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Sustainable, 'Green' Vinyl Ester Resin (VER) from Renewable Resources

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List of Acronyms, Keywords, and Acknowledgment

BPA – Bisphenol A

BADGE – Bisphenol A Diglycidyl Ether

Br-VER – Brominated Vinyl Ester Resin

CF – Carbon Fibers

DoD – Department of Defense

FT-IR – Fourier Transform- Infra Red spectroscopy

FVER – Formulated Vinyl Ester Resin

FVP – Flash Vacuum Pyrolysis

GCMA – Glycerol Carbonate Methacrylate

GVER – Green Vinyl Ester Resin

GMA – Glycidyl Methacrylate

^{1}H NMR – Nuclear Magnetic Resonance Spectroscopy

HPLC – High-Performance Liquid Chromatography

HRR – Heat Release Rate

NAVAIR – Naval Air System Command

NAVSEA – Naval Sea System Command

RD – Reactive Diluent

TBBPA – Tetrabromobisphenol A

THF – Tetrahydrofuran

UML – University of Massachusetts Lowell

US – United States

VARTM – Vacuum Assisted Resin Transfer Molding

VER – Vinyl Ester Resin

VHER – Vinyl Hydroxyl Ether Resin

Acknowledgment

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SERDP Final Report

3/31/2017

Sustainable "Green" Vinyl Ester Resin (VER) from Renewable Resources

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Abstract

Sustainable "Green" Vinyl Ester Resin (VER) from Renewable Resources

Objective: Carbon-fiber reinforced composites of Vinyl Ester Resin (VER) are largely used in Department of Defense (DoD) weapons platforms. Critical composite structures for ship hulls and transportation vehicles can be made using a low-cost VER that can be processed at ambient temperature using vacuum-assisted resin transfer molding (VARTM). Current precursors for making VER are isolated from petroleum feedstock, which is subjected to fluctuating prices and limitations in supply. In addition, the synthetic route uses epichlorohydrin as one of the precursors, which is a potential carcinogen.

The objective of this SERDP project was to develop a sustainable, environmentally safe VER for military structural composite weapons systems starting with low-cost lignin and glycerin biowaste streams, prepare various formulations and their carbon fiber reinforced composites that can completely or in part replace the current commercial resin manufactured from petroleum feedstock.

Technical Approach: The development of bioderived VER was conducted in following steps:

1. Isolation of bioderived phenol from pyrolysate from lignin and its conversion to BPA.
2. Synthesis of glycidyl methacrylate (GMA) from glycerin via conversion to glycidol followed by reaction with meth methacrylate.
3. Synthesis of VER via reaction of BPA with GMA, eliminating the use of toxic epichlorohydrin.
4. Developing one-pot synthesis method for VER using glycerin and BPA as reactants.
5. Prepare various formulations of GVER and examine their cure kinetics.
6. Carbon fiber reinforced composites of various formulations using VARTM.
7. Mechanical and flammability testing to determine structural equivalence.

Results: BPA from the green phenol from lignin pyrolysis and GMA from biodiesel based glycerin were successfully synthesized. The monodisperse VER was prepared, purified and its various formulations were prepared. The commercial resin with 40 wt. % of styrene have similar viscosity

like GVER with 20 wt. % of styrene. Carbon fiber reinforced composites of GVER have similar mechanical and flammability performance compared with commercial resins. In addition, three different syntheses of VER from glycerin and BPA were developed and examined for marine coating.

Benefits: This program provided a sustainable, environmentally safe source of vinyl ester resin monomer from bio-waste streams of lignin and glycerin. This will enhance the independence of the United States from foreign oil. The proposed synthetic route to produces GVER eliminates the usage of epichlorohydrin. In addition, the GVER has significantly lower down the usage of reactive diluent styrene compare with commercial resins.

Executive Summary

SERDP WP-2317 is aimed at developing sustainable, environmental friendly green vinyl ester resin (GVER) which can completely or in part replace the current petroleum-based resin applied for US Department of Defense (DoD) composite weapon system. The scientific objectives of this work are 1) isolation of precursors for vinyl esters (VEs) monomer from the waste stream of the biodiesel and paper/pulp industries, 2) development of the process to produce GVER using various novel synthetic approaches and 3) preparation of various formulations to examine the possibility of replacing the petroleum-based resin completely or in part, 4) fabrication of highly durable lightweight composite through vacuum assisted resin transfer molding (VARTM) process and investigating their mechanical and flammability performances.

The VEs are generally composed of aromatic components such as bisphenol A (BPA) or tetrabromobisphenol A (TBBPA) and an aliphatic component such as glycidyl methacrylate (GMA), and VEs property can be tuned by modification in their precursors. We have developed various synthetic methods for VEs using either glycerin, GMA or glycerol carbonate methacrylate (GCMA) as aliphatic precursors and BPA or TBBPA as aromatic precursors. In addition to that, an entirely new class or resin vinyl hydroxy ethers (VHEs) was developed.

Lignin was pyrolyzed at elevated temperature and the lab scale setup was optimized in such a way that maximum amount of phenol can be isolated. The oil was purified by various methods and green phenol was isolated which was used further to demonstrate the synthesis of BPA. Along with pyrolysis and isolation of green phenol; different depolymerization methods were examined, which selectively produces a high amount of food flavoring agents such as vanillin. The biodiesel based glycerin was purified at lab scale and was used further to demonstrate synthesis of GMA, GCMA and subsequently VEs and VHEs.

The VEs were purified and mixed with 40 wt. % of styrene to prepare base formulation, which was subsequently mixed with 20, 50 or 80 wt. % of commercial petroleum-based resin. Other formulations with a lower amount of styrene in 20 and 30 wt. % were also prepared. Carbon fibers (CFs) reinforced composites were prepared and their mechanical and flammability performance was investigated. The GVER reaches a similar viscosity as the commercial resin with only half the styrene monomer content, thereby reducing the volatile organic compounds associated with manufacturing. The mechanical performance of the GVER compares favorably with commercial resin and provide a route for composites manufacturing from sustainably sourced vinyl ester matrix. All GVER formulations have similar or slightly improved flammability performance compared with petroleum-based commercial resin. These results provide a pathway to transition from petroleum-based vinyl ester resins to their bio-based counterparts while maintaining existing processing conditions and comparable mechanical and flammability performance.

This work has benefited DoD by reducing production cost and environmental burden. For example, source materials are renewable low-cost bio-waste, thus will eliminate dependency on oil-based production cost. Furthermore, our novel synthesis method can eliminate the use of toxic chemicals such as epichlorohydrin from GVER synthesis route compared to the current process. The reactive diluent (RD) which is essential for the current formulation can be significantly reduced according to our new methods.

.

1. Objective

The primary objective of the program was to apply the sustainable, environmentally safe 'green' vinyl ester resin (GVER) technology demonstrated to be feasible to replace the current petroleum feedstock based resin completely or in part for US Department of Defense (DoD) composite weapon system during the SERDP program. The developed process utilizes waste from the biodiesel and paper industry, these source materials are renewable, low-cost, and are becoming increasingly abundant, which will subsequently eliminate the dependence on the fluctuating crude oil supplies. In addition, the design of process was aimed such a way that eliminate the use of extremely toxic chemicals such as epichlorohydrin and reduces usage of reactive diluent (RD) styrene significantly.

Materials and processes have been refined and scaled up to produce enough quantities of GVER to fabricate their CF reinforced composites through VARTM and examine material properties. Various novel synthetic approaches for GVER were explored and their different formulations were prepared. Performance equivalent to currently used DoD composite weapons systems components were demonstrated via mechanical property testing. UML's sponsorship includes the US Air Force, Navy, and Army. Ashland Inc., a VER manufacturer, has been approached to guide UML toward the development of appropriate military composite materials and component structures. Finally, the performance of all refined materials produced in the program was demonstrated by standard characterization tests. The amount of reactive RD for the formulation was also reduced significantly.

2. Background

Use of the composite materials for the construction of DoD weapons platforms is approaching 200 million pounds per year. Vinyl ester resin (VER) is a low-cost resin that can be processed at ambient temperature using vacuum-assisted resin transfer molding (VARTM) into massive carbon-fiber-reinforced composite structures such as ship hulls and transportation vehicles. But since VER production is highly dependent on oil, it is subject to fluctuating prices and supplies limitations. The continued viability of this strategic DoD weapons material is further jeopardized by the manufacturing need for hazardous materials, epichlorohydrin, and styrene. Because of its increasing use of military weapon systems, VER is considered a strategic DoD resource. However, the resin as currently manufactured has three important disadvantages. First and foremost, VER is currently synthesized from petroleum feedstock, so as mentioned it is subject to price volatility with the supply unreliable and limited in times of oil shortages. Second, VER is synthesized from epichlorohydrin, a known environmental hazard that produces acute toxicity from inhalation, oral, and dermal exposure. It is also classified by the EPA as a Group B2 probable human carcinogen. Third, the styrene monomer, a major RD component of VER, is environmentally hazardous, being volatile, flammable, and toxic, and in addition to being an irritant, styrene can affect the gastrointestinal and central nervous systems and has been categorized by the EPA as a hazardous air pollutant and possible carcinogen for humans. To ensure the continued viability of this strategic VER material, it is essential to develop VER synthesis routes that are not dependent on petroleum. In this task, UMass-Lowell (UML) also intends to investigate VER synthesis routes that eliminate the use of epichlorohydrin and to conceive resin formulations that do not contain hazardous components such as styrene. To assure sustainability of the new processing route, starting materials should be derived from readily available renewable resources. Finally, the resultant VER must retain the desirable economic and performance characteristics of the current products. Figure 1 illustrates the UML's approach to 'Green' Vinyl Ester Resin from Renewable Resources.

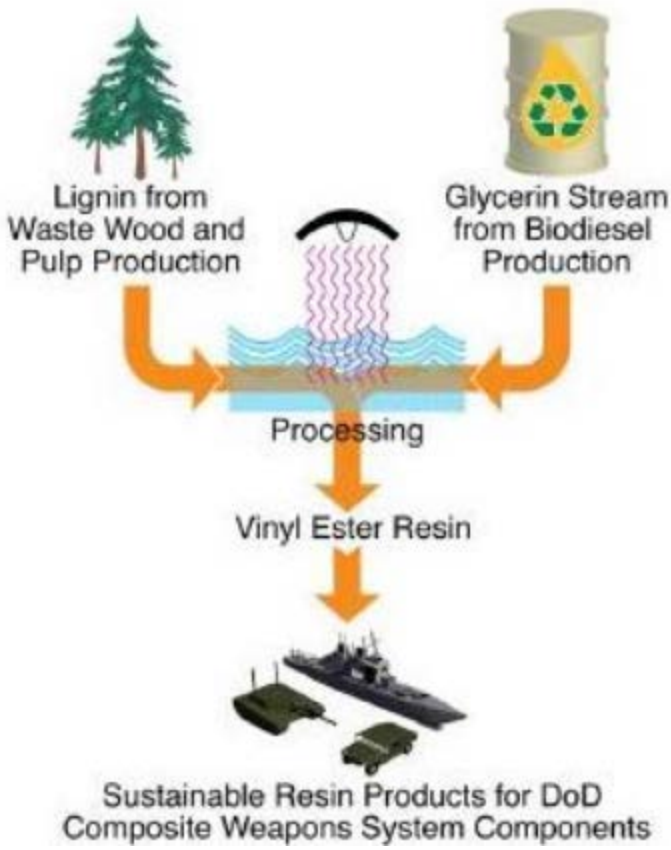


Figure 1. The UML approach

2.1. Summary of Process /Technology

GVER production from renewable sources consisted four steps: 1) Recovery of phenol from lignin and wood wastes; 2) conversion of the recovered phenolics into BPA; 3) synthesis of GMA from waste glycerin; and 4) synthesis of GVER from BPA and GMA. The efficiency of flash pyrolysis methods for converting lignin and wood waste into phenols at high yield and purity were examined [2-9]. Economic and environmental impacts were major determinants in the selection/evaluation of each synthesis step. Furthermore, the modification of the GVER was conducted to adapt the viscosity such that it can be modified with various processing techniques. Resin impregnation techniques were conducted to ensure the material resilience of the final product. The brominated resin was also developed to increase the flammability resistance of the final product. Figure 2 shows the sequence of reactions leading from lignin and/or wood wastes to GVER monomer.

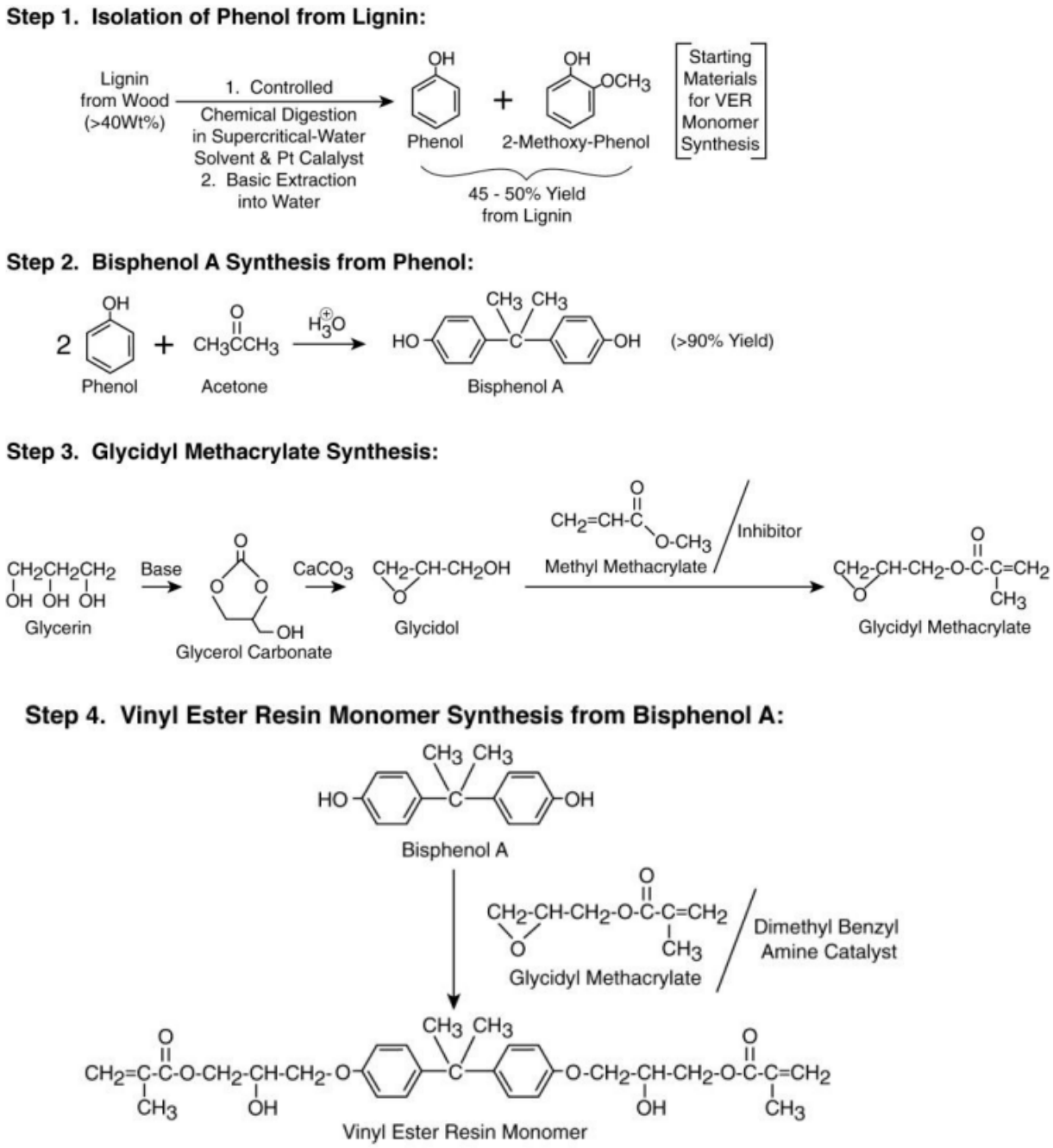


Figure 2. Sequence of reactions leading from lignin and/or wood wastes to GVER monomer

2.2. Benefit

Fiber-reinforced composites produced from vinyl ester resins (VER) have become the material of choice for marine applications, especially next-generation Navy ships. VER is a low-cost material that can be processed to form a matrix of fiber-reinforced composites that are excellent materials for hulls, transportation vehicles, and many other militaries and commercial

systems. VER is finding increasing application in the transportation, construction, marine, and wind energy industries. In the year 2000 alone, over 60 million pounds of VER were sold in North America. Since then, the US Navy's need for VER has significantly increased. For example, the 500-ton deckhouse structure for the DDG 1000 is fabricated from carbon/VER composites. Current plans are for up to two ships per year, to a total of 20-32 ships. The Navy also has recently used Derakane 510A brominated VER on the advanced enclosed mast/sensor (AEM/S) mast on *USS Radford* (DD 968), LPD-17 masts, composite advanced sail, and composite high-speed vessel as well as the DDG1000. Vinyl ester resins are formulated from VER monomer, a solvent/reactive diluent, typically styrene, as well as additives to meet specific needs. In general, VER has several advantages over other polymers. For example, toughened and brominated VER produces resins with higher strengths than polyesters and lower viscosities than epoxies. This low viscosity is critical for fabricating large ship structures by vacuum infusion. Fiberglass-reinforced VER composites are preferred for many topside applications where low detectability and radar transmission are important. Recent advances in compatible sizings have enabled stiffer reinforcements of VERs using carbon fiber [10, 11]. In this SERDP program, it was demonstrated that UML 'green' VER composites are structurally equivalent and also equivalent in the fire, smoke, and toxicity standards to already specified material systems, and are acceptable for refinement, scale up, and use as components in DoD composite-weapons systems.

3. Results and Discussion

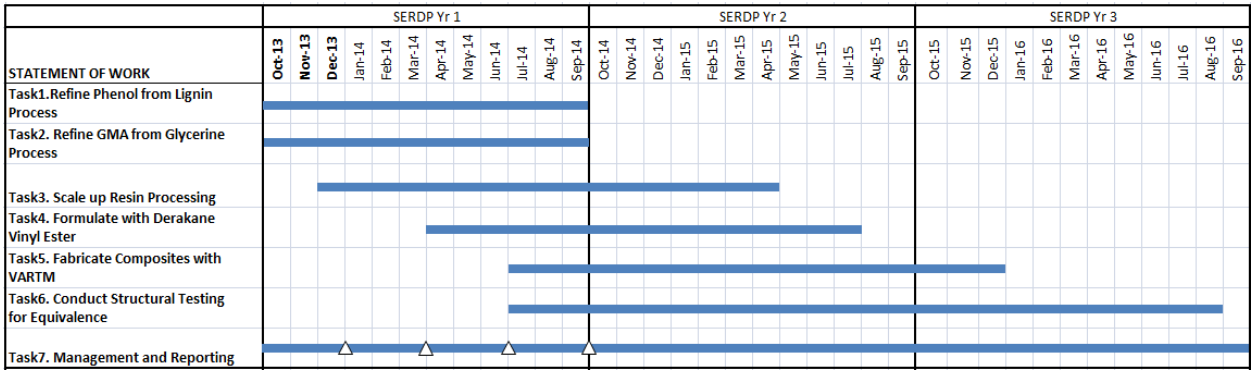


Figure 3. SERDP WP2317 Execution Plan

3.1. Task 1 - Refine Phenol from Lignin Process

BPA is considered one of the most important building blocks of today's plastics industry. Many plastics such as polycarbonates, epoxy resins, and vinyl ester resins are synthesized using BPA as a precursor[12]. BPA is considered a high production volume chemical; 2.2 million pounds of BPA was produced worldwide in 2009[13]. BPA is synthesized by the reaction of phenol and acetone[14]. Forty percent of worldwide phenol production is used for BPA production. Currently, the petroleum industry is the entire source for phenol and thus BPA production. Therefore, it is desirable to explore sustainable phenol and BPA production.

Lignin as a biomass is abundantly available worldwide and in many cases considered to be a part of waste streams[15-17]. It is a major side-product in the pulp and paper, and agro-based industries[18]. Lignin cannot be digested by cattle and therefore is not suitable for use in animal husbandry as a feed source. Also, as a material, it possesses limited applications, and its conversion to high-value chemicals is a challenge for paper and agro-based industry[19]. Hence, the conversion of lignin biomass into commercially relevant starting chemicals is a highly important and attractive area.

Lignin is a highly branched, substituted, mononuclear aromatic polymer that is often bound to cellulose and hemicellulose fibers[20]. It is typically obtained through the hydrolysis of wood, which removes the "waste lignin" from the cellulose and hemicellulose fibers[21]. Because it has very complex structure, one of the protocols used for the deconstruction of lignin into useful chemicals is pyrolysis which produces a liquid phase called pyrolysate. Typically phenols and many other commercially attractive aromatic chemicals with one or two hydroxyl groups are

significant components of the pyrolysate obtained from the pyrolysis of lignin, such as guaiacol, vanillin, and catechol[22].

Pyrolysis of lignin can be challenging because the thermoplastic properties of lignin create feeding and agglomeration issues in continuous reactors typically used for pyrolysis of biomass[23, 24]. However, it can be depolymerized using supercritical water[25], flash vacuum pyrolysis[26], solvolysis[27], base-catalyzed hydrolysis[28], catalytic reactions that use hydrogen[29, 30], and formate-assisted pyrolysis[31]. Despite some advantages of the various thermo-conversion methods of lignin, each has its potential drawbacks including the limited ability to scale up and use of catalysts (sometimes based on expensive noble metals) and added chemicals. In this work, we utilized a less-complicated pyrolysis method to demonstrate BPA synthesis from lignin.

Thermal decomposition of lignin results in the production of char and condensable vapors during Flash Vacuum Pyrolysis (FVP)[32, 33]. FVP process was carried out in the absence of oxygen with a high rate of heating around 500 ºC followed by a rapid cooling of the produced vapors. The reactor temperature was carefully selected after preliminary GC/LC-MS experiment. Inert gas flow system was procured to get rid of a trace of oxygen in the furnace reactor during FVP. This may increase the yield by reducing the possible oxidation/side reaction of pyrolyzed intermediate during the high-temperature pyrolysis in the quartz reactor.

Recently, lignin-based composite materials have gained significant attention. Some compounds in bio-oil derived from pyrolysis of lignin can be used as reactants in prepolymer synthesis or as reactive diluents in different thermosetting materials.[34] Until now, bio-derived composites are made either using bio-mimicking commercial compounds,[35] or lignin with limited purification.[36] In the present work, we have combined different purification methods, which will be helpful in isolation of other high-value precursors.

The objective of the present study is to demonstrate a synthesis of high-value building block BPA from the pyrolysate of lignin. We performed a systematic investigation of the effect of temperature on phenol production from lignin pyrolysis. Phenolics were isolated from the pyrolysate by solvent extraction and vacuum distillation. Purified phenolics were used for the synthesis of BPA and the reaction mixture was purified by column chromatography.

3.1.1. Experimental

3.1.1.1. Equipment and Materials

- Tube furnace reactor (Thermolyne 21100, Barnstead) with thermocouple embedded
- Heating mantle with on/off temperature controller and sand (50-70 mesh particle)
- Clear fused quartz tube (25mm ID x 28.8mm OD, 24” length) with a 24/40 female taper joint on each end

- Water-cooled condenser
- Vacuum pump
- Digital weight scales
- Accessories: high temperature resistant joint grease, ring stands and clamps, Dewars for cold trap with glassware, round bottom quartz flask, vertical lift, glass wool, glass adapters, glass scintillation vials, filter paper, funnel glasswares, crucible holders, foil tape
- Solvents: All solvents for the extraction procedure were of ACS grade and purchased from PharmcoAaper Inc; THF (Tetrahydrofuran), methanol, hexanes, ethyl acetate and methylene chloride.

3.1.1.2. Lignin Resources

Lignin was procured from four different sources (1) Sigma-Aldrich's alkaline lignin, (2) Sigma-Aldrich's dealkaline lignin, (3) Tokyo Chemical Industries (TCI's) alkaline lignin, (4) Tokyo Chemical Industries (TCI's) dealkaline lignin, (5) Lignin from Maine Seed Company (Wales, ME), and (6) Flambeau river papers LLC (Park Falls, WI). All lignin materials were dried in vacuum oven overnight before pyrolysis (Figure 4)

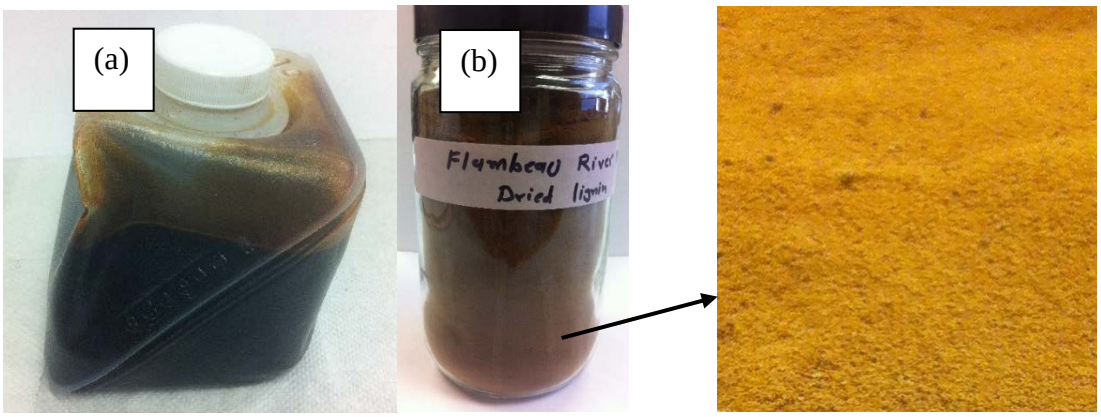


Figure 4. (a) Liquid lignosulfonate and (b) solid lignosulfonate obtained from Flamebeau River Papers, LLC.

In order to scale-up GVER, the higher amount of green BPA is required. We have received 10 gallons of black liquor from our collaborator Maine Seed Company (MSC) as shown in Figure 5. Black liquor is highly viscous material, which was dried at elevated temperature and pyrolyzed subsequently. We have pyrolyzed black liquor repeatedly, as it is producing the highest amount of phenol among phenolic compounds in comparison with other lignin materials. Collected pyrolysate was purified using solvent extraction followed by column chromatographic purification.

Figure 5. Black liquor (10 gallons) received from Maine Seed Company (MSC) to scale-up lignin pyrolysis.

3.1.1.3. Characterization

NMR Spectroscopy. ^{1}H NMR spectra of the synthesized materials were recorded at 25 °C on a Bruker 500 MHz spectrometer using DMSO (Cambridge Isotope Lab., Inc.) as the solvent and tetramethylsilane (TMS) as the internal reference (δ H 0.00).

GC-MS Analysis. The pyrolysate samples were analyzed by a previously reported modified method[9]. We used the GC-MS instrument of Agilent (Santa Clara, CA) 7890 GC equipped with 5973 MS. It has a column of Restek Corporation (Bellefonte, PA) Rtx Wax 30 m x 0.25 mm. It has an SP1Temperature Program with 40 °C for 3 min then 4 °C/min ramp to 100 °C and hold for 3 min; then 6 °C/min ramp to 240 °C and hold for 10 min; total run time 54.3 min with splitless injection mode and 2.0 µL injection volume. We used a column flow of 1.0 mL/min UHP He. All mass spectra were analyzed using the NIST Mass Spectral Library 2008. A revised, semi-quantitative GC-MS data analysis method was applied to analyze the extraction yield of phenol. Percentage information was calculated based on the peak area calculation using the GC software (Chemstation software from Agilent, Santa Clara, CA). Ten major phenolic standard samples were analyzed, and the relative output of each standard was compared on a percentage basis. Using GC-MS, the presence of more than 25 different phenol-based constituent compounds in the pyrolysate was identified, as shown in Table 1. List of Phenolic Compounds Identified in the Pyrolyzed Mixture by GC-MS, Retention Time, and Chemical Structure

Semi-quantitative GC/MS analysis using standards

We generally used output yield (%) calculated from the total peak area. In the case of diluted samples which have more background effect, we applied semi-quantitative analysis. Among the phenolic compounds identified between 20-54 min retention time range; we selected

eleven, the most expected species during pyrolysis as standards. The filtered lignin pyrolysis samples were analyzed by the method of Du et al.[41], with modifications.

High-Performance Liquid Chromatography (HPLC). HPLC was analyzed on a Waters 2695 instrument equipped with a Waters 2996 PDA UV detector, and an HYPERSIL ODS (C18) column of 5-micron size, 250 mm length with the flow rate of 1 mL/min. Water and methanol (70:30) were used as a mobile phase at the temperature of 30 °C. The chromatogram was obtained by monitoring at 254 nm.

3.1.2. Process Development

3.1.2.1. Design overview of pyrolysis

Lignin pyrolysis under critical-water condition[3] produces phenol, guiacol (2-methoxy-phenol) and catechol (3-hydroxyphenol). However, the method is not efficient enough for a high amount of lignin pyrolysis. Phenol could react immediately as formed under conditions of the high-pressure reaction into undesirable side-products. Therefore, it was difficult to increase the batch size using the supercritical water-based setup(Figure 6).

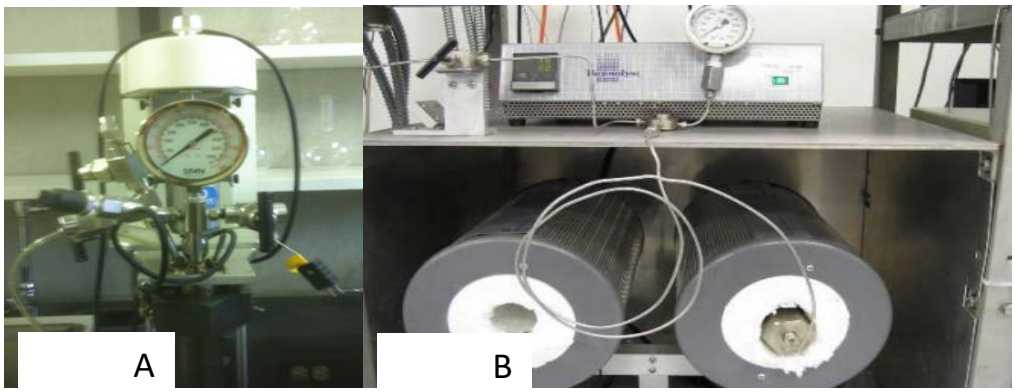


Figure 6. Procured supercritical-water lignin hydrolysis instrument at UML

In order to overcome the limitation of small batch pyrolysis in the supercritical water conditions, we investigated an alternate pyrolysis method called flash vacuum pyrolysis. It was expected that this technique will lead to the isolation of a higher quantity of phenolics, which can subsequently be purified into phenol, guaiacol (2-methoxyphenol) and catechol (1,2-dihydroxybenzene). In lab scale, the design of pyrolysis setup was changed (Figure 7, Figure 8) significantly over the period to isolate higher amount of phenolic.

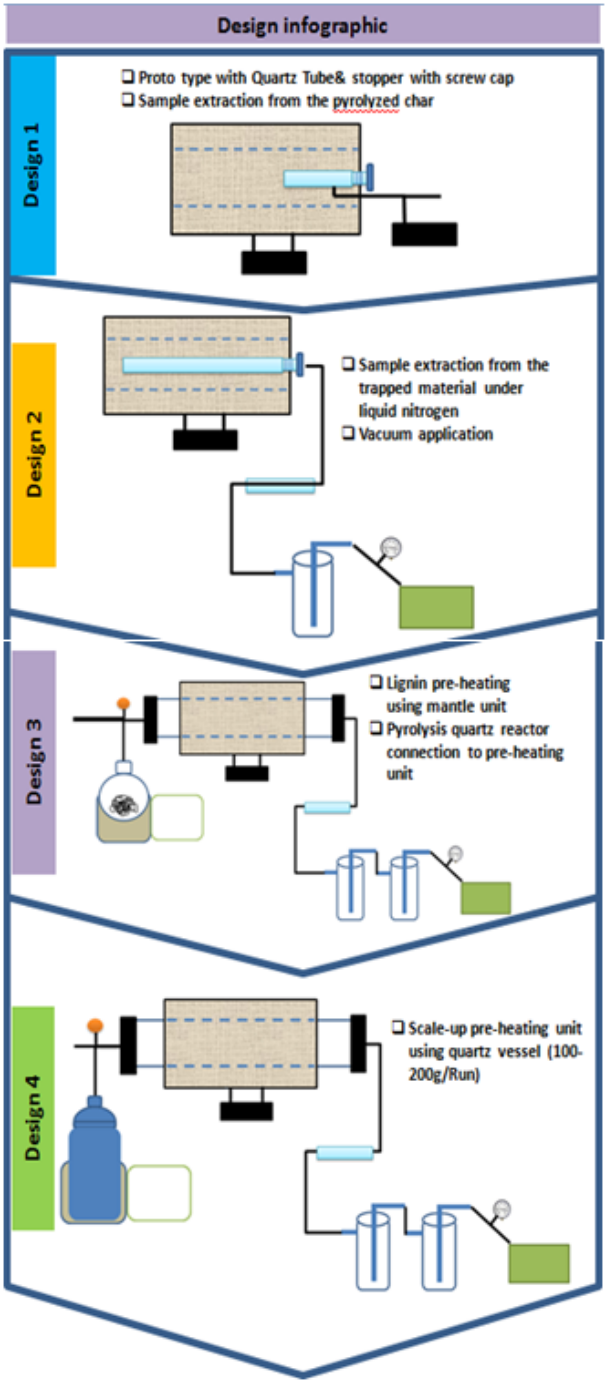


Figure 7. FVP design infographic over the project period.

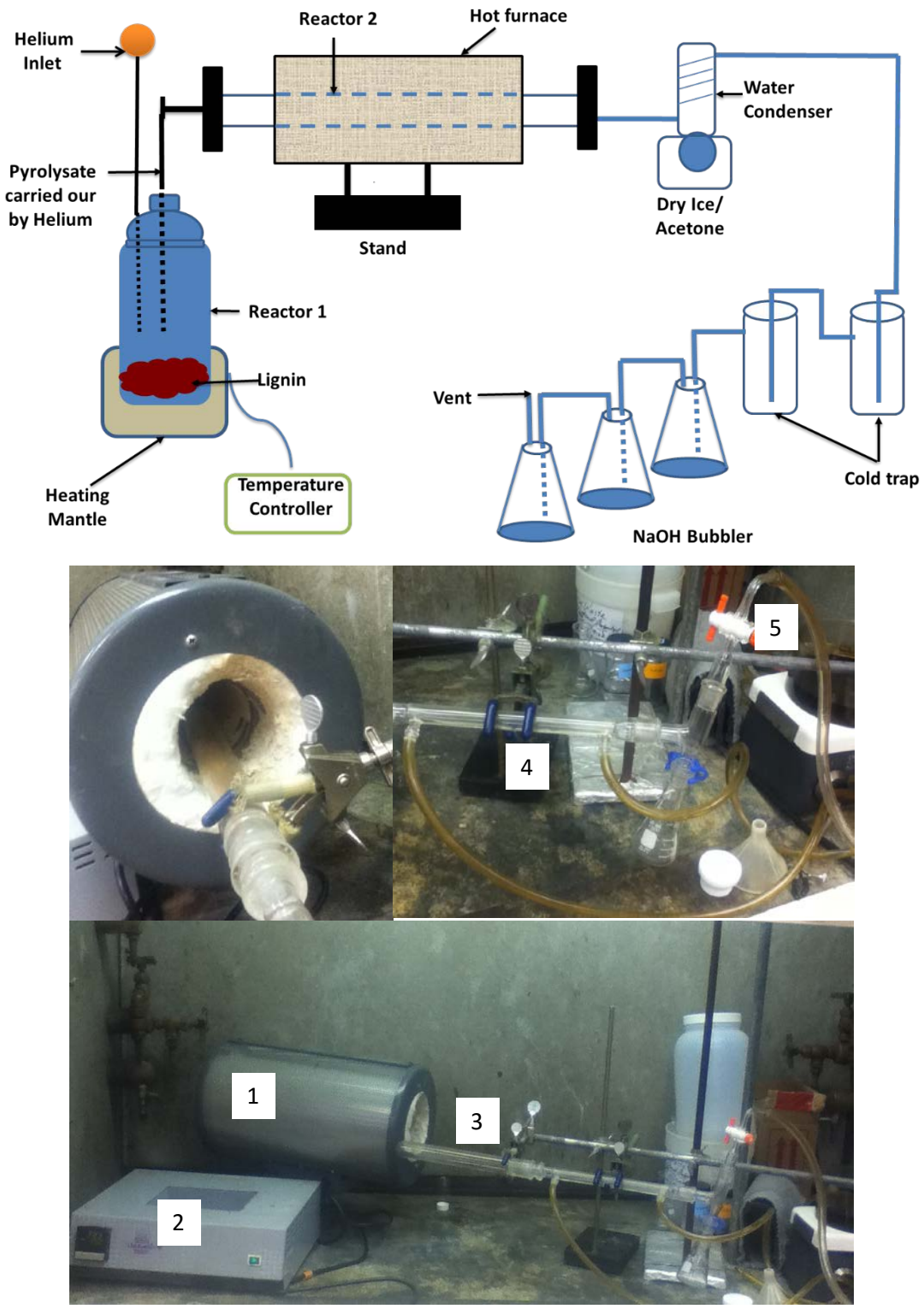


Figure 8. Pyrolysis reactor.

1. Furnace chamber, 2. Control base with a pyrometer, 3. Pyrolysis reactor, 4. Water-cooled condenser, 5. Vacuum lining

3.1.2.2. Preliminary Test

The LC/MS analysis (UV at 254 nm) suggested that as the temperature increases the amount of phenol increases significantly. Data from LC/MS (Figure 9, Figure 10) suggested that we had performed pyrolysis of lignin successfully. However, due to the difficulties in the identification of each peak with low intensity of the signals. GC/MS analysis (semi-quantitative) was preferred for the following analysis [40].

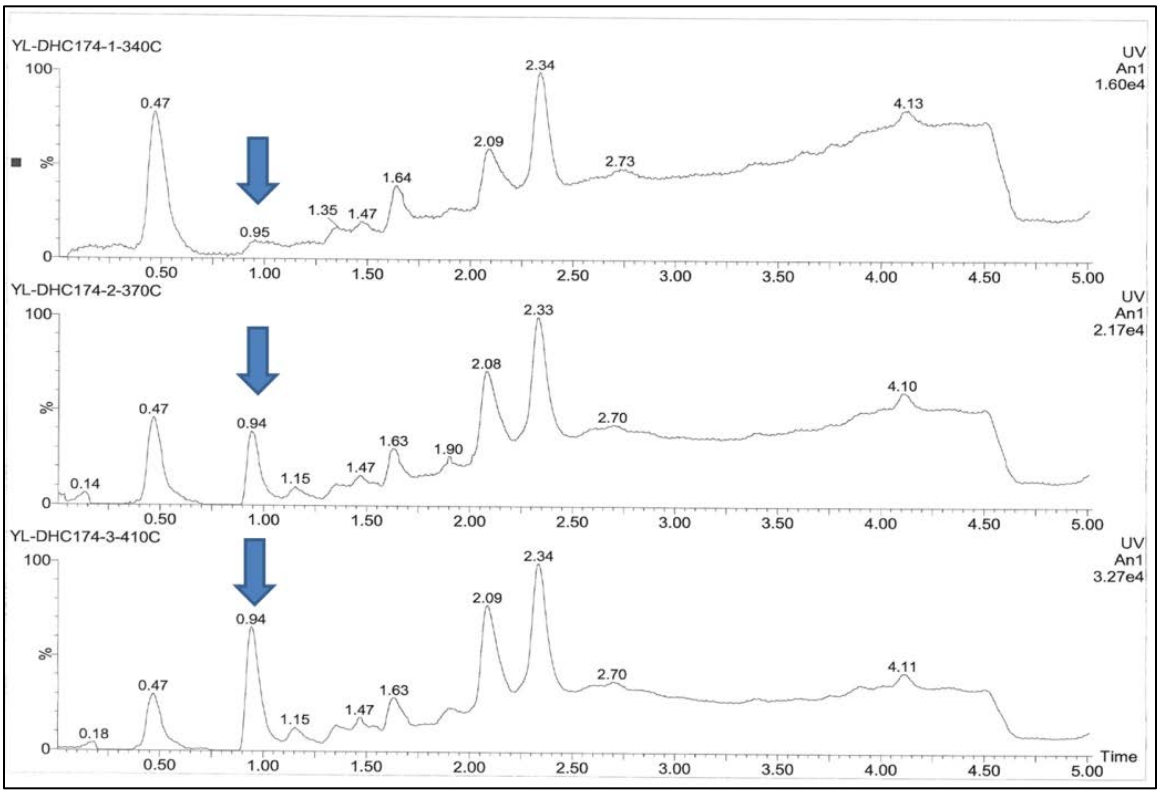


Figure 9. LC-MS spectra of lignin pyrolysis at (a) 340 ºC, (b) 370 ºC, and (c) 410 ºC.

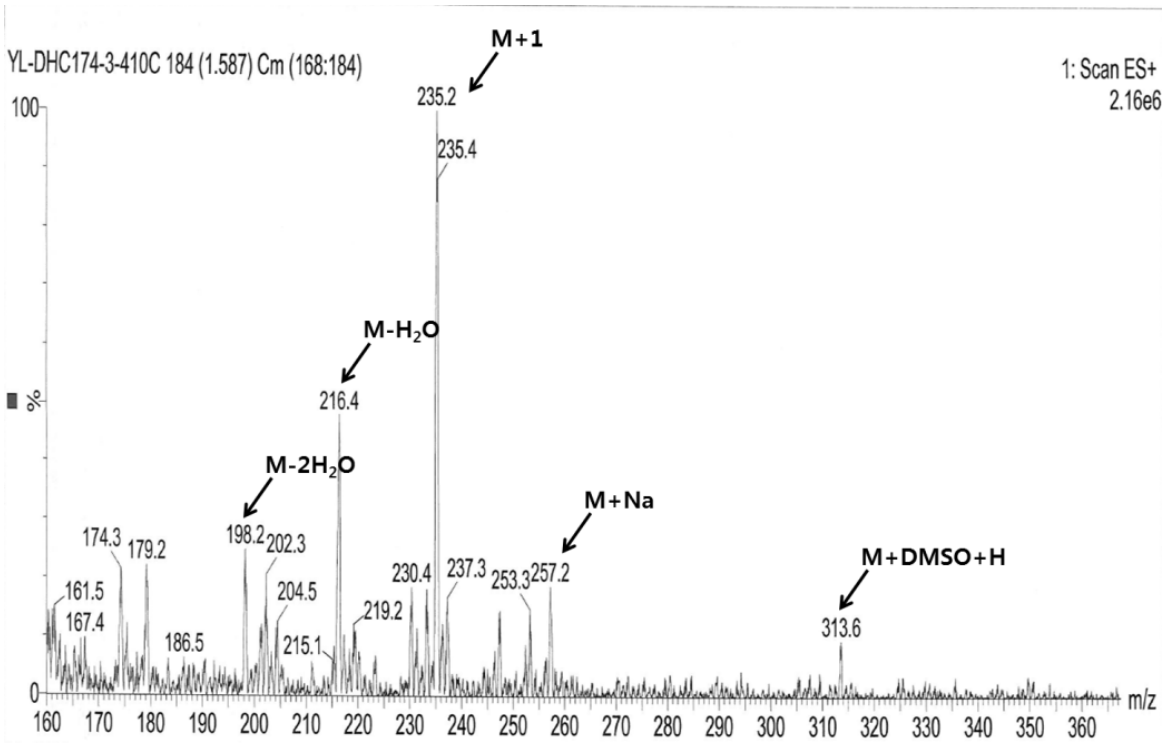


Figure 10. LC/MS data confirms pyrolysis of lignin at 410 ºC

Peak Identification: The peak at a retention time (Rt) 0.94 increases with increase in temperature. The type of material observed at peak 0.94 is unclear due to the weak signal. The samples were also analyzed by HPLC equipped with DAD. The peaks in HPLC-DAD at Rt 1.50 and Rt 1.63 seem to be the same as those of Rt 0.94 in HPLC-UV. Furthermore, the peak at Rt 2.40 is the same as the peak at Rt 2.34 and the intensity of peaks at Rt 1.50 and Rt 1.63 with an increase in pyrolysis temperature. The peak at Rt 2.16 was relatively increased with higher temperature, but no related MS was detected. The peak at Rt 1.50 shows m/z 235 as M+1. Some other relative peaks identified were marked M-18 (H_2O). Therefore, the compound at Rt 1.50 might contain at least two hydroxyl groups. The peak at Rt 2.40 shows m/z 219 as M+1. If the compound consists of only C, H, O, N, there are 36 formulas available with formula mass of 218.

Recovery Yield: The weight loss of lignin was calculated based on weight measurement on the char and the trap samples after pyrolysis (Figure 11). The unrecovered weight loss of lignin was attributed to the gaseous aerosol, materials in the lines and moisture. Total recovery yield based on char and trap samples was 82.3 % (helium flow) and 59.6 % (vacuum pyrolysis), respectively. The temperature in the preheating mantle was 400 ºC while maintaining 500 ºC in the pyrolysis quartz reactor using the furnace. The reaction time was set for 1 hour.

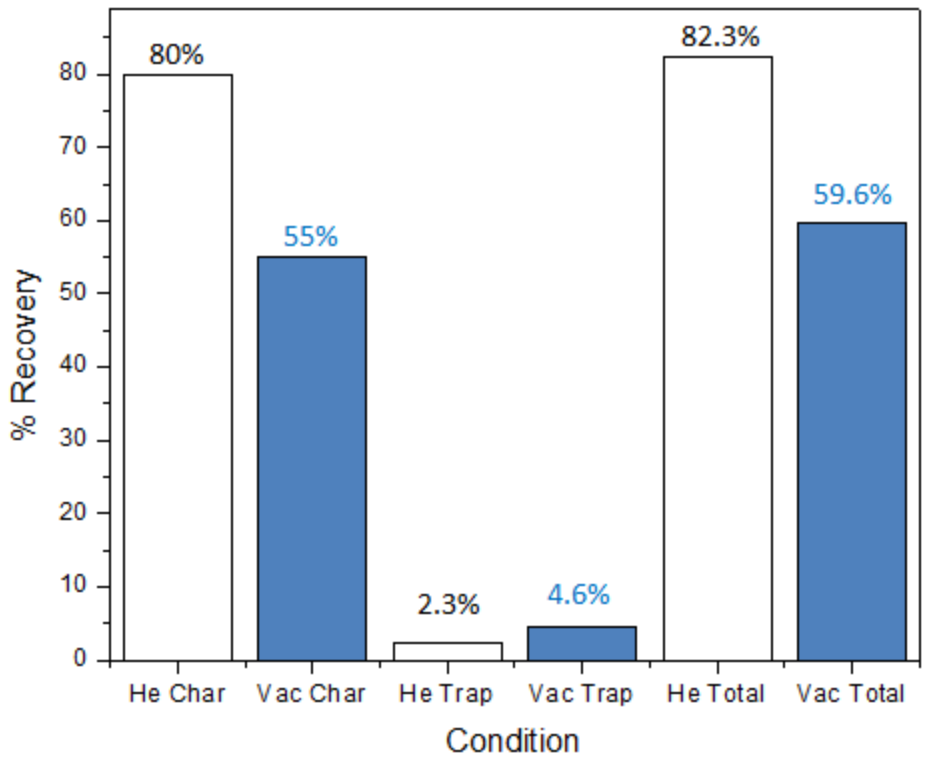


Figure 11.The comparison of recovery yield between helium and vacuum pyrolysis

The yield of standard compounds was compared between helium flow pyrolysis and vacuum pyrolysis. There was a noticeable difference in catechol and guaiacol concentration due to the exposure time during the pyrolysis. It is highly possible that guaiacol converted to catechol efficiently on helium gas flow pyrolysis due to the longer exposed reaction time. However, the output of other phenolic compounds was very similar (Figure 12).

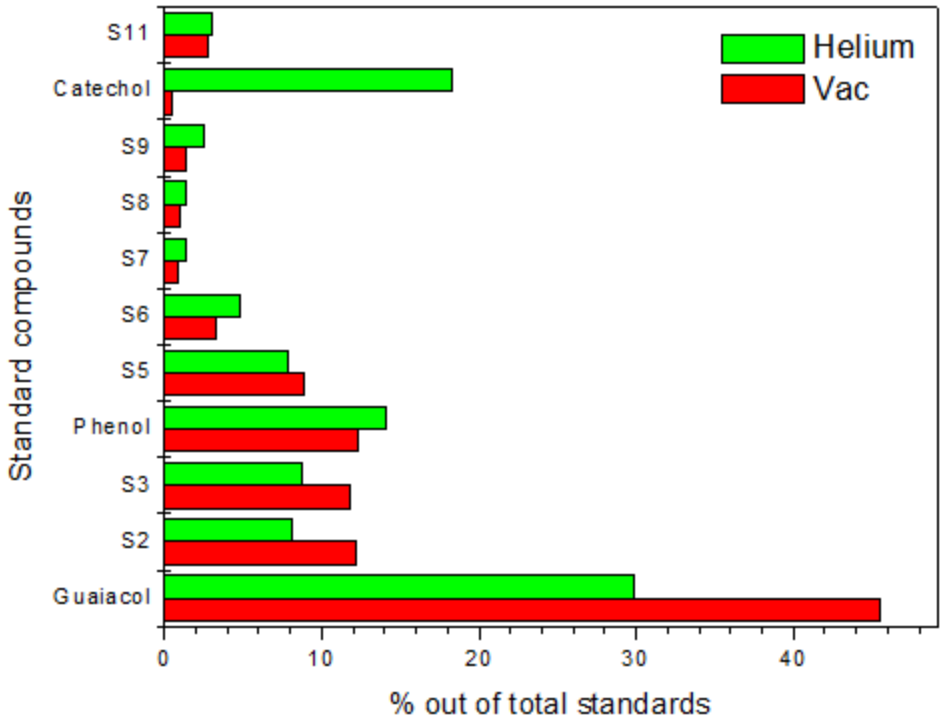


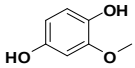
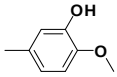
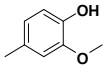
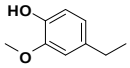
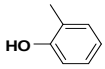
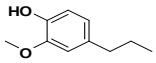
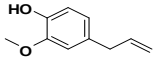
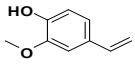
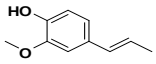
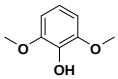
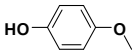
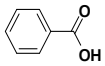
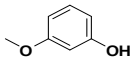
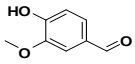
Figure 12. The relative percentage of standard compounds measured by GC-MS.

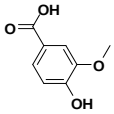
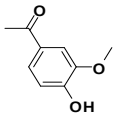
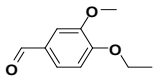
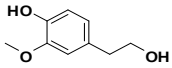
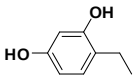
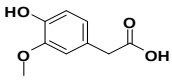
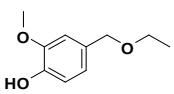
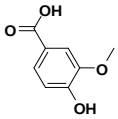
The result showed a promising approach for an efficient separation of phenolic compounds including phenol, guaiacol (2-methoxyphenol), and catechol (1,2-dihydroxybenzene) out of lignin. The extracted phenol, especially, can be directly used for BPA synthesis.

3.1.2.3. Analysis of pyrolysate by GC-MS

GC/MS analysis was performed with the help of Professor Dave Ryan at UML to determine phenolic compound more effectively. Preliminary LC/MS data of pyrolyzed crude mixture showed the existence of phenol in our Char (crude) samples clearly. The same pattern of the peak can be identified in GC/MS analysis with better sensitivity. Generally, GC/MS has better resolution in terms of selectivity due to its ionization technology and detection method. GC/MS has an advantage over LC/MS in small molecules detection. Semi-quantitative yield will be prepared based on the data for comparison of different temperature conditions.

Table 1. List of Phenolic Compounds Identified in the Pyrolyzed Mixture by GC-MS, Retention Time, and Chemical Structure

No	Retention time	Name	Label	Structure
1.	27.253	4-Hydroxy guaiacol		
2.	28.471	Guaiacol	S1	
3.	28.654	3-Methyl guaiacol		
4.	30.032	5- Methyl guaiacol		
5.	30.289	4- Methyl guaiacol	S2	
6.	30.834	Phenol	S3	
7.	31.376	4-Ethyl guaiacol	S4	
8.	32.563	2-Methyl phenol		
9.	32.693	3-Methyl phenol		
10.	33.023	4-Propyl guaiacol		
11.	33.965	4-Allyl guaiacol		
12.	34.110	2-Ethyl phenol		
13.	34.388	4-Vinyl guaiacol	S5	
14.	35.325	4-Propenyl guaiacol		
15.	35.477	2,6-Dimethoxy phenol	S6	
16.	37.421	4-Methoxy phenol (Mequinol)		
17.	37.747	Benzoic acid		
18.	38.038	3-Methoxy phenol		
19.	39.559	Vanillin	S7	

20.	40.182	4-Hydoxy,3-methoxy benzoic acid		
21.	40.569	4-Acetyl guaiacol (Apocynin)	S8	
22.	40.956	1,2-Dihydroxy, 3-methyl benzene		
23.	41.433	4-Ethoxy-3-anisaldehyde		
24.	41.523	Catechol	S9	
25.	43.228	Homovanilyl alcohol		
26.	43.469	1,3-Dihydroxy,4-ethylbenzene		
27.	44.853	Homovanillic acid	S10	
28.	45.016	4-(Ethoxymethyl)-guaiacol		
29.	52.182	p-vanillic acid		

Among all the phenolic compounds identified between the retention time range of 26 and 46 min in the GC chromatogram, ten representative standard compounds (S1-S10) were selected,

$$Amount\ of\ phenol = \left(\frac{Area\ under\ the\ peak\ of\ phenol\ in\ GC\ chromatogram}{Total\ area\ under\ the\ all\ peak\ of\ GC\ chromatogram}\right) X\ 100$$

whose presence was consistently found in pyrolysate obtained under various conditions as shown in Table 1. The amount of phenol and other phenolics was calculated by the equation below. The area under the phenol peak was divided by the total area under all the peaks of the GC chromatogram and then multiplied by 100, which provided the amount of phenol in total pyrolysate.

3.1.2.4. Temperature Condition

Temperature is one of the important variables to test the yield of pyrolysis of lignin under low-pressure vacuum. Slow pyrolysis at low temperatures and long residence times produces char majorly. Fast pyrolysis [23, 37, 38] or flash pyrolysis produces a high yield of liquid products (60 wt. % moisture free organic liquids on dry feed)[39]. The temperature setup above 700 ºC maximizes gas yields (up to 80 wt. %). Product selectivity during the pyrolysis is poorly

understood. Most of the studies were conducted at low temperature (<450 ºC) with long residence times (>5 min) or slow heating rates. We increased the yield of various phenolic compounds as well as phenol itself using FVP technique.

Lignin was pyrolyzed at different temperature conditions with or without vacuum on a small scale. The furnace was heated up to three different temperature conditions (330, 370 and 410 ºC) to see the output and yield of the pyrolysis products. The inside of the tubular chamber of the furnace was insulated with ceramic fiber insulation. The temperature was controlled by a thermocouple and was displayed on a pyrometer in a control base. The pyrolysis reactor tube made of Pyrex was directly placed in the furnace for 10 minutes. Cleaved materials were dissolved either in THF, filtered and dried. A basic/neutral form of lignin was purchased from Sigma-Aldrich Chemical. Output yield was calculated based on the weight measurement between product (pyrolyzed lignin) and reactant. Char was ground and dissolved in THF to extract pyrolysis products by stirring for 1 h at 450 rpm. The final solution was filtered through filter paper in a funnel and concentrated using rotary evaporator.

3.1.2.5. Reactor temperature

Based on the preliminary result of high vacuum, the effect of temperature was carefully investigated under low-pressure vacuum to test the yield of pyrolysis. The Preliminary LC/MS data suggested that the amount of phenol recovery could be increased at high temperatures compared to low-temperature output. Remained char part was cooled after pyrolysis in the closed reactor, ground and stirred overnight in tetrahydrofuran (THF) to extract all the products generated during the pyrolysis using THF. Stirring time was expanded up to overnight to increase the recovery yield (w/w) out of a crude mixture of char. Samples were analyzed using GC-MS.

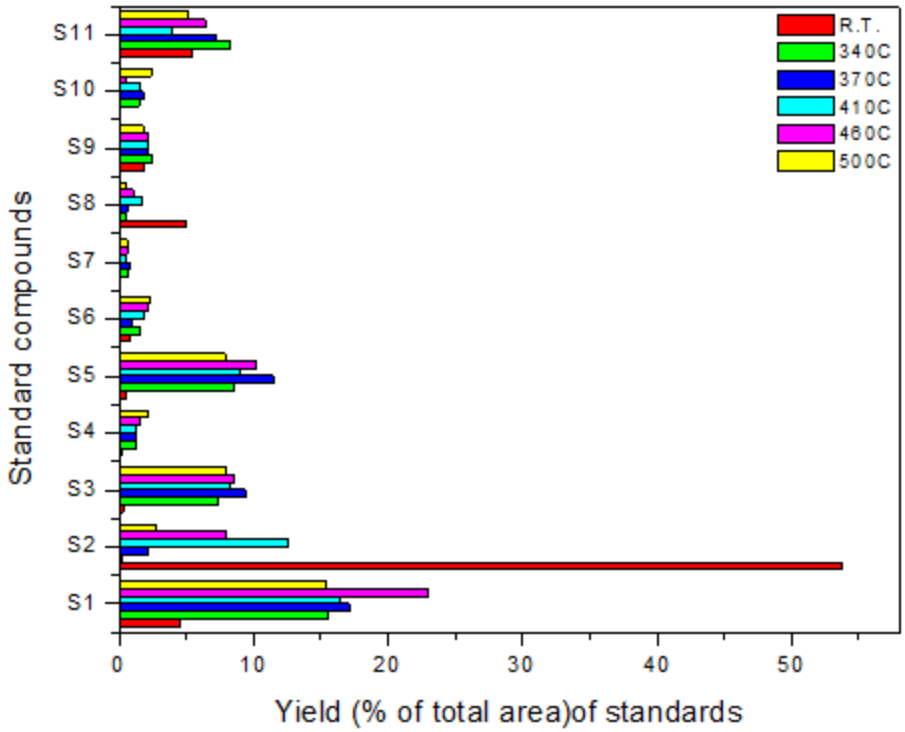


Figure 13. Recovery yield of standards at different reactor temperature.

In order to improve the efficiency of our proposed setup (Design 1 in Figure 7). Under the inert condition, we tried the 6 different reactor temperature conditions (Figure 13). Standard compounds were identified using GC-MS. We conducted multiple pyrolyzes at various temperatures to make semi-quantitative data set, which suggested that different heating temperature had a significant impact on the amount of each fractionated standards.

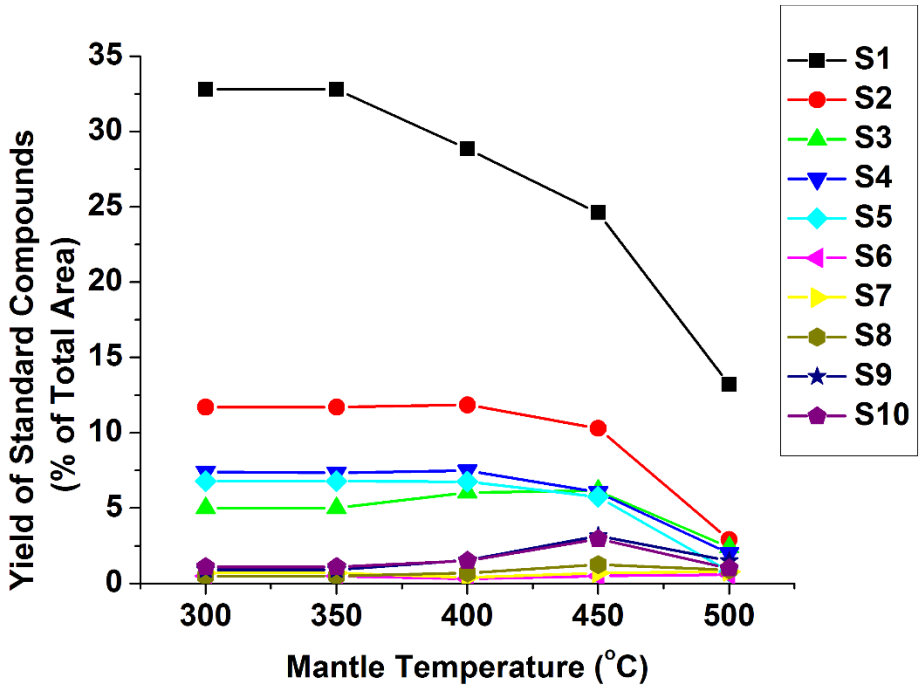


Figure 14. The recovery yield of standards at different temperature of the primary reactor. S1 = guaiacol; S2 = 4-methyl guaiacol; S3 = phenol; S4 = 4-ethyl guaiacol; S5 = 4-vinyl guaiacol; S6 = 2,6-dimethoxyphenol; S7 = vanillin; S8 = 4-hydroxy-3-methoxyacetaphenone (apocynin); S9 = catechol; S10 = homovanillic acid.

The effect of variation of the primary reactor temperature on the product composition of the pyrolysate was investigated. Five different temperature conditions of the primary reactor were examined in the range of temperature of 300 °C to 500 °C while keeping the temperature of the secondary reactor constant at 500 °C. The amount of ten representative standard compounds (S1-S10) were quantified using GC-MS to produce the semi-quantitative data set shown in Figure 14. We have used Sigma-Aldrich's lignin for this analysis as it was highly dry and easy to handle. The phenol recovery rate was highest when the pyrolysis reaction was run at 450 °C.

The lignin depolymerization mechanism is rather complicated to understand, therefore, it is difficult to predict a particular condition for higher phenol generation from pyrolysis. Lignin depolymerization is guided by several bond cleavage reactions at various temperatures, depending on the bond energies. The α- and β- alkyl-aryl ether bonds have a prominent presence in lignin[42] which cleave by heat treatment, and lead to the formation of various phenolics.[43] We have used a two reactor system to avoid prolonged exposure of the pyrolysates at the elevated temperature in order to reduce further decomposition.

During pyrolysis, it was expected that in the primary reactor, the C-C and C-O bonds would break because of their low bond dissociation energy, and the larger aromatic structures (more than one aromatic ring) would remain and be exposed to higher temperature for a short retention time,

enabling further pyrolysis to take place in a secondary reactor. In the secondary reactor, the C−OCH_3 bond will cleave at higher bond dissociation energy of 410 kJ mol^{-1}, compared with other ether linkages. It is also well known that the aromatic components start to decompose at 500 °C. Therefore, prolonged exposure to high temperatures may decrease the yield of phenolics. In addition, a short retention time at a high temperature is highly desirable and can be achieved in our setup.

Lignin can be isolated from both softwood and hardwood because they have very high amounts of guaiacyl and syringyl units, respectively. We have used lignin from the soft wood as they have less syringyl and more guaiacyl units. Because our pyrolysis was aimed at the isolation of high amounts of phenol, the dissociation of C−OCH_3 linkages was desirable and can occur during the secondary pyrolysis at high temperatures resulting in more phenol being achieved. Moreover, it has been already well established that different groups of products will dominate at different temperatures, such as low-molecular-weight oxygenated products at 250 to 400 °C, phenolic compounds at 350 to 500 °C, and aromatic hydrocarbons (benzene, toluene, and styrene) at 500 to 700 °C.[44]

The yield of compounds S1, S2, S4, and S5 decreased with primary reactor temperature. The yields of the remaining compounds showed maximums near 450 ºC. This may have occurred because of the excess decomposition that was taking place in the preheater, which resulted in even further decomposition in the quartz furnace. The increase in S3 (phenol) and S9 (catechol) is consistent with increased temperatures in the primary reactor explained by the increase in demethoxylation of compounds like S1 (guaiacol). Catechol is known to be a precursor to coke formation and further increasing pyrolysis temperatures could favor some coke formation and reduce liquid yields.

3.1.2.6. Preheating temperature

Lignin is not volatile even in a high vacuum. It does, however, decompose at a temperature above 300 ℃, with the maximum formation of phenolic products occurring between 400-450 ºC, according to literature reports. Lignin pre-heating units for vapor production was attached at the entrance of pyrolysis reactor so that the vaporized lignin only entered the hot zone in the furnace for pyrolysis as shown in Design 3 of Figure 7. Although the furnace has a quite good heat-up rate, it is not fast enough to reach the desired temperature in a flash time period (<0.1 seconds) which is essential for FVP. The lignin was weighted into a quartz vessel before and after pyrolysis. Lignin was vaporized using heating mantle at 300-500 ºC which is attached directly to the quartz pyrolysis reactor placed inside of the furnace at 500 ºC. We could separate vapor/liquid state of products easily from the char residue using a cold trap. The yield comparison between vacuum and non-vacuum condition will be prepared after GC/MS analysis. The phenol production yield (6.2%) from trapped sample ~3 times larger than that of char extraction (2.2%) under non-vacuum condition. It was shown that the trapped materials contained more phenolic compounds (over 70%

out of total peaks identified within our GC retention time frame during 20-50 min) than that of char extract (49%) (data are not shown)

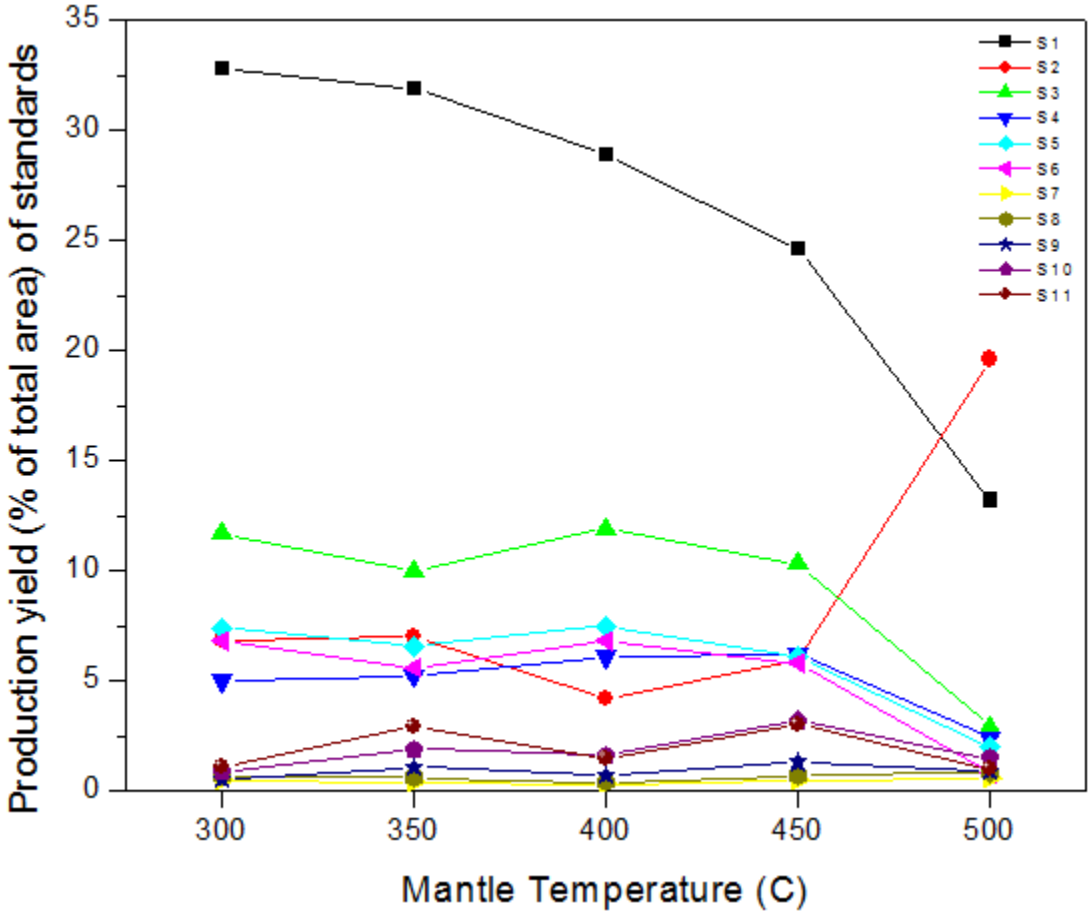


Figure 15. Lignin preheating effect on phenol production.

Pyrolysis was performed at various mantle temperatures maintaining the reaction temperature at 500 ºC. Pyrolyzed samples were collected in the cold trap unit and analyzed using GC/MS. The amount of the most of the phenolic standard compounds decreased as pre-heating temperature increased. In the case of phenol (simplest form among phenolics), when we apply the percentage (% of total peaks) within the retention (20-50min) range, the production yield increased until 450 ºC was attained (Blue line in Figure 15 & Figure 16). The phenol production was significantly decreased when the temperature reached 500 ºC.

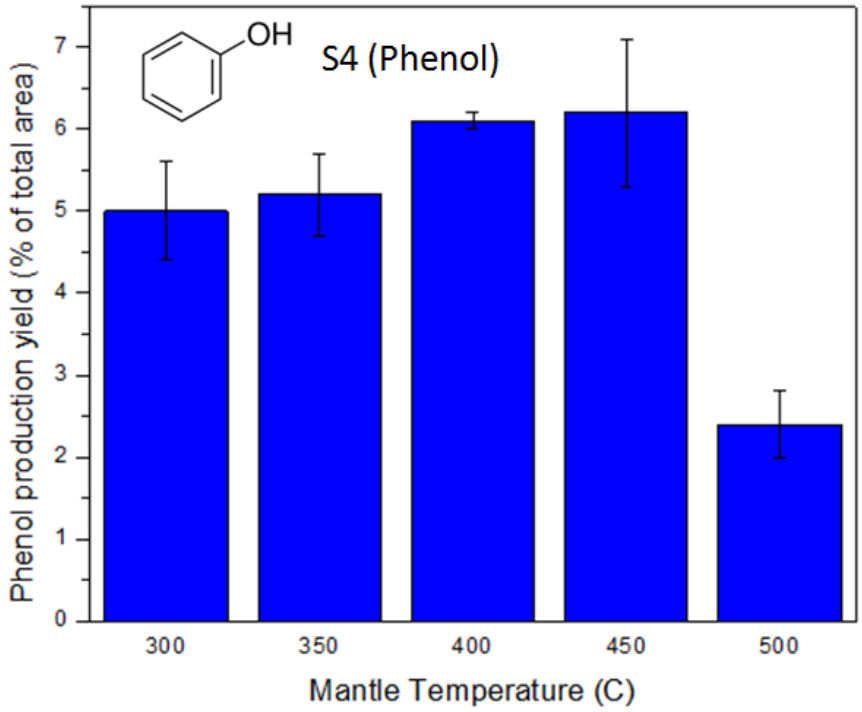


Figure 16. Phenol production yield at various temperatures in pre-heating units.

The total phenolic compounds production was gradually decreased as temperature increased as shown Figure 17. The correlation between the yield of total phenolics and weight loss was prepared as in Figure 18 to investigate the validation of optimum temperature set up in the pre-heating unit.

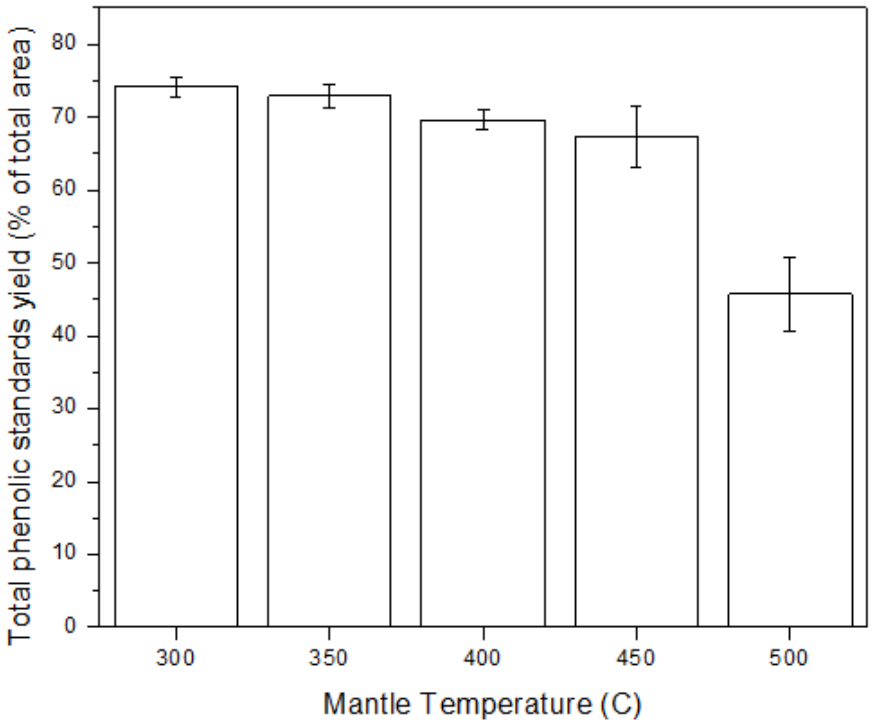


Figure 17. The yield of total phenolic compounds at various mantle temperatures

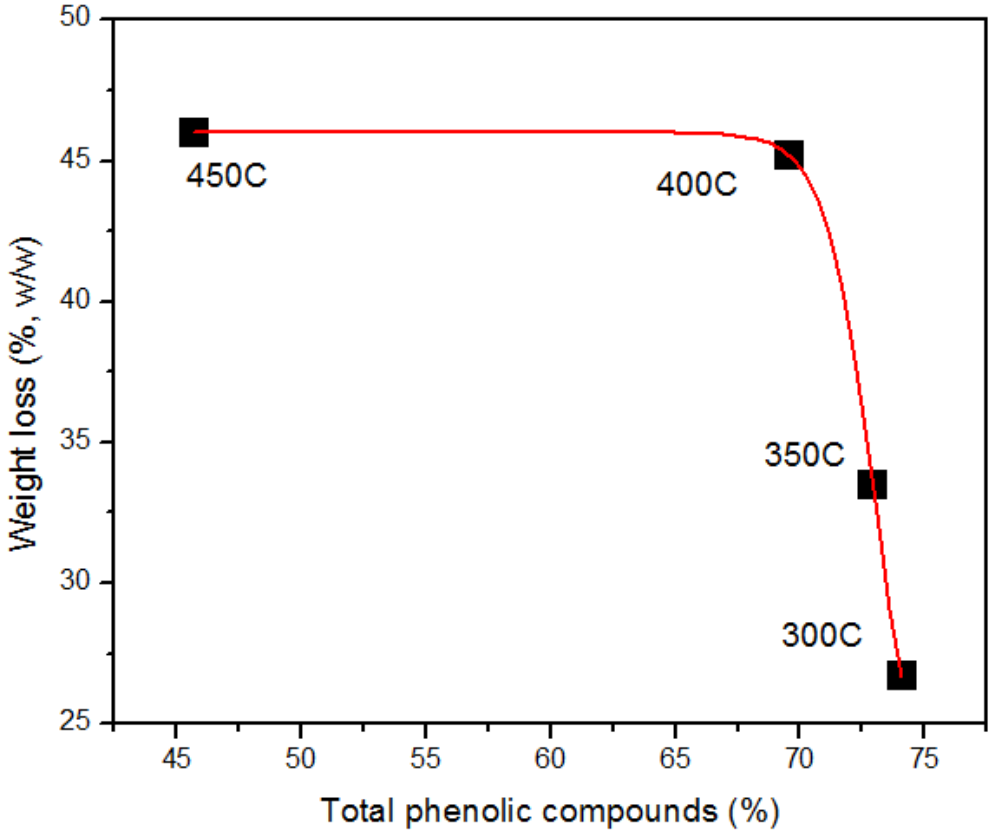


Figure 18. Correlation plot between weight loss and total phenolic output.

High temperature might help to reduce the overall reaction time needed for full decomposition of lignin. However, it also decreased production yield of total phenolic standard compounds when the temperature reaches over 400 ºC. Phenol production could be directly affected by this condition. The contour plot made by DOE program (MODDE by Umetrics) showing that we could reach our maximum % output in terms of phenol production when we have high temperature both on reactor and mantle (Figure 19). However, this contour information only shows the percentage distribution of phenol out of total peaks identified. It does not consider the loss of total phenolics, our interest, in the system. Further investigation might be required to understand this issue. The weight loss of lignin by vaporization at the pre-heating units did not directly increase the total phenolic compounds.

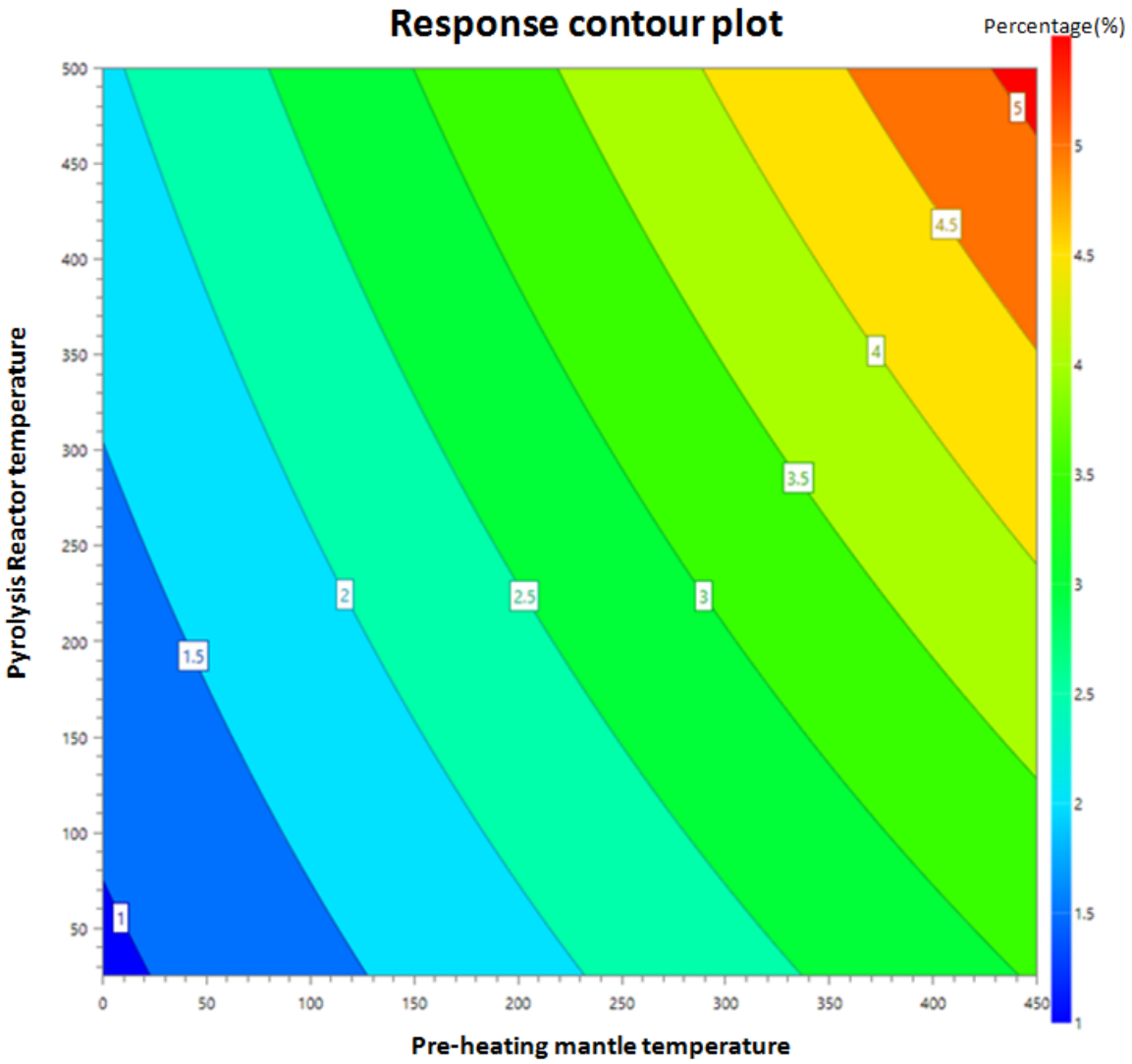


Figure 19. Response contour plot made by DOE program (MODDE by UMetrics)

The contour plot shows the correlation between reactor temperature and preheating mantle temperature corresponding to the weight loss of lignin after pyrolysis.

3.1.2.7. Effect of the raw material (lignin) on the yield of phenolics

The oil product generated from pyrolysis at a primary reactor temperature of 420 ºC and a secondary reactor temperature at 500 ºC was analyzed using GC-MS. Six different kinds of lignin were obtained from various suppliers and pyrolyzed under the same condition. The amount of pyrolyzed material was analyzed gravimetrically and analytically. These materials are listed below.

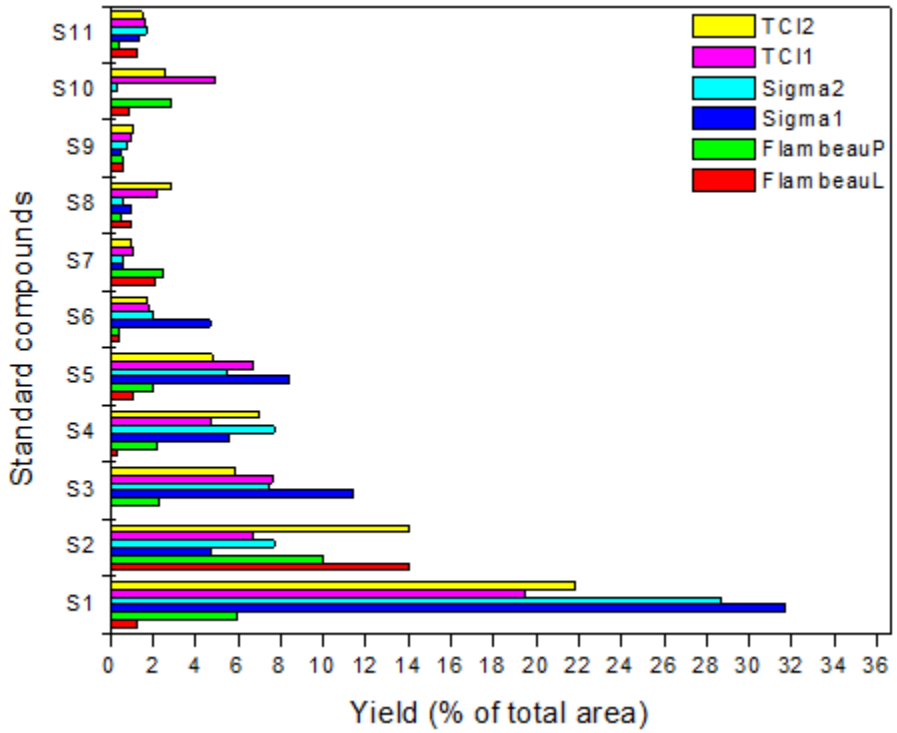


Figure 20. Raw lignin materials were tested using various supplier's material.

The intensive semi-quantitative GC-MS analysis was performed on pyrolyzed product of lignin obtained from a various source (Figure 20). Depending on the wood process, commercial lignin is treated in a different way and results in different final phenolic composition. For example, Flambeau River Paper LLC, our collaborator, process wood (mostly maple and birch) to produce pulp out of it to make the paper product. Water soluble lignosulfonate will be easily separated during the acidification process with sulfur and limestone. Alkali form of lignin will be obtained when the process uses magnesium and ammonia in the step. Different kind of sugar units might be attached to lignin. Birch, for example, will produce xylose attached lignin and followed by xylitol production process. In general, S1 was observed in the highest amount compare with all standards, and using Flambeau River Paper lignin, very small amount of phenol was isolated.

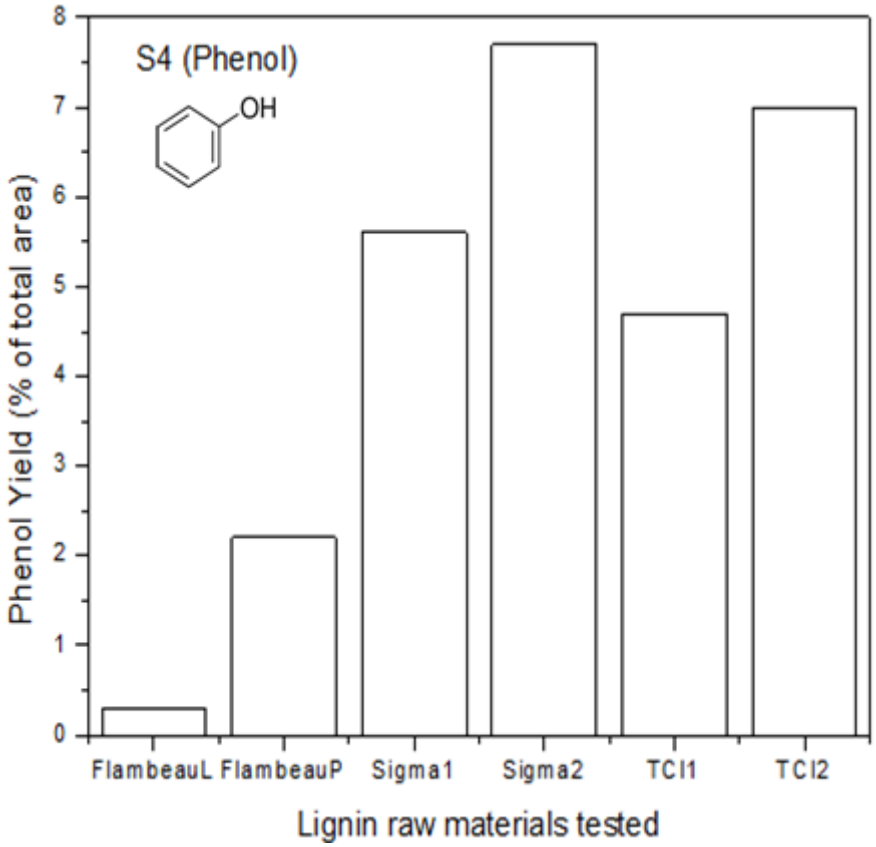


Figure 21. Phenol production from different raw materials.

FlambeauL-Sugared lignosulfonate, FlambeauP-Desugared lignosulfonate, Sigma1-alkali lignin with a low sulfonate, Sigma2-alkali lignin, TCI1-dealkaline lignin, TCI2-alkaline lignin.

Most of the lignin raw materials produced a decent amount of phenol except Flambeau liquid lignin (Figure 21). It is expected features because it is sugared lignosulfonate containing only 55 % of lignin. We found Sigma2 (alkali lignin containing 5% moisture impurities) has highest lignin production yield among them. We used this product as our model material for the conditional test to get comprehensive GC-MS analysis. Figure 20 and Figure 21 shows an initial trend of the source of the lignin on the final phenol or all phenolic derivatives in the pyrolyzed product; which suggests that the source of lignin is very critical.

3.1.2.8. Mass balance of the pyrolysis process;

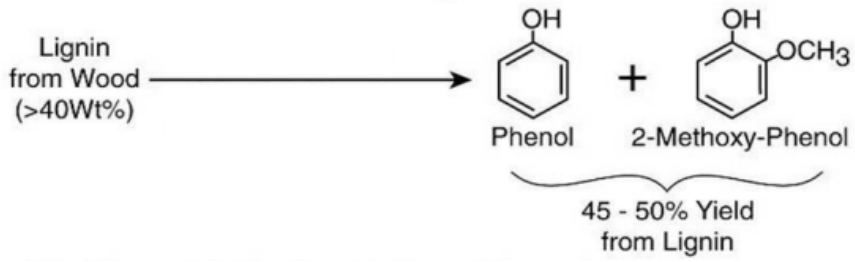


Figure 22. Isolation of phenol from lignin by pyrolysis

Mass balance for the lignin pyrolysis was performed by carefully weighing each component of the pyrolysis setup prior and after the pyrolysis run. This was performed for four different types of lignin and the results are summarized in Table 2. Mass balance and phenolic yields for different lignin starting materials. The yield of standard compounds was compared between the different lignin used in the helium flow pyrolysis.

Table 2. Mass balance and phenolic yields for different lignin starting materials.

Mass balance between different phases	Vacuum Setup (SA)	Helium Setup			
		SA	TCI (alk)	TCI (dealk)	FRP-LLC
Char (Solid) (wt. %)	55.0	54.9	62.6	54.9	52.7
Phenolics (Liquid) (wt. %)	7.1	12.6	11.5	3.2	17.9
(Gases)	37.9	32.5	25.9	41.9	29.4
Main phenolics identified					
Guaiacol	31.43	10.32	9.48	2.84	4.35
2-methoxy-4-methylphenol	9.40	1.95	1.34	0.45	0.65
Phenol	6.30	9.41	20.22	4.59	3.97
4-ethyl-2-methoxyphenol	6.83	1.85	0.91	0.40	0.58
2-methoxy-4-vinylphenol	3.70	0.66	1.44	0.00	0.22
2,6-dimethoxyphenol	0.53	0.57	0.25	0.15	0.64
vanillin	0.87	0.03	0.92	0.89	0.83
4-hydroxy-3-methoxyacetaphenone	0.63	0.55	0.61	0.46	0.37
catechol	0.10	11.66	2.27	2.02	4.15
Homovanillic acid	1.40	0.50	0.43	0.22	0.18

3.1.3. Phenol purification and refinement

3.1.3.1. Purification by solvent extraction

Phenols are very important organic compounds used as starting materials or intermediates for the preparation of many aromatic derivatives [9]. Phenol also found as an important feature in biologically and pharmacologically active substances. A large amount of phenol can be obtained from the pyrolysis of lignin. However, it has a small portion of the mixture of pyrolyzed lignin product. In order to isolate pure phenol material from the pyrolysate, various purification methods were employed. Firstly, a solvent extraction was performed and phenolics were isolated by slightly alkaline phase. Secondly, a fractional distillation was performed on the concentrated phenolics. Lastly, the phenol-enriched fraction was purified by column chromatography. A solvent gradient was used for purification of the pyrolysate. Firstly, a neat hexane was used and phenolics were collected, then the amount of ethyl acetate in the eluent solvent was increased gradually and at a different stage, different fractions were collected. At last, the column was rinsed with neat ethyl acetate.

The pH of the aqueous layer was adjusted between 10 to 12. Phenolics forms sodium salt in basic conditions and stays in aq. layer. After that, the organic layer was separated and washed three times with NaOH solution. The organic layer was separated, dried over anhydrous sodium sulfate, concentrated and analyzed by GC-MS, which has mostly non-phenolics. The aqueous layer was acidified using concentrated HCl and the pH was adjusted to 4-5. The aq. layer was again extracted using dichloromethane three times. In acidic conditions, phenolics stay in the organic layer, which was separated, dried over anhydrous sodium sulfate, concentrated as shown in Figure 23. This layer has a high amount of phenolics as analyzed by GC-MS. Using the solvent extraction method, we could successfully increase the amount of phenol in the total pyrolysate.

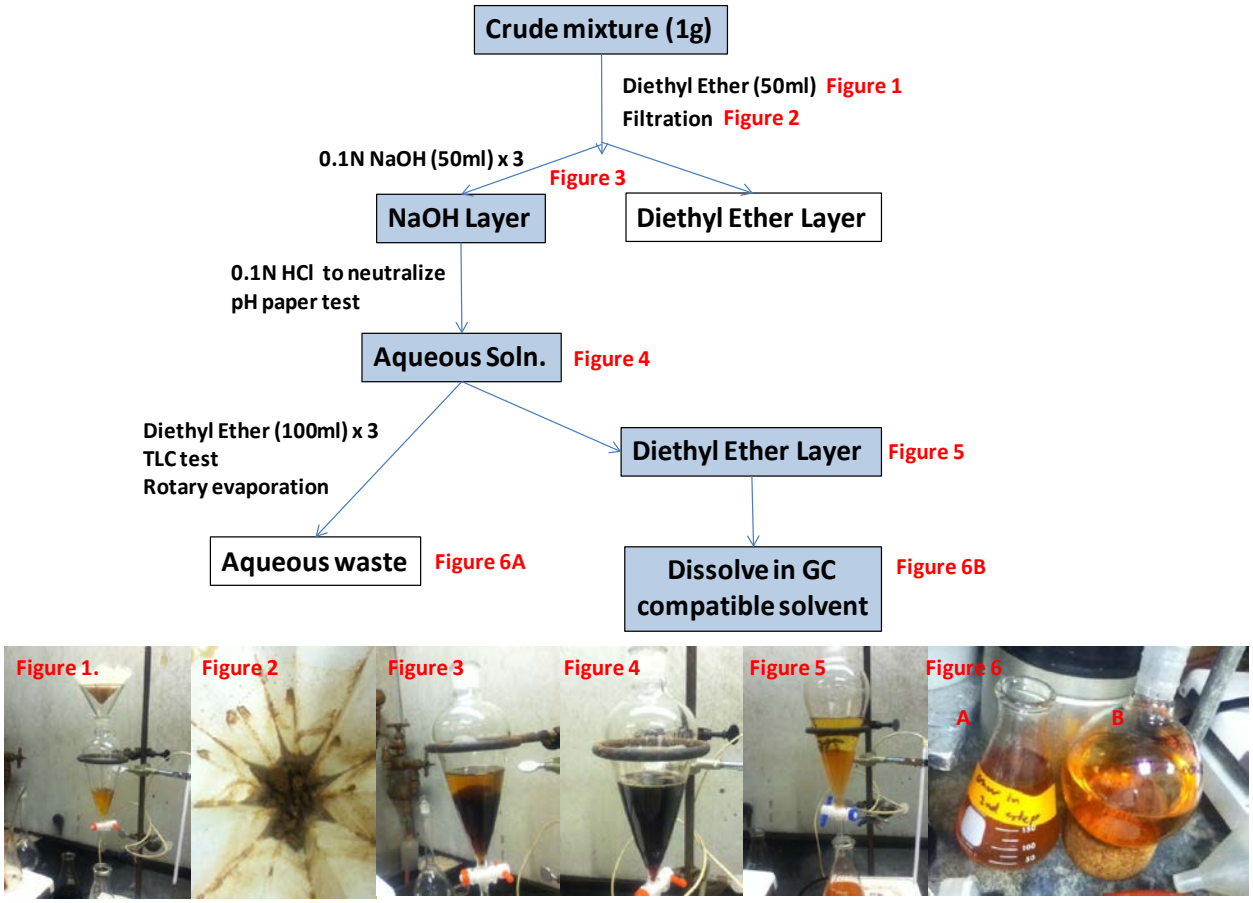


Figure 23. Scheme of phenol refinement steps.

Step by Step procedure of solvent extract using pyrolysate:

- 1.0 g of the lignin pyrolysis reaction mixture was weighted in the 250 mL conical flask.
- 50 mL diethyl ether was added to the conical flask.
- Precipitant which is not solubilized with diethyl ether were filtered out using filter paper in a 250 mL separating.
- 0.1N NaOH was added and mixed together vigorously.
- Washing was repeated 3 times with same 0.1 NaOH.
- The aqueous phase was separated using a separating funnel. Phenolic components were moved to the aqueous phase, leaving most of the others in the ether layer.
- 0.1N HCl was added to neutralize the mixture. Neutralized mixture was placed in a separating funnel (500ml ca.).
- Ether was added to extract acidified solution. The phenolic compound was transferred into the ether layer. The ether layer was concentrated with a rotary evaporator.
- The presence of phenol was tested on TLC plate with fluorescence indicator.

We have examined various solvents for the extractions of the phenolics in order to investigate the efficiency of the extraction method. Concentrated ether soluble pyrolysate was used as a starting material for further refinement and isolation step.

Figure 24. Products of pyrolysis of lignin.

The char (left) after pyrolysis was used for the solvent extraction and phenol isolation (Figure 24). Highly concentrated phenolics (black liquid on the right) prepared from cold trap units were dissolve in the ether after several refinement steps as shown in Figure 23, which was distilled further. MSC lignin produced the highest amount of phenol among phenolics when it is pyrolyzed. The increased phenol amount using the solvent extraction was reported in Table 3The aqueous lay was acidified using concentrated HCl with pH 4-5. The aqueous layer was extracted using dichloromethane three times. In the acidic condition, phenolics stay in the organic layer, which was separated, dried over anhydrous sodium sulfate, concentrated. This layer has a high amount of phenolics as analyzed by GC/MS.

Table 3. Product composition of phenolics in different fractions of solvent extractions.

Representative phenolics	Fractions after solvent extraction	
	Nonphenolic	Phenolics
Guaiacol	1.20	17.2
2-methoxy-4-methylphenol	0.82	1.86
Phenol	0.00	15.2
4-ethyl-2-methoxyphenol	1.90	1.88
2-methoxy-4-vinylphenol	0.00	0.00
2,6-dimethoxyphenol	0.00	14.5
vanillin	0.00	0.00
4-hydroxy-3-methoxyacetaphenone	0.00	0.00
catechol	0.00	2.58
Homovanillic acid	0.00	0.00

3.1.3.2. Purification by distillation.

Phenolics obtained after the solvent extraction were concentrated and distilled using fractional distillation setup as shown in Figure 25. Fractional distillation is an industrially viable protocol for refinement and isolation of a multitude of organic chemicals.

Figure 25. Lab-scale Vacuum Distillation Setup for Phenolics.

Different fractions were collected (Figure 26) at a different temperature under constant vacuum pressure. The first, the second, and the third fraction were isolated at 70 °C, 100 °C, 140 °C with fourth residual fraction, respectively. The first fraction has the highest amount of phenol, followed by the second and the third fraction with reduced amount of phenolics (Table 4).

Table 4. Product Composition During Fractional Distillation of Phenolics.

Representative Phenolics	First fraction	Second fraction	Third fraction	Fourth fraction
Guaiacol	29.6	23.3	14.4	0.00
2-methoxy-4-methylphenol	0.00	2.64	4.16	0.00
Phenol	61.6	24.5	10.1	0.00
4-ethyl-2-methoxyphenol	0.00	0.00	4.21	2.62
2-methoxy-4-vinylphenol	0.00	0.00	0.00	0.00
2,6-dimethoxyphenol	0.00	2.78	8.92	25.2
vanillin	0.00	0.00	0.00	0.00
4-hydroxy-3-methoxyacetaphenone	0.00	0.00	0.00	0.00
catechol	0.00	0.00	4.28	12.6
Homovanillic acid	0.00	0.00	0.00	0.00

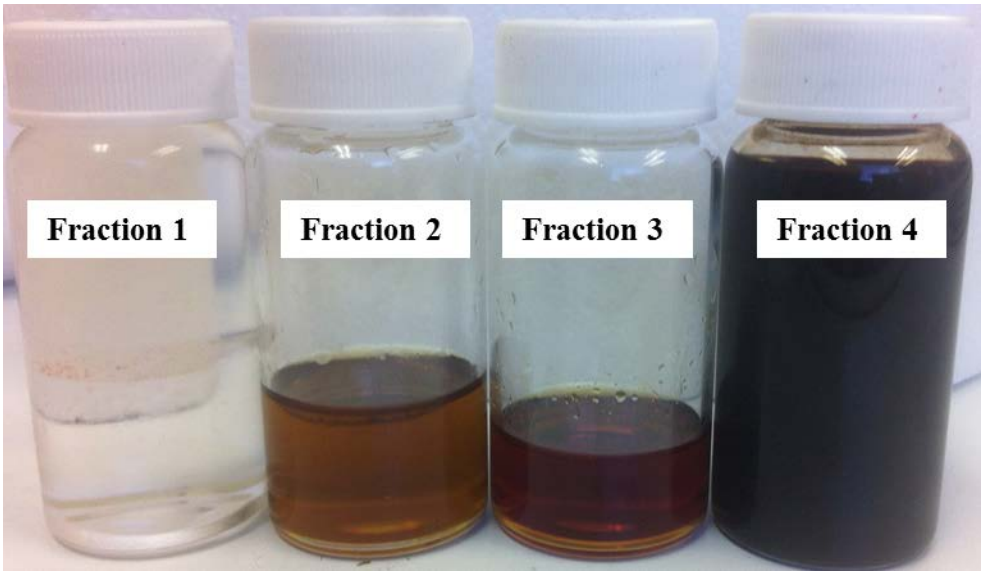


Figure 26. Different fractions (Phenolics) isolated during fractional distillation.

3.1.3.3. Flash chromatography

The phenol-enriched fraction from the distillation setup was further purified by column chromatography as shown in Table 5. Each fraction has different distribution pattern of phenolic compounds as in Figure 27. Using the flash chromatography technique, we could increase the purity of phenol produced during pyrolysis followed by refinement.

Table 5. Various fractions isolated during the column chromatographic separation using hexane /ethyl acetate.

Main phenolics identified	*Different Fractions*				
	1st	2nd	3rd	4th	5th
Guaiacol	10.96	12.29	8.51	0.00	0.00
2-methoxy-4-methylphenol	5.82	5.69	3.70	2.24	0.00
Phenol	1.10	2.16	3.03	0.00	0.00
4-ethyl-2-methoxyphenol	5.67	4.82	3.37	1.85	0.00
2-methoxy-4-vinylphenol	1.96	1.29	1.28	4.16	6.11
2,6-dimethoxyphenol	0.00	1.42	1.05	0.00	0.00
Vanillin	0.00	1.77	2.74	1.07	0.00
4-hydroxy-3-methoxyacetaphenone	0.00	3.04	6.72	2.87	0.00
Catechol	1.74	3.38	8.90	3.34	0.00
Homovanillic acid	0.00	1.48	10.39	33.81	0.00

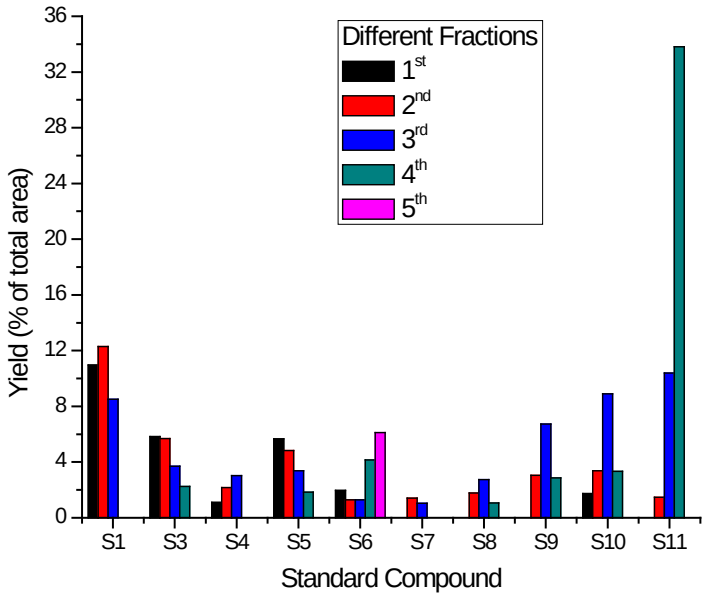


Figure 27. Different fractions isolated after column purification of pyrolysate.

The column chromatography was used in a gradient condition, where first we started with 100 % hexane and then increased the amount of ethyl acetate as phenolics started to elute. Different fractions were collected, separated and isolated by evaporation of solvents. The fractions were then analyzed by GC-MS as shown Table 5 and Figure 27. The material was still in mixture form, which was purified using the same method again, but decreasing the amount of ethyl acetate.

Table 6. Phenolic composition during chromatographic purification of the first fraction.

Main phenolics identified	Separation of First Fraction	
	1-2	1-3
Guaiacol	9.686	0.822
2-methoxy-4-methylphenol	9.686	0.213
Phenol	3.573	0.131
4-ethyl-2-methoxyphenol	7.016	0.223
2-methoxy-4-vinylphenol	2.306	0.180
2,6-dimethoxyphenol	0.000	1.158
Vanillin	0.000	0.777
4-hydroxy-3-methoxyacetaphenone	0.000	0.341
catechol	0.000	10.396
Homovanillic acid	0.000	0.879

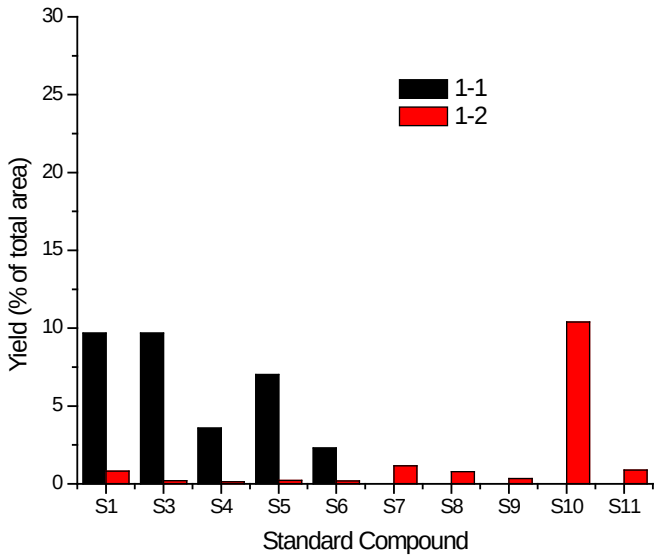


Figure 28. Graphical representation of the phenolic composition during chromatographic purification of the first fraction.

The first fraction was again purified using a similar method as shown in Figure 28 and Table 6 demonstrates the product composition. A decent separation was observed; in the second fraction, a very high amount of guaiacol was found. The second fraction from the first column was also purified using a similar method as shown in Figure 29. A good separation was observed in the column purification. Phenol was isolated with ~10 % of the total in the mixture (Table 7).

Table 7. Phenolic composition during chromatographic purification of the second fraction.

Main phenolics identified	Separation of Second Fraction					
	2-1	2-2	2-3	2-4	2-5	2-6
Guaiacol	5.12	26.6	0	0	0	0
2-methoxy-4-methylphenol	1.52	11.5	0	0	0	0
Phenol	0	9.78	2.02	0	0	0
4-ethyl-2-methoxyphenol	0	7.11	0	0	0	0
2-methoxy-4-vinylphenol	0	1.40	0	0	0	0
2,6-dimethoxyphenol	0	0	0	3.48	1.93	3.47
Vanillin	0	0	0	0	8.99	0
4-hydroxy-3-methoxyacetaphenone	0	0	0	0	13.9	15.9
Catechol	0	0	8.09	37.2	14.7	1.46
Homovanillic acid	0	0	0	0	0	0

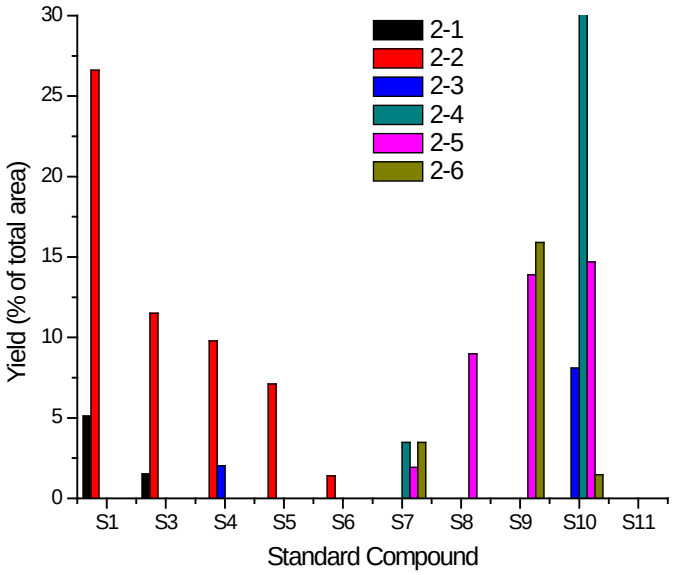


Figure 29. Graphical representation of the phenolic composition during chromatographic purification of the second fraction.

Table 8. Phenolic composition during chromatographic purification of the third fraction

Main phenolics identified	Separation of First Fraction		
	3-2	3-3	3-4
Guaiacol	13.54	0.290	0.422
2-methoxy-4-methylphenol	7.276	0.296	0.175
Phenol	5.259	0.000	0.000
4-ethyl-2-methoxyphenol	7.734	0.191	0.000
2-methoxy-4-vinylphenol	2.919	0.716	1.646
2,6-dimethoxyphenol	0.000	2.144	0.000
Vanillin	0.000	5.647	0.000
4-hydroxy-3-methoxyacetaphenone	0.000	20.29	1.436
Catechol	0.000	1.893	1.079
Homovanillic acid	0.000	0.290	34.12

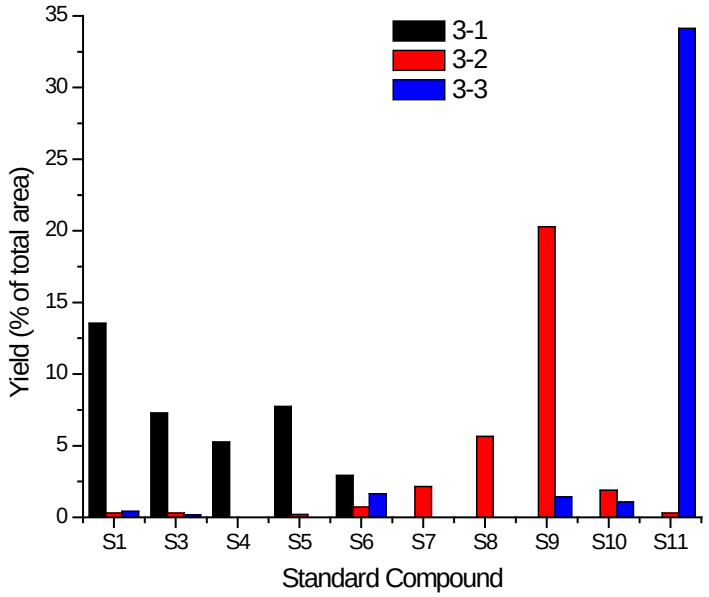


Figure 30. Graphical representation of the phenolic composition during chromatographic purification of the third fraction.

The third fraction was purified using gradient method and pure homovanilic acid was observed in the last fraction as shown in Figure 30 and Table 8.

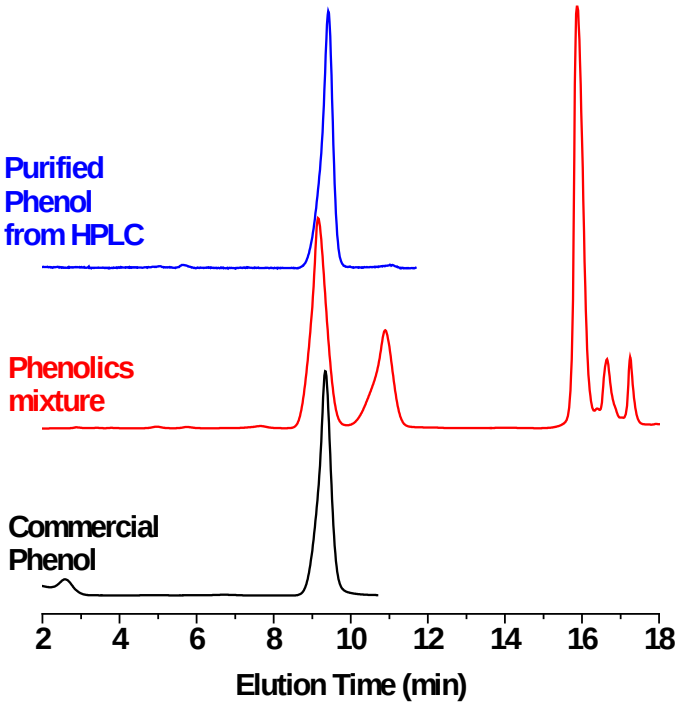


Figure 31. HPLC of the commercial phenol and purified phenol.

The second fraction from the column chromatography of the second fraction (2-2) was used for HPLC analysis using reverse phase column and water and methanol as an eluent, we have seen peaks of more than five chemicals in the HPLC plot of column purified phenolics as shown in Figure 31. For, reference, we have also analyzed pure commercial phenol by same HPLC system and it shows peak ~9.2 min. Our column purified phenolics also exhibited a peak at ~9.2 min, which confirmed the presence phenol in our purified material. The fraction of phenol was collected from the drain of the HPLC and concentrated at rotary evaporator. The concentrated phenolic of the drain has an identical peak with commercial phenol.

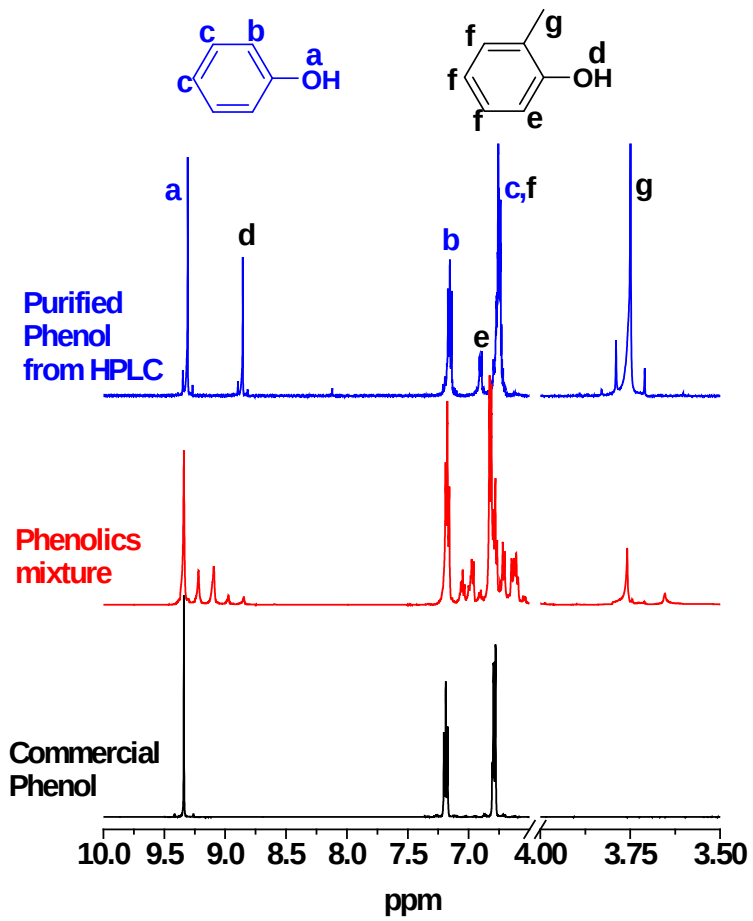


Figure 32. ^{1}H NMR of the commercial phenol and purified phenol.

^{1}H NMR spectra of the column purified phenolics, commercial pure phenol, and HPLC purified phenol is shown in Figure 32. ^{1}H NMR of column purified phenolic showed many peaks in the aromatic region confirming the presence of more than one chemical. However, the column purified phenolics has two very strong peaks in aromatic region matching with commercial phenol exactly. The concentrated fraction from HPLC drain showed a peak for phenol and methyl phenol. The green phenol was successfully purified with a slight amount of methyl phenol from a mixture of more than 40 phenolics.

3.1.4. Investigation of additional methods for depolymerization of lignin.

The polyphenolic structure in the lignin is chemically very stable, and therefore difficult to transform or structurally modify. Harsh reaction conditions are required to break down lignin [2]. In addition, lignin contains a large amount of oxygen which prevents the simple depolymerization products from being used as a substitute or additive for conventional liquid fuels. When

considering the use of lignin as a renewable raw material, crude bio-oil need to go to the way to high value added products such as phenolics (phenolic compounds) and other fine chemicals. Not only searching for the low material resources but also searching effort for the efficient conversion processes are required to get a high yield of products with low cost of operation. Fast pyrolysis aims exclusively at the maximum production of liquid products and does not regard the chemical composition of the pyrolysate. Phenolics are extremely interesting building blocks for various application. We have investigated several depolymerization techniques to improve the yield of the phenol-enriched pyrolysate.

3.1.4.1. Depolymerization by microwave irradiation:

The depolymerization of lignin under pyrolysis conditions is extremely energy intensive process. This reaction generally follows a radical mechanism, which can also be produced using microwave irradiation or sonication, which are relatively environmentally benign sources of energy. We have depolymerized lignin using microwave irradiation as shown in Figure 33 & Figure 34. The product composition after the microwave irradiation is shown in Table 9. A significant difference was observed during microwave irradiation compared with pyrolysis.

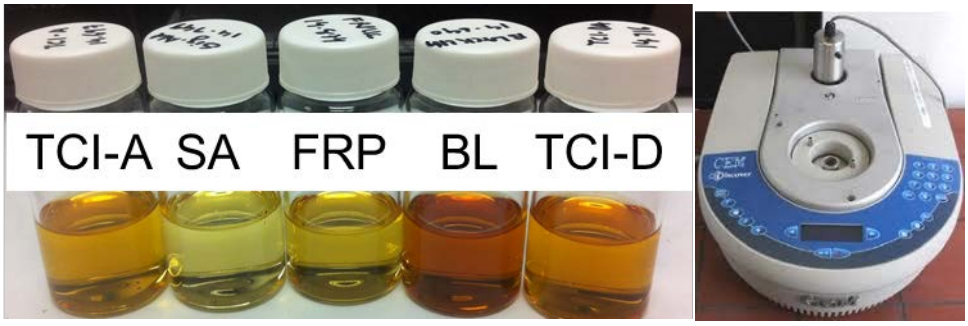


Figure 33. Microwave reactor for depolymerization

(a) Phenolic samples after depolymerization of lignin under microwave in ethyl acetate and (b) microwave reactor.

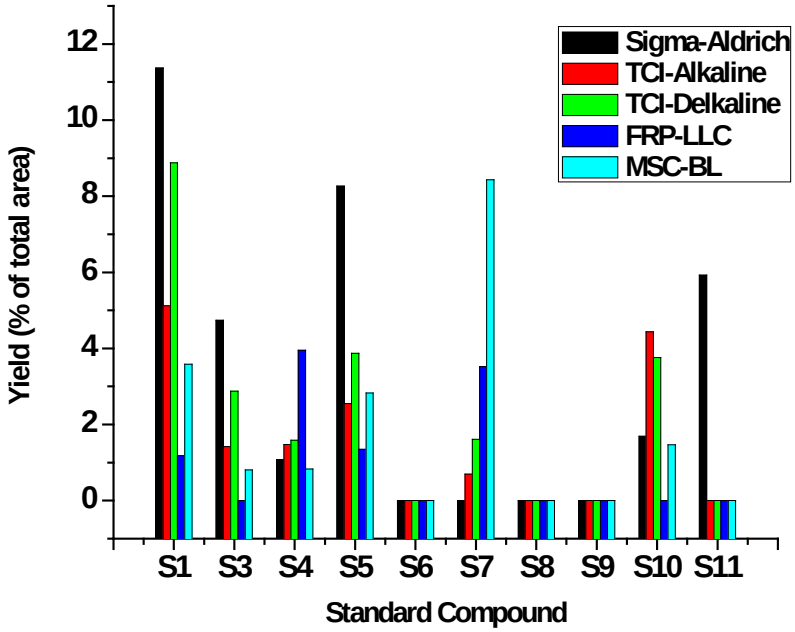


Figure 34. Product composition in various lignin after depolymerization under microwave irradiation.

Table 9. Depolymerization of lignin under microwave irradiation.

Phenolics	Lignin Materials				
	SA	TCI (alk)	TCI (dealk)	FRP-LLC	MSC-BL
Guaiacol	11.371	5.122	8.876	1.177	3.582
2-methoxy-4-methylphenol	4.742	1.420	2.878	0.000	0.805
Phenol	1.078	1.473	1.583	3.951	0.827
4-ethyl-2-methoxyphenol	8.265	2.552	3.868	1.346	2.827
2-methoxy-4-vinylphenol	0.000	0.000	0.000	0.000	0.000
2,6-dimethoxyphenol	0.000	0.692	1.611	3.519	8.432
vanillin	0.000	0.000	0.000	0.000	0.000
4-hydroxy-3-methoxyacetaphenone	0.000	0.000	0.000	0.000	0.000
catechol	1.693	4.436	3.762	0.000	1.464
Homovanillic acid	5.927	0.000	0.000	0.000	0.000

3.1.4.2. Depolymerization using ultrasonication

Base-catalyzed depolymerization of lignin can be assisted through ultrasonication. Sonication is one of the environmentally benign approaches for the depolymerization of lignin. The temperature of the lignin dispersion was maintained at 23 °C using a water bath as shown in Figure 35. The product composition is described in

Table 10, where a very high amount of vanillin was observed as one of the product.

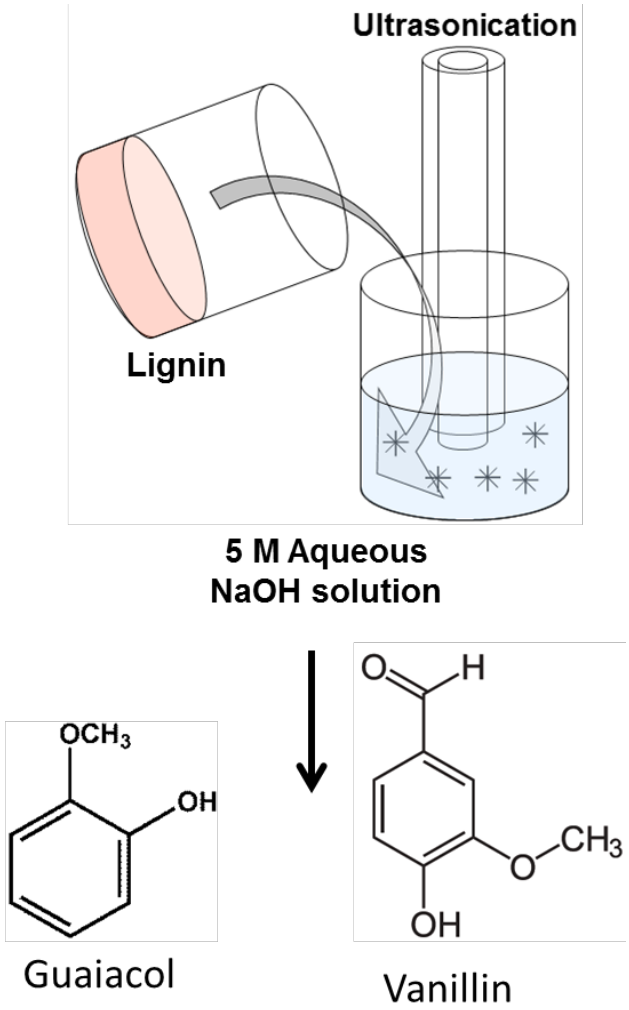


Figure 35. Sonication of black liquor under alkaline condition.

Table 10. Product composition during sonication of black liquor under severe alkaline condition.

Compound name	Retention time (min)	% of the total

Guaiacol	27.917	5.647
2-methoxy-4-methylphenol	Not Detected	0.000
Phenol + Methylphenol	Not Detected	0.000
4-ethyl-2-methoxyphenol	Not Detected	0.000
2-methoxy-4-vinylphenol	Not Detected	0.000
2,6-dimethoxyphenol	Not Detected	0.000
Vanillin	39.149	17.060
4-hydroxy-3-methoxyacetaphenone	Not Detected	0.000
Catechol	Not Detected	0.000
Homovanillic acid	Not Detected	0.000

3.1.4.3. *Formate-assisted pyrolysis*.

The formate-assisted pyrolysis was performed at Prof. William DeSisto's laboratory at the University of Maine (Orono,ME). The calcium compounds were incorporated in the preparation of feedstock of the lignin and the pine sawdust by forming a solution/suspension with the salt in deionized water and then incorporating the dry powder. The pretreated lignin and pine sawdust were dried in an oven to 5–10 % moisture and sieved to achieve particles smaller than 1.5 mm. The prepared feedstock was pyrolyzed with 40–60 mesh sand as a heat transfer medium in a 3.5 cm X 30 cm entrained flow reactor. The reactor temperature was measured using two thermocouples located on the vertical axis measured 3.0 and 9.5 in. from the top of the reactor. The pine/calcium formate mixture was metered through a screw feeder and pneumatically fed into the reactor, using a nitrogen flow rate of 6 L/min.

The feed rate of the pretreated pine was approximately 1 g/min, and up to 1 kg of material could be processed in a run. The pyrolysis temperature was 500 °C. Immediately downstream of the reactor, char was separated using a hot gas filter (HGF) also maintained at 500 °C. The total vapor residence time in the fluidized bed reactor [45] and the HGF was 12 s, with about 90% of that time in the HGF. After the vapor passed through the hot gas filter the liquid was collected in a condenser operated at 6 ºC, followed by an electrostatic precipitator (ESP) to collect aerosols. The gas exhaust from the ESP was periodically sampled and analyzed by GC. The exhaust gas flow rate was measured using a dry gas meter. The liquid yield was determined by weighing the condenser and electrostatic precipitator before and after pyrolysis. The char yield was determined by weighing the material collected in the reactor and the char filter, and then subtracting the mass of calcium compounds)[46].

During the formate-assisted pyrolysis, all material is getting in their reduced form. In order to transform bio-oil into a transportation fuel, oxygen must be removed and hydrogen must be

added. The material was analyzed by GC-MS and purified by solvent extraction method. Firstly, the material was dissolved in methylene chloride and extracted with 0.1 M NaOH solution. All phenolics moves to the aqueous solution, which was later acidified using HCl solution and isolated by solvent extraction. The phenolic composition, before and after solvent extraction is shown in Table 11. As can be observed, the amount of phenol increased significantly after the extraction process.

Table 11. The composition of Phenolics in Formate-Assisted Pyrolysate

Representative Phenolics	Sawdust		Lignin
	Pyrolysate without treatment	Phenolics	Pyrolysate without treatment
Guaiacol	1.66	1.92	0.000
2-methoxy-4-methylphenol	1.38	1.34	0.000
Phenol	8.38	12.2	12.30
4-ethyl-2-methoxyphenol	0.00	0.00	0.000
2-methoxy-4-vinylphenol	0.00	0.00	1.835
2,6-dimethoxyphenol	0.00	0.00	0.000
vanillin	0.00	0.00	0.000
4-hydroxy-3-methoxyacetaphenone	0.00	1.58	0.000
catechol	4.03	3.50	1.477
Homovanillic acid	0.00	0.00	0.000

The amount of phenol increased significantly after the extraction process (Table 12).

Table 12. Phenolics Distribution and composition during Fractional Distillation of Phenolics.

Representative Phenolics	PhOH fraction-1	PhOH fraction-4	Phenolics 2nd Fraction	Bio-oil Lignin-aged 1month	Bio-oil-Lignin
Guaiacol	0.000	37.60	33.24	0.000	0.000
2-methoxy-4-methylphenol	0.000	0.000	0.000	0.000	0.000
Phenol	2.995	24.60	27.10	11.67	10.92

4-ethyl-2-methoxyphenol	0.000	0.000	0.000	3.439	0.000
2-methoxy-4-vinylphenol	0.000	0.000	0.000	0.000	0.000
2,6-dimethoxyphenol	0.000	0.000	0.000	0.000	0.000
Vanillin	0.000	0.000	0.000	0.000	0.000
4-hydroxy-3-methoxyacetaphenone	0.000	0.000	0.000	0.000	0.000
Catechol	0.000	0.000	0.000	0.000	0.000
Homovanillic acid	0.000	0.000	0.000	0.000	0.000

Bio-oil generated through fast flash pyrolysis in a continued fluidized reactor gave out concentrated bio-oils either from saw-dust or from lignin itself. The production distribution of aromatic compounds was narrowed down to two or three phenolic compounds.

3.1.4.4. Catalytic depolymerization

Depolymerization of lignin was investigated using various catalytic conditions. We have used BPEI/TCA MOF, TM-728-1.25 and aluminum fumarate as a different catalyst. MOF-Catalyzed pyrolysis of lignin was performed. 28.5 g of lignin was mixed with 1.5 g of MOF and pyrolysis was performed under same conditions. The main purpose for catalytic depolymerization was to make it more economical, environmentally benign and easy for operation. MOFs and nanoparticles are considered excellent heterogeneous catalyst due to their unique properties. Graphene-Oxide based MOF has exhibited great selectivity towards cleaving of methoxy and converting it to the hydroxy group thus, high amount of phenol and catechol observed compared with guaiacol as shown in Table 13 and Figure 36.

Table 13. Pyrolysis of lignin using a different catalyst.

Main phenolics identified	*Sigma-Aldrich (Kraft-Coniferous) lignin*			
	Without Catalyst	GO-Cu MOF	Ca-TA MOF	Iron Oxide NP
Guaiacol	10.32	2.82	4.81	12.7
2-methoxy-4-methylphenol	1.95	0.63	0.35	4.91
Phenol	9.41	10.73	3.83	5.16
4-ethyl-2-methoxyphenol	1.85	0.39	1.31	5.52
2-methoxy-4-vinylphenol	0.66	0.14	0.18	1.74
2,6-dimethoxyphenol	0.57	0	0	0.76
vanillin	0.03	0	0	0.80
4-hydroxy-3-methoxyacetaphenone	0.55	0.18	0.34	1.01
catechol	11.66	10.23	8.64	8.21
Homovanillic acid	0.50	0	0.28	2.47

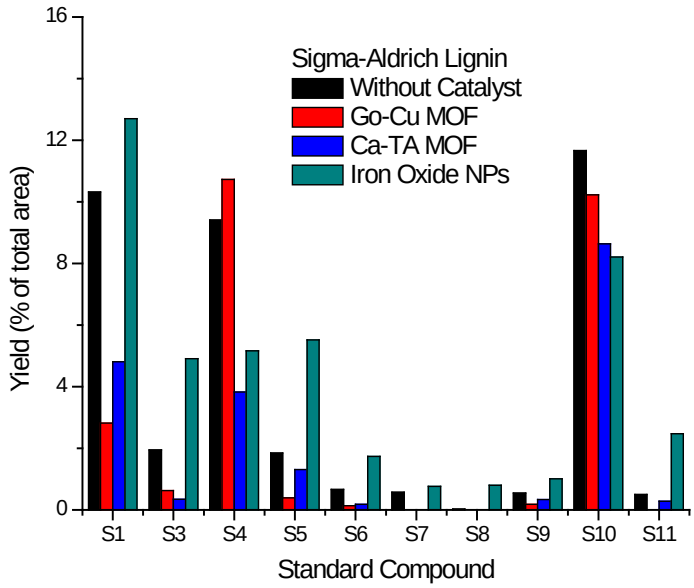


Figure 36. Catalytic depolymerization of lignin.

MOF-Catalyzed pyrolysis of lignin was performed. 38.0 g of lignin was mixed with 2.0 g of MOF and pyrolysis was performed under same conditions. The main purpose for catalytic depolymerization was to make it more economical, environmentally benign and easy for operation. MOFs are considered excellent heterogeneous catalyst due to their unique properties.

Table 14. Pyrolysis of lignin using different catalyst (second group)

Representative Phenolics	*TCI (Kraft-Coniferous) lignin*			
	Without Catalyst	TM-728	BPEI/TCA MOF	Aluminum Fumarate
Guaiacol	9.48	29.1	18.9	29.1
2-methoxy-4-methylphenol	1.34	5.71	2.11	5.11
Phenol	20.2	15.7	18.8	14.6
4-ethyl-2-methoxyphenol	0.91	3.94	0.00	1.88
2-methoxy-4-vinylphenol	1.44	0.00	0.00	0.00
2,6-dimethoxyphenol	0.25	3.99	4.33	4.55
vanillin	0.92	3.94	0.00	4.97
4-hydroxy-3-methoxyacetaphenone	0.61	0.00	0.00	0.00
catechol	11.7	10.2	8.64	8.21
Homovanillic acid	0.50	0.00	0.28	2.47

As described in Table 14, lignin was pyrolyzed using different MOFs as a catalyst. We tested BPEI/TCA MOF, TM-728-1.25 and aluminum fumarate as a different catalyst. Although we could not observe a significant difference in product composition, we could easily observe a slight increase in the amount of vanillin while using BPEI/TCA MOF and aluminum fumarate. We will stop usage of MOF for catalysis of lignin as it is not significantly producing phenolics with higher selectivity**.**

3.1.4.5. Acid/base catalyzed reaction

We have performed base-catalyzed depolymerization of lignin using sodium hydroxide as shown in Figure 37. The results were quite interesting as we have obtained a high amount of vanillin and homovanillic acid, which has high market values.

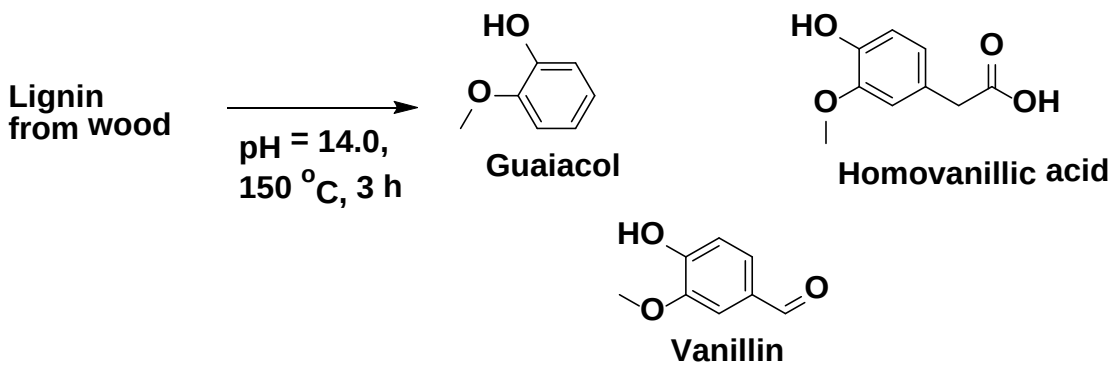


Figure 37. Isolation of high value phenolic from lignin by depolymerization using sodium hydroxide.

Base-catalyzed depolymerized of lignin was performed using high concentration sodium hydroxide solution. Lignin was placed in a high-pressure tube and the pH of the solution was maintained at 14.0. The tube was placed in an oil bath and the temperature was increased to 150 °C. After the reaction, the reaction mixture was acidified and the organic material was extracted with dichloromethane and analyzed by GC-MS. The isolated material exhibited poor yield of ~ 1.0 %; as a result, we investigated the oxidation of lignin using potassium permanganate.

Table 15. Product composition in extracts of oxidized lignin.

NaOH-Based Oxidation of Lignin		
Compound name	**Retention time (min)**	**% of the total**
Guaiacol	28.047	8.06
2-methoxy-4-methylphenol	Not Detected	0.00
Phenol	Not Detected	0.00

4-ethyl-2-methoxyphenol	Not Detected	0.00
2-methoxy-4-vinylphenol	Not Detected	0.00
2,6-dimethoxyphenol	Not Detected	0.00
Vanillin	39.258	32.86
4-hydroxy-3-methoxyacetaphenone	40.264	13.27
Catechol	Not Detected	0.00
Homovanillic acid	44.566	45.81

As shown in Table 15, the major products which are isolated by oxidation of Sigma-Aldrich's lignin under high alkaline conditions were guaiacol, vanillin, 4-hydroxy-3-methoxyacetaphenone and homovanillic acid. The total depolymerized fraction was isolated in very small amount and it was concluded that the higher yield can be obtained at higher temperature and pressure.

3.1.4.6. Oxidative depolymerization of lignin.

In another attempt to increase the yield of phenolic material, lignin was oxidized in THF/Water mixture at 70 °C for 2 h using $KMnO_4$ as shown in Figure 38. The product was extracted from the reaction mixture using dichloromethane. The higher amount of vanillin was isolated by oxidation of lignin using both alkali and $KMnO_4$ based oxidation methods.

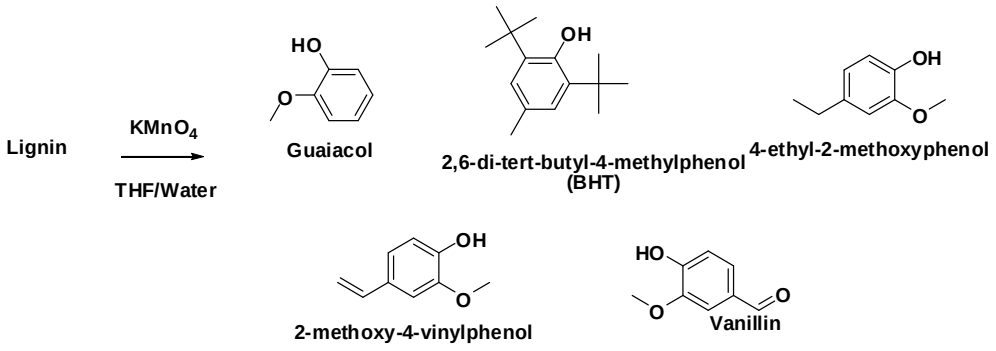


Figure 38. Oxidation of lignin using $KMnO_4$.

For $KMnO_4$ catalyzed oxidation of lignin, we have used four different kinds of lignin, which were obtained from various suppliers.

Table 16. Extraction of organic material after oxidation of lignin.

Compound	Types of lignin

	Flambeau River Paper LLC	TCI (Alkaline)	TCI (Dealkaline)
Guaiacol	1.96	0.00	0.00
2-methoxy-4-methylphenol	0.00	0.00	0.00
Phenol	0.00	0.00	0.00
4-ethyl-2-methoxyphenol	0.00	0.00	0.44
2-methoxy-4-vinylphenol	0.00	0.00	1.39
2,6-dimethoxyphenol	0.00	0.00	0.00
Vanillin	0.00	3.81	55.98
4-hydroxy-3-methoxyacetaphenone	0.00	2.25	16.40
Catechol	0.00	0.00	0.00
Homovanillic acid	0.00	2.42	3.10

Table 17. The organic layer of oxidized lignin after treatment with HCl.

Compound	**Types of lignin**			
	Sigma-Aldrich	**Flambeau River Paper LLC**	**TCI (Alkaline)**	**TCI (Dealkaline)**
Guaiacol	8.11	1.75	0.00	0.00
2-methoxy-4-methylphenol	0.00	0.00	0.00	0.00
Phenol	0.00	0.00	0.00	0.00
4-ethyl-2-methoxyphenol	0.53	0.00	0.00	0.00
2-methoxy-4-vinylphenol	1.68	0.00	0.00	0.00
2,6-dimethoxyphenol	0.00	0.00	0.00	0.00
Vanillin	12.32	0.00	32.21	65.34
4-hydroxy-3-methoxyacetaphenone	3.67	0.00	5.27	16.40
Catechol	0.00	0.00	0.00	0.00
Homovanillic acid	6.16	0.00	0.00	3.10

As shown in Table 16 and

Table 17, we have oxidized four different kinds of lignin using potassium permanganate. We have oxidized (a) Sigma-Aldrich alkaline, (b) TCI alkaline, (c) TCI-dealkaline and (d) Flambeau River Paper LLC lignin. Lignin was oxidized in THF at 70 °C and water were added drop-wise during the reaction. After completion of oxidation, THF was evaporated on a rotary evaporator and the organic material was extracted using dichloromethane. The organic layer was washed with 0.1 N HCl and analyzed again by GC-MS. Table 17 exhibits amount of each phenolics after immediate extraction using dichloromethane from the reaction solution. Very high amount of vanillin was observed in both TCI alkaline and dealkaline lignin. Washing of organic layer with mild acid helped in improving the composition of vanillin.

3.1.5. Bisphenol A (BPA) synthesis

- Pyrolysis was performed continually to obtain a higher amount of pyrolysate, which was later used for purification and isolation of higher amount of phenol.
- A mixture of phenolics, which was obtained after pyrolysis of lignin, was purified by column chromatography. The phenol-enriched phenolic was used for BPA synthesis. The reaction of acetone and green phenolic in presence of Amberlyst-15 catalyst produces green BPA. As acetone is a low-boiling solvent, a hermetically sealed high-pressure reactor was utilized in the synthesis. We have confirmed conversion of green phenol to BPA by GC-MS and ^{1}H NMR.
- Isolation of higher amount of phenol and other valuable phenolic compounds from pyrolysate is one of the main goals. Hence, in an alternative to the pyrolysis approach, we performed sodium hydroxide based depolymerization and potassium permanganate based oxidation of different kinds of lignin.

3.1.5.1. Conversion of Phenol into Bisphenol A

In order to evaluate the setup and material efficiency, we synthesized BPA from a commercially available phenol according to a literature procedure [47-51] as shown in Figure 39. In the first approach, no solvent was used and phenol was first melted in an oil bath at 60 ºC then combined with acetone and hydrochloric acid (HCl) in the presence of thioglycolic acid promoter. The reaction was performed in a Pyrex round-bottom flask equipped with a water condenser in a hood on a hot plate with an oil bath. The mixture reacted immediately, which yielded crude product subsequently identified as a mixture of BPA and unreacted phenol. The reaction mixture was characterized by TLC, ^{1}H NMR, and LC-MS. After completion of the reaction, it was observed that a significant amount of phenol remained in the final product and it was presumed that a water-condenser-based system was not efficient enough to hold the acetone vapor, and loss of acetone in the system resulted in the poor conversion. The overall goal was to eliminate phenol from the final product mixture as much as possible, so the procedure was then altered. In the second approach, the reaction was performed in a reactor sealed with a plastic cork. Several reactions were performed, mainly by varying phenol-to-acetone ratio, temperature, and reaction time. A high-

pressure closed system could function at high pressure with almost zero leakage; thus, the significantly higher conversion was observed and phenol remained in the system. In addition, the molar quantity of phenol was lowered significantly.

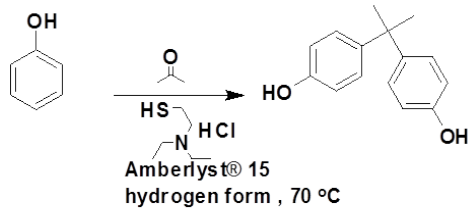


Figure 39. Acid-catalyzed coupling reaction of phenol with acetone

Basically, two systems, one at ambient pressure and another at high pressure, were successfully investigated in different phenol-to-acetone ratio, temperature, and reaction time. It suggested that high-pressure reactor was more efficient compared with the ambient pressure system. Under ambient pressure and 60 ℃, a TLC of reaction product did not exhibit any sign of BPA. However, when the sample was analyzed by LCs equipped with UV at 254 nm and diode array detector (DAD), the sample showed λ_{max} of 278nm at Rt 2.40 which represents BPA as shown in Table 18. The literature value of λ_{max} of BPA is 277 nm, but the instrument worked over 190~600 nm with an interval of 2 nm. Therefore, no odd number of wavelength on the results could be observed. Moreover, it exhibited λ_{max} of 268 nm at Rt 1.44, which was well in accordance with literature λ_{max} of phenol. The ^{1}H NMR of the crude product was analyzed in DMSO. The peak of water, DMSO, and unreacted acetone was observed at 3.4 ppm, 2.5 ppm, and 2.0 ppm respectively. A trace amount of ArH peak from BPA was observed at ~7.0 ppm, and the integrations value (2.00:0.11) suggested the presence of ~5% of BPA in sample 1.

Table 18. Effect of setup and phenol-to-acetone ratio on the conversion of phenol to bisphenol

Sample	Reactant					Amber lyst-15	T(C)	cMR (1:X) X	Time (h)	Pressure
	Phenol		Acetone							
	g	mol	g	mol	mL	mg				
[a]11/25/2013-03	9.95	0.106	0.78	0.01	0.98	105	70	7.9	48	ambient
[b]12/03/2013-05	9.11	0.097	2.21	0.04	2.80	100	95	2.5	72	ambient
[d]12/09/2013-07	8.85	0.094	2.21	0.04	2.80	95.5	90	2.5	22	yes, pressure flask
[d]12/10/2013	9.07	0.096	2.55	0.04	3.22	99.6	90	2.2	4	yes, pressure flask
[d]12/10/2013	9.22	0.098	2.61	0.04	3.30	100	90	2.2	16	yes, pressure flask
[d]12/11/2013	8.49	0.090	2.37	0.04	3.00	91.1	90	2.2	1	yes, pressure flask
[d]12/11/2013	8.42	0.089	2.37	0.04	3.00	90.6	90	2.2	2	yes, pressure flask

[d]12/11/2013	4.17	0.044	1.19	0.02	1.50	46.0	70	2.2	24	yes, pressure flask

[a]TLC analysis indicated no sig. product; allowed to react overnight again; samples sent for LC-MS and ^{1}H-NMR.[b] TLC analysis indicated no sig. product; additional acetone and catalyst (2.8ml and 100mg respectively) were added and allowed to react overnight again; samples sent for LC-MS and ^{1}H-NMR. [c]MR = initial acetone/phenol molar ratio. [d] TLC analysis indicated the presence of bisphenol A; samples sent for LC-MS and H-NMR.

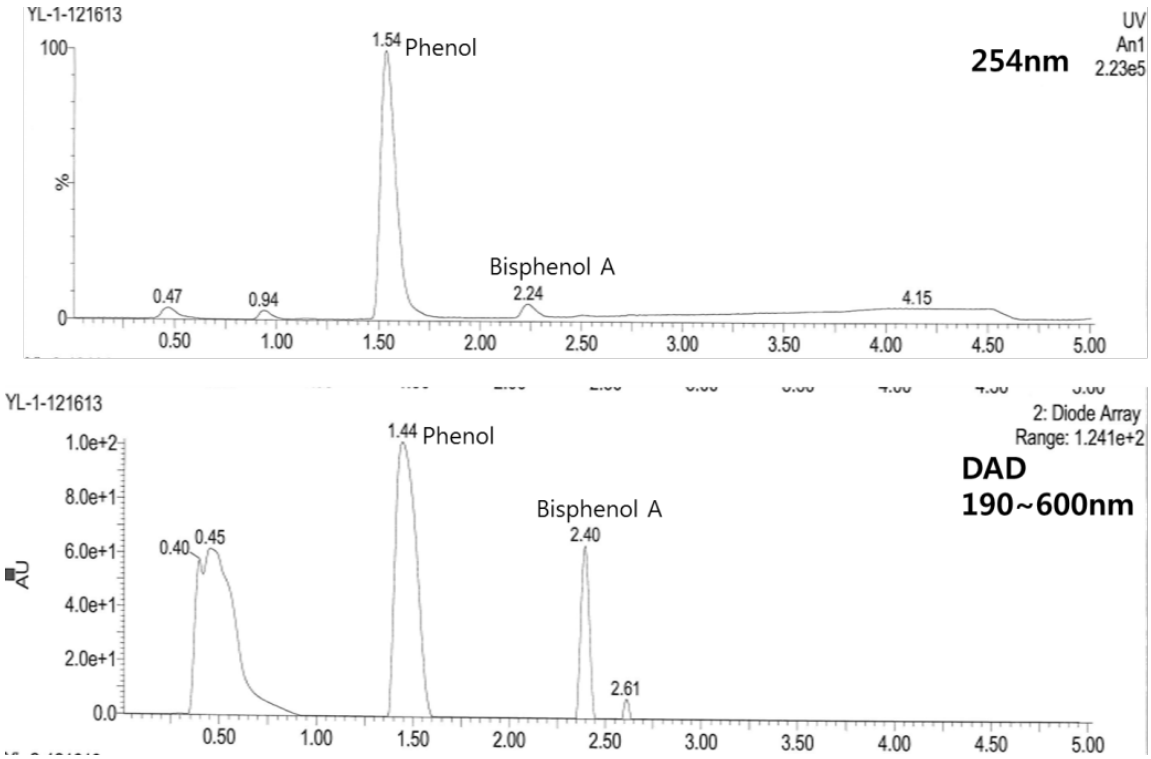


Figure 40. LC-MS spectra at (a) 254nm and (b) DAD of bisphenol A synthesized under ambient pressure

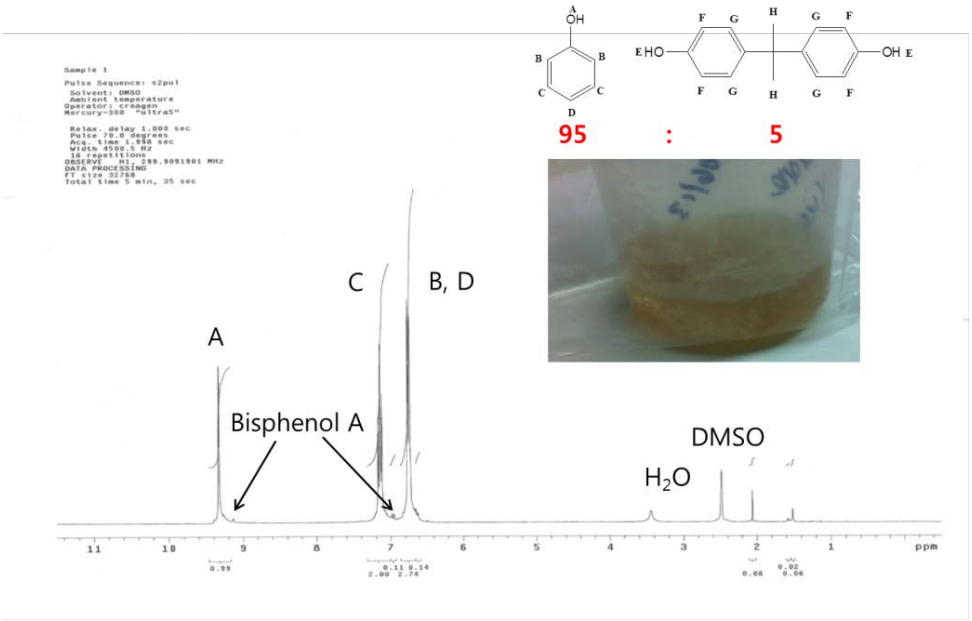


Figure 41. ^{1}H NMR and image of bisphenol A synthesized under ambient condition

In the second approach under sealed high-pressure glass reactor, BPA was successfully obtained by reaction of a commercial sample of phenol under acidic conditions and in the presence of a catalyst. The crude product mixture was analyzed by LC/MS which showed the parent ion peak for BPA in the reaction product, and comparing with sample 1, bisphenol A peaks on both spectra were significantly increased as shown in Figure 42. TLC analysis confirmed the presence of phenol impurity in bisphenol A product. Rf values for authentic BPA and authentic phenol samples were identical with Rf values obtained for synthesized BPA product and phenol impurity respectively. In a mass spectroscopy, a peak observed at Rt 2.22 was showing 229.1(M+1), which represents BPA as shown in Figure 43. The ^{1}HNMR spectra showed a quartet chemical shift between 6.6 ppm and 7.0 ppm, corresponding to the hydrogens located on the benzene rings on the BPA molecule. Both had a singlet peak at 4.5ppm, representing the phenoxy off both rings as well. On top of that, there was a peak at 2.6ppm representing the two internal methyl groups. The integration value (2.00:1.77 and 0.84:0.71) suggested that ~ 47.0 of BPA was present in the final product as shown in Figure 44. Although LC/MS confirmed the possibility of bisphenol A within the sample, it was ^{1}HNMR that provided concrete proof.

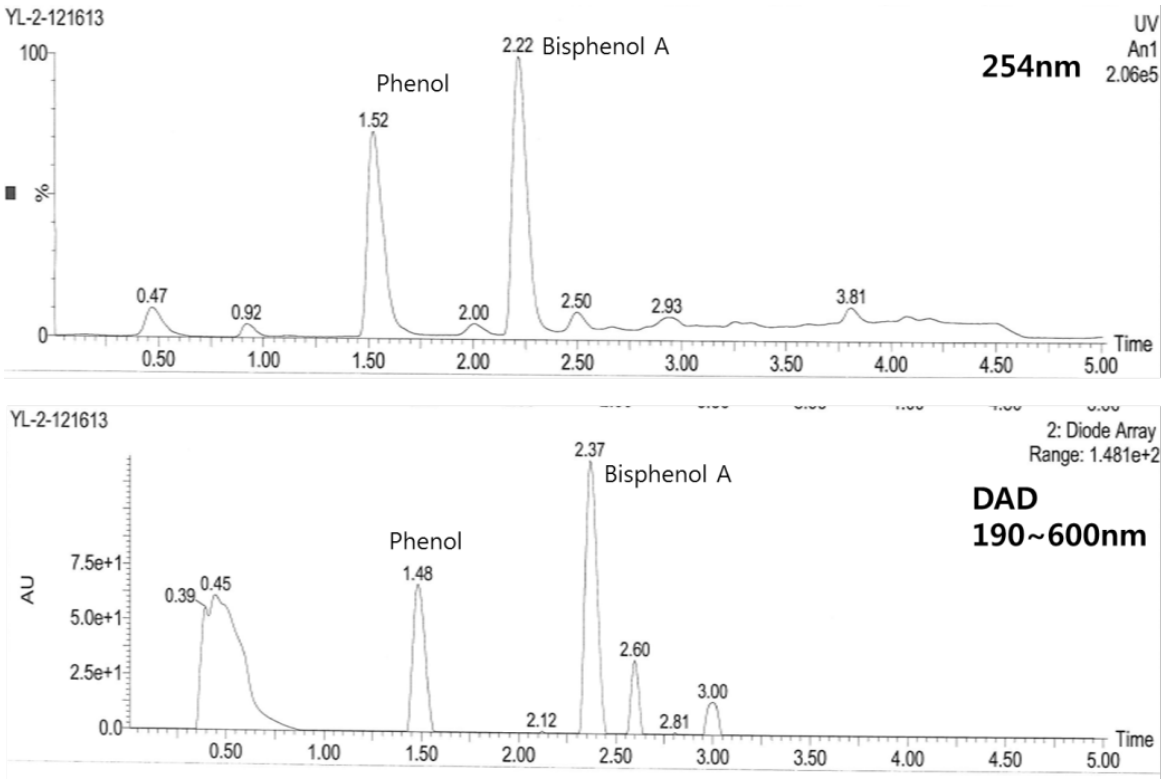


Figure 42. LC-MS spectra at (a) 254 nm and (b) DAD of bisphenol A synthesized in a high-pressure reactor

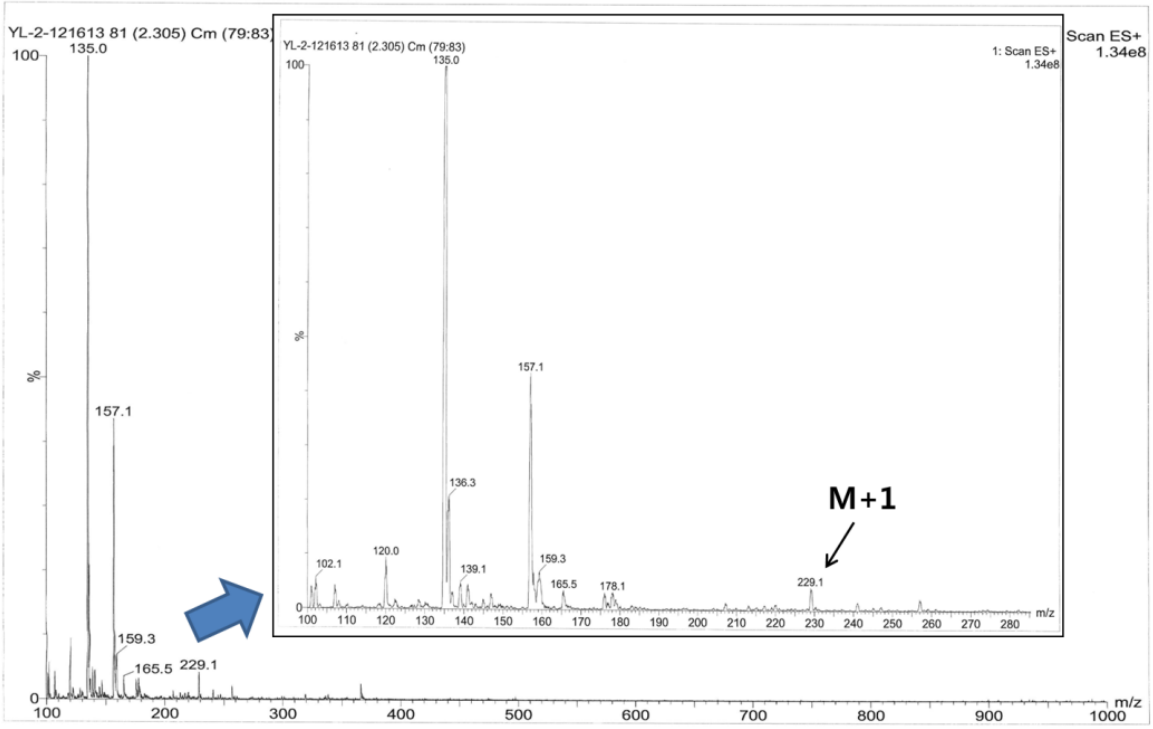


Figure 43. Mass spectra of bisphenol A synthesized in a high-pressure reactor.

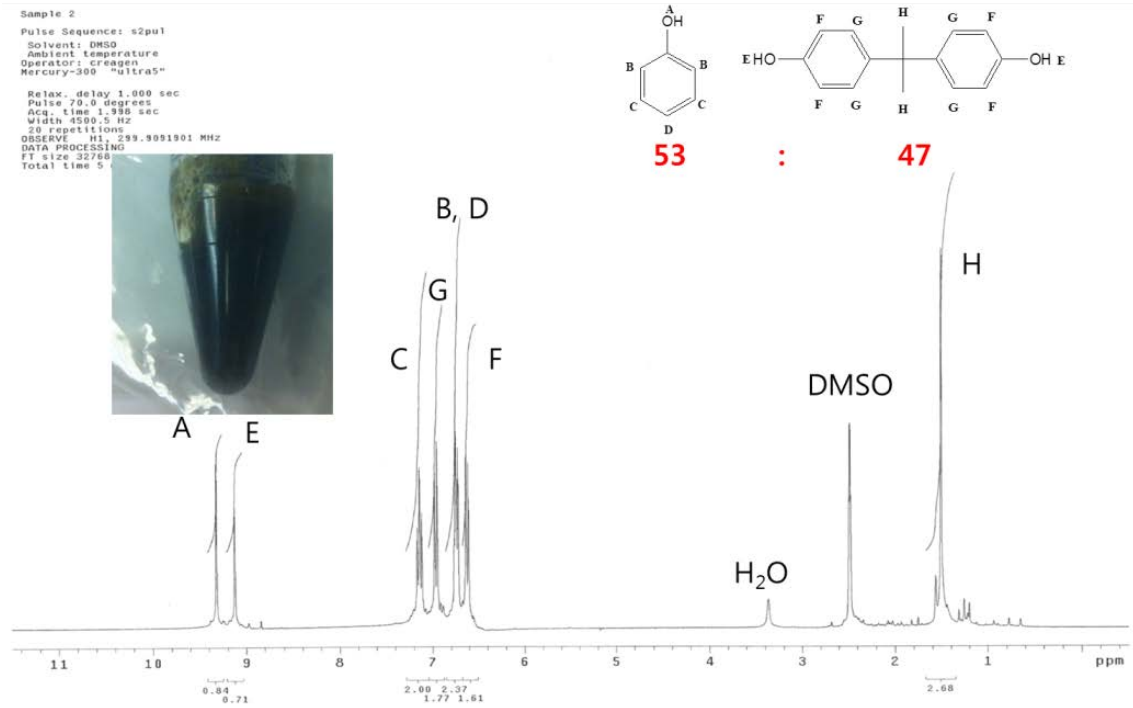


Figure 44. ^{1}H NMR and image of bisphenol A synthesized in high-pressure reactor

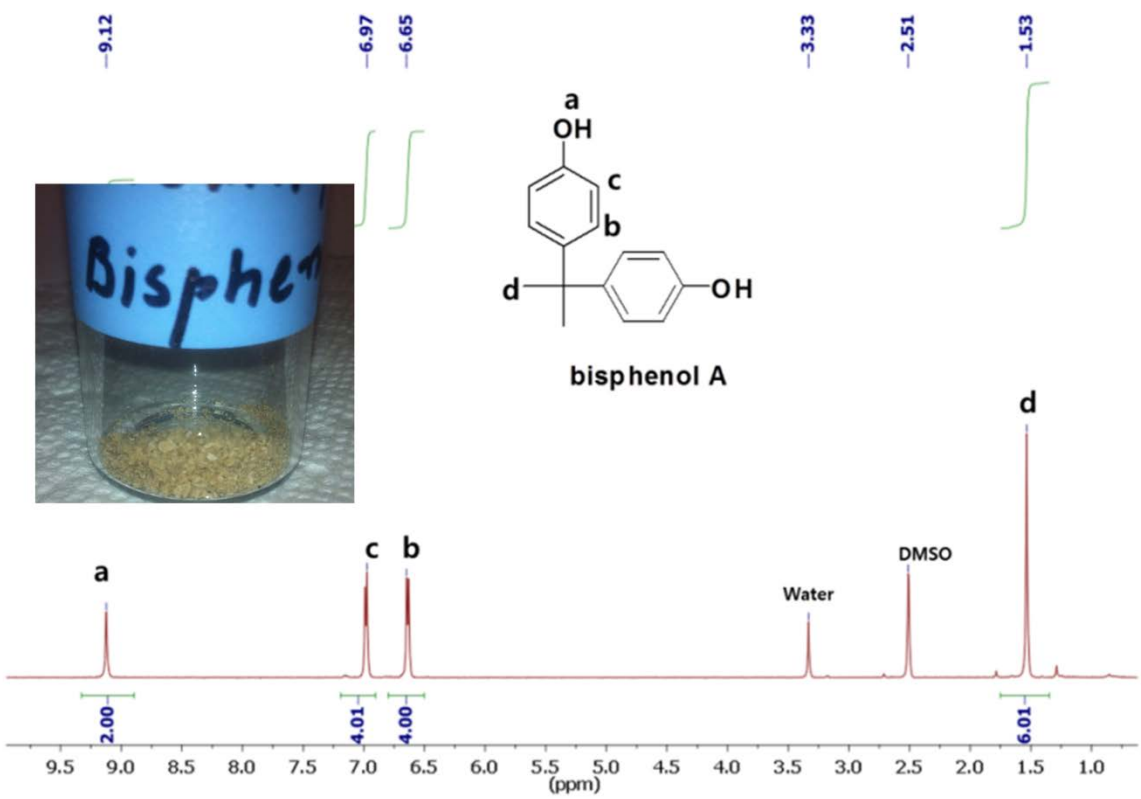


Figure 45. ^{1}H NMR of column separated BPA.

The synthesized BPA was purified by column chromatography using hexane: ethyl acetate in 7:3 as a solvent mixture. The BPA was isolated with 7.0 % yield and product was confirmed by ^{1}H NMR as shown in Figure 45 The IR of the purified BPA is shown in Figure 46, which shown a clear peak of –OH at 3320 cm^{-1}.

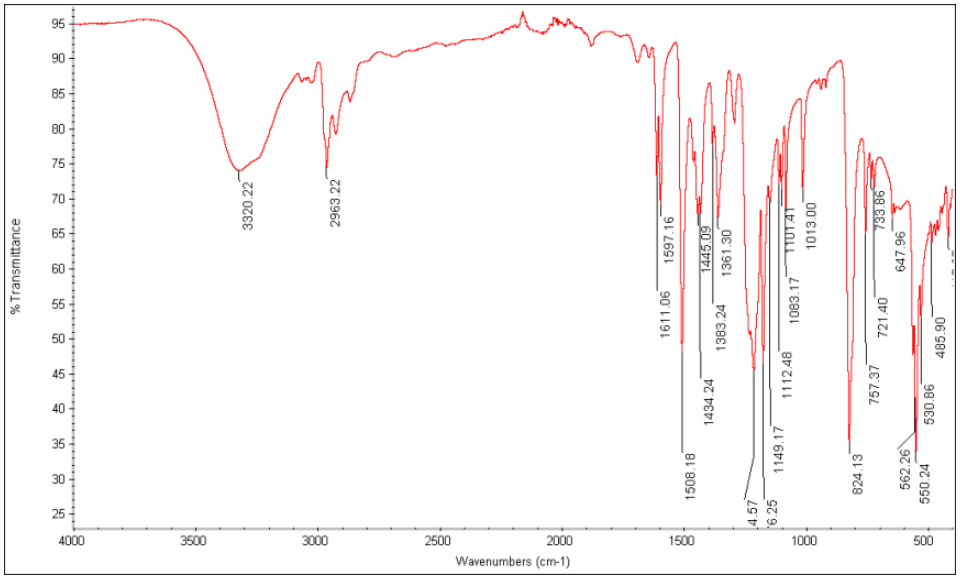


Figure 46. FT-IR of column separated BPA.

3.1.5.2. Synthesis of bisphenol A from green phenolics.

We have performed synthesis of BPA using same method and column purified the second fraction from phenolics. The conversion of phenol to BPA using phenolic will be very small, and it will be desirable to detect it using GC-MS. BPA standard was analyzed by GC-MS at 1160 ppm. BPA has degraded into two compounds at given GC-MS conditions and two peaks were obtained one of phenol and other of isopropyl phenol. Each peak was identified using a mass spectrum of each compound. The fragmentation of BPA is shown in Figure 47.

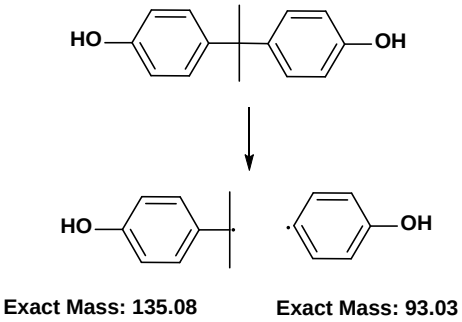


Figure 47. Fragmentations of BPA

The reaction mixture of BPA synthesis was analyzed at the same GC-MS condition. We expected to observe two peaks at the same retention times as observed in BPA standard to confirm

the presence of BPA in the samples. Since the BPA concentrations in samples were very low, both "total ion" and "selective ion" chromatograms were obtained. The GC spectra of pure BPA exhibited sharp peaks at 7.891 and 10.640 min. The mass spectra of the peak at 7.881 displayed presence of phenol and 10.642 min confirmed the presence of p-isopropyl phenol.

BPA was synthesized using pyrolysate, which was purified using column chromatography. The GC-spectra using total ion method was quite unclear. Therefore, a selective ion method was used to analyze the sample, which gave a relatively clear spectrum. The fragmented BPA peaks at 7.891 and 10.640 min was observed in GC spectra of green BPA. The mass spectra of the peak at 7.885 and 10.663 confirmed the presence of phenol and p-isopropyl phenol, respectively. The GC-data confirmed that we have successfully synthesized BPA starting from lignin.

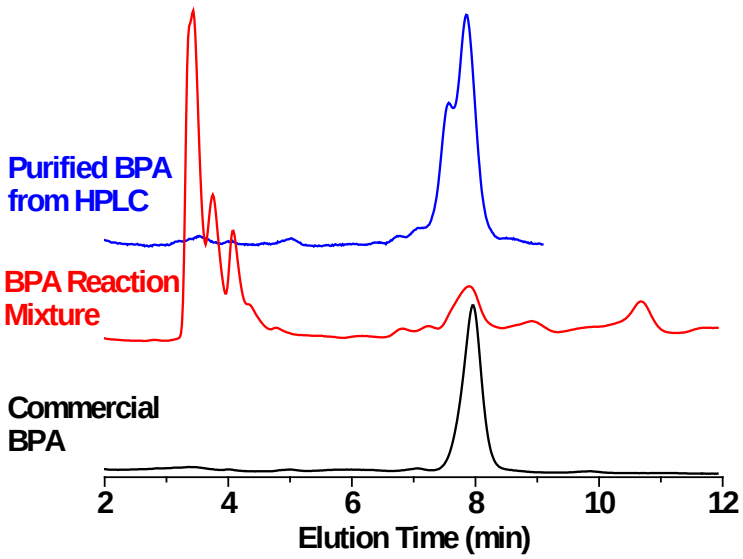


Figure 48. HPLC of the commercial BPA and purified BPA.

The reaction mixture of BPA was analyzed by reverse phase HPLC using methanol and water mixture as an eluent as shown in Figure 48. Upon analysis by HPLC using reverse phase column with water and methanol as an eluent, we have seen peaks of more than five chemicals in the HPLC plot of BPA reaction mixture as shown in Figure 48. For reference, we have also analyzed pure commercial BPA by same HPLC system and it shows peak ~8.0 min. Our BPA reaction mixture also exhibited a peak at ~8.0 min, which confirmed the presence of BPA in our reaction mixture. The fraction of BPA was collected from the drain of the HPLC and concentrated using a rotary evaporator. The concentrated BPA of the drain has an identical peak with commercial BPA.

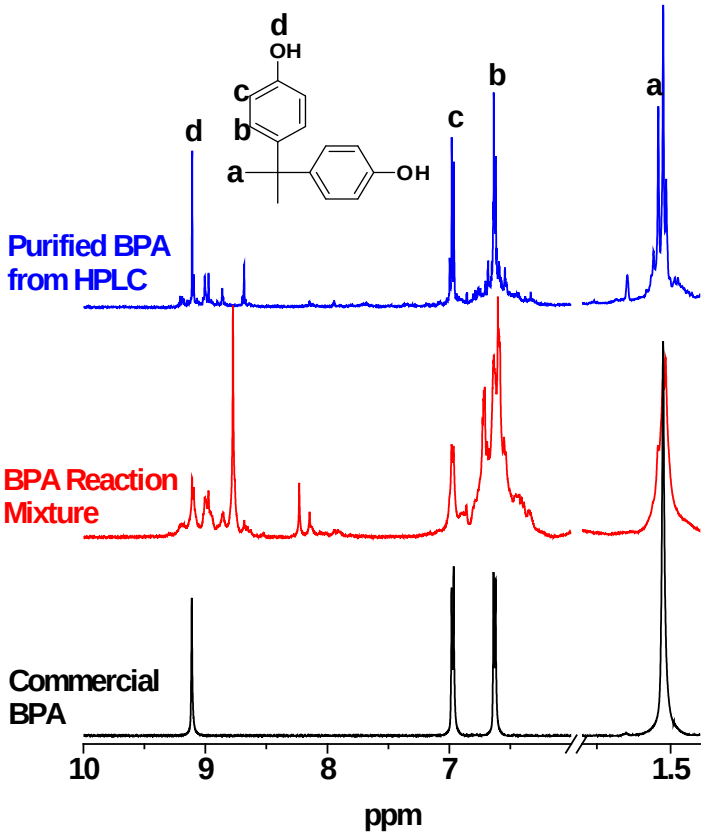


Figure 49. ^{1}H NMR of the commercial BPA and purified BPA.

^{1}H NMR spectra of the BPA reaction mixture, commercial pure BPA and HPLC purified BPA is shown in Figure 49. ^{1}H NMR of BPA reaction mixture showed many peaks in the aromatic region confirming the presence of more than one chemical. However, as can be seen in Figure 49, the BPA reaction mixture has two very strong peaks in aromatic region matching with commercial BPA exactly. The concentrated fraction from HPLC drain showed identical peaks with commercial BPA. The green BPA was successfully synthesized and purified, which was confirmed by ^{1}H NMR.

In summary, we have successfully purified pyrolysate and isolated phenol, which was confirmed by GC-MS, HPLC, and ^{1}H NMR. We have used phenol-enriched phenolics for the synthesis of BPA, the BPA was isolated in pure form, which was confirmed by GC-MS, HPLC, and ^{1}H NMR.

3.1.6. Synthesis of tetrabromobisphenol A (TBBPA)

TBBPA is an important precursor for the synthesis of flame retardant vinyl ester resin. It is being synthesized by simple bromination of bisphenol A as shown in Figure 50.

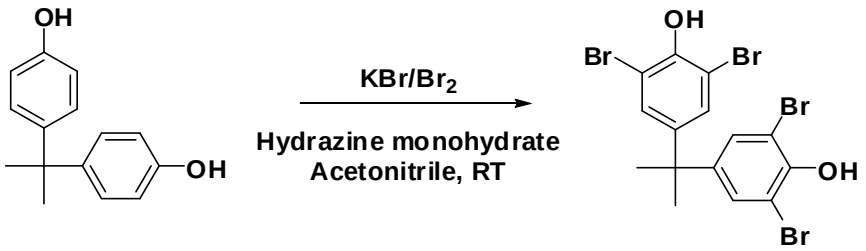


Figure 50. Synthesis of tetrabromobisphenol A (TBBPA) at room temperature

3.1.6.1. Equipment for the process

Magnetic stirrer with a power cord, lab jack, ring stand, two thermometers, two magnetic stir bars, 1000mL 3-neck round bottom flask, two ring stand clamps, 250mL dropping funnel, ground-glass joint grease, glass stopper, ground glass thermometer adapter, analytical balance, weigh boats, spatulas, Eppendorf pipet, TLC developing chamber, aluminum-backed TLC plates, tweezers, pencil, permanent marker, handheld UV lamp, culture tubes and rack, disposable glass Pasteur pipettes and rubber bulbs, 20mL glass scintillation vials, disposable glass capillary tubes (10uL), scissors or paper cutter, ruler

3.1.6.2. Setup

Two magnetic stirrers were used, one was equipped with a 500mL beaker and stir bar, other was equipped with a 1000 mL 3-neck round bottom flask with a dropping funnel and a magnetic stir bar inside the flask.

3.1.6.3. Synthesis of Tetrabromobisphenol A

A 1000 mL round-bottom flask was charged with bisphenol A (42.23g, 185 mmol) and acetonitrile (277.5 mL). In a 500 Ml beaker, a solution of KBr (88.06 g, 740 mmol) in water (185 mL) was prepared, to which bromine (148 g, 925 mmol) was added, and the resulting mixture was stirred to form an aqueous solution of KBr_3 at 30 °C. This solution was added rapidly to the bisphenol A solution by utilizing a 250 mL pressure-equalizing funnel within 10-12 min. The bromine color disappeared immediately, and white crystals of TBBPA were obtained within 5-10 min of reaction time at 30 °C. Hydrazine hydrate (80%) was added to destroy the residual bromine, and the mixture was poured into water to separate the precipitated TBBPA. The precipitated reaction mass was separated from the mother liquor by vacuum filtration, utilizing a Buchner funnel, and then was washed twice with deionized water and dried in an oven at 100 °C. The total isolated yield of TBBPA was 96.0 %, and the purity of the crystals was found to be 99.38% with a bromine content of 58.74%.

Bromination of bisphenol A is a simple reaction as it is performed at room temperature with short reaction time; moreover, the workup procedure for the isolation of the brominated bisphenol A is also simple. The TBBPA was isolated by pouring the final reaction mixture in water and filtering the solid material. The material was dried in a vacuum oven, and slightly yellow color material was isolated. The ^{1}H NMR, ^{13}C NMR, and FT-IR proved that the material was 100 % pure without any impurity or side product as shown in Figure 51, Figure 52, and Figure 53 respectively.

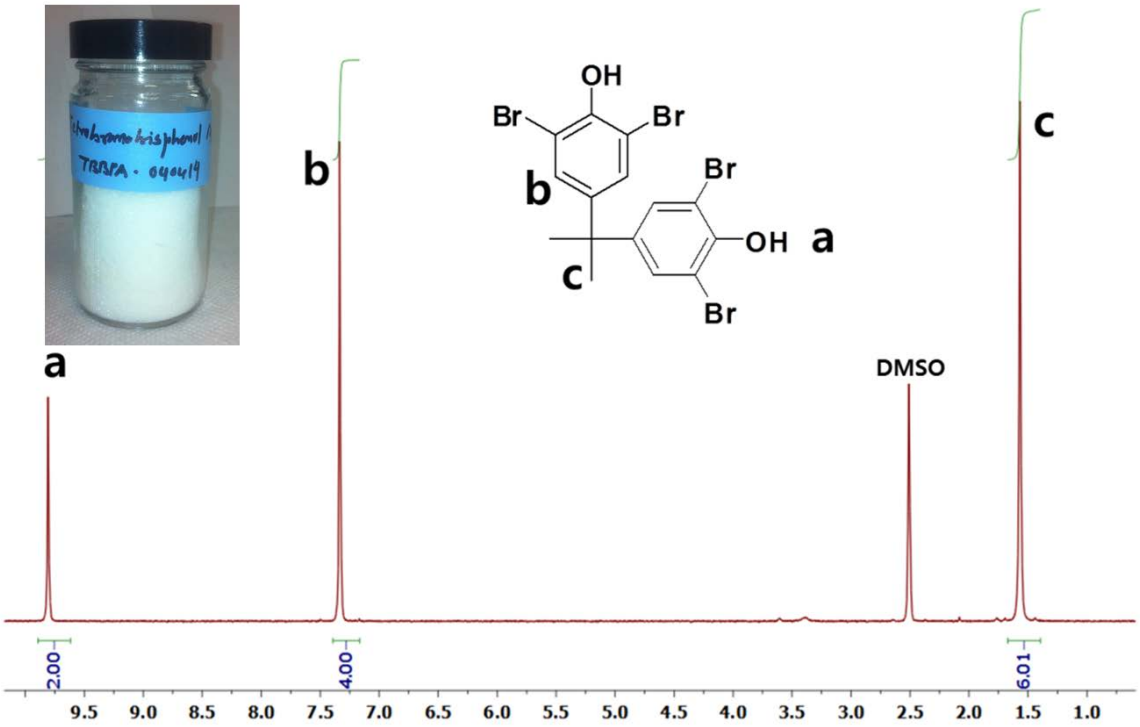


Figure 51. 1H NMR and image of tetrabromobisphenol A synthesized under ambient condition

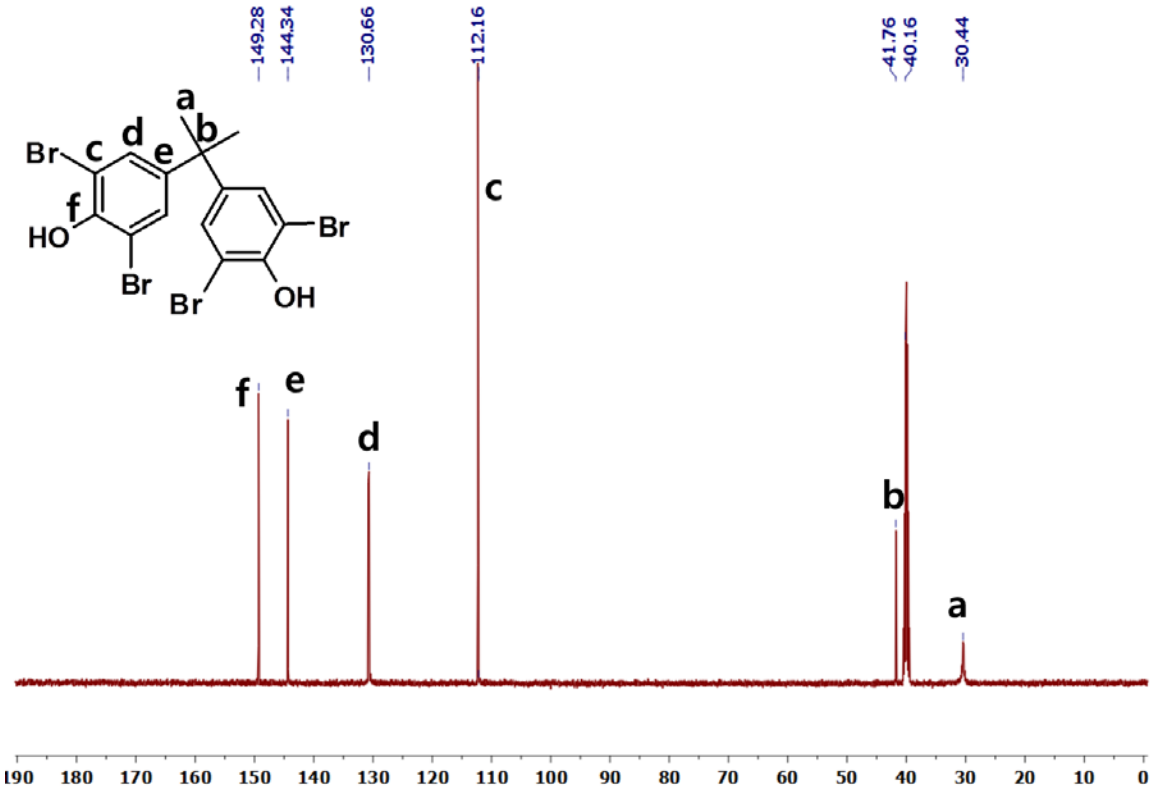


Figure 52. ^{13}C NMR and image of tetrabromobisphenol A synthesized under ambient condition

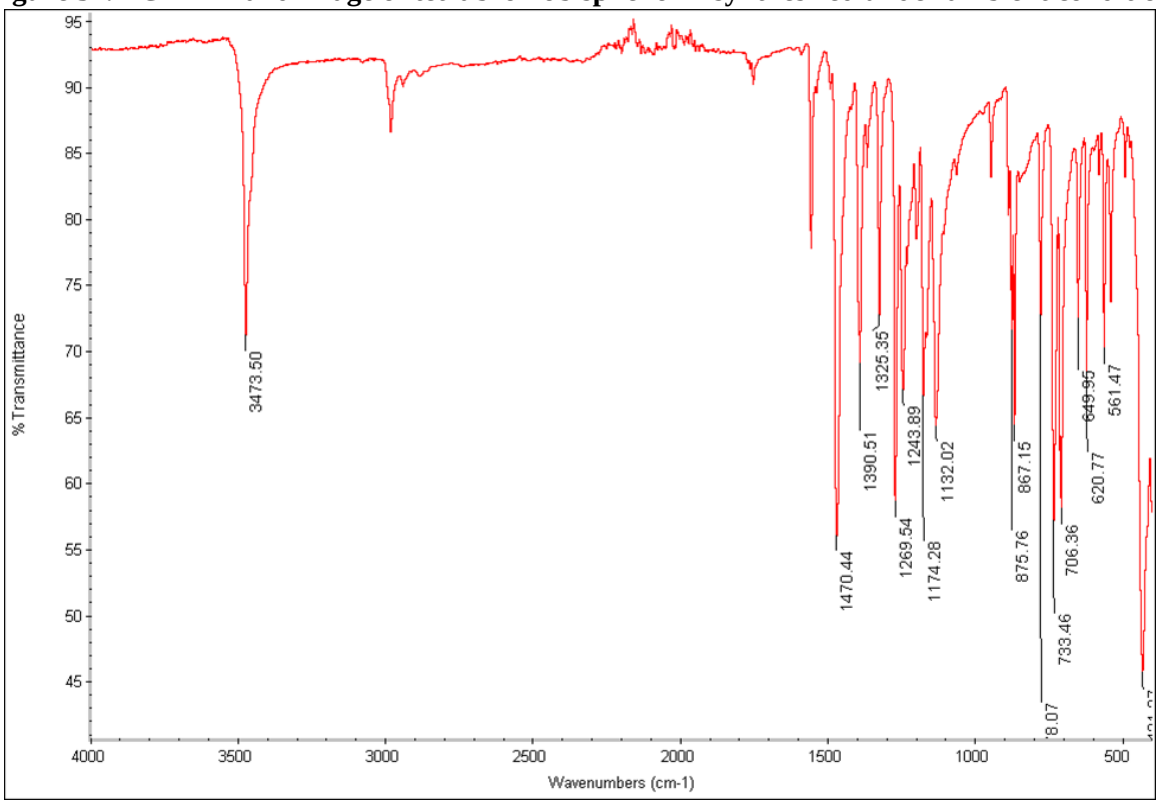


Figure 53. FT-IR and image of tetrabromobisphenol A synthesized under ambient condition

3.2. Task 2 - Refine GMA from Glycerin Process

In Task 1, the isolation of the first precursor BPA from the lignin was demonstrated. In Task 2, the synthesis of second precursor glycidyl methacrylate from glycerin was demonstrated. Glycerin is a side-product from the transesterification of triglyceride in the manufacturing of biodiesel or by hydrolysis of triglyceride during saponification.

Recently, significant advances have been made for obtaining biodiesel, a renewable biofuel for use in diesel engines and heating applications. Biodiesel can be produced by base catalyzed the hydrolysis of rapeseed oil, soybean, and wastes of cooked oil, rice straw, vegetable oil mixtures of cottonseed, soybean and castor oils, jatropha oil, and crude palm oil. Biodiesel is environmentally beneficial because it is biodegradable, nontoxic and has a low emission. [52] During manufacturing of biodiesel, approximately a 10 % volume of glycerin is produced as a by-product or waste. [53] Therefore, the effective utilization of glycerin enlarges the economy of biodiesel production; moreover, the conversion of glycerin to value added chemicals can expand the scope of green chemistry. [54] Although biodiesel uses non-petroleum feedstocks, it is still subject to the price fluctuations of the petroleum liquid fuels market. Subsidization also plays an important role in the overall market price of biodiesel. These two market factors often make it very important for biodiesel manufacturers to sell as many of their byproducts as possible.

To obtain the glycerin from the waste stream of biodiesel production material, we collaborated with Maine Standard Biofuels (Portland, ME), which is a manufacturer of biodiesel as shown in Figure 54a. We have also obtained vegetable glycerin from the local vendor named Bulk Apothecary (Streetsboro, OH) as shown in Figure 54b.

Figure 54. Glycerin obtained from (a) Main Standard Biofuels, and (b) Bulk Apothecary

Maine Standard Biofuels Inc. (MSB, www.mainestandardbiofuels.com) is one of the leading small scale Biodiesel producers in Maine. The major raw material used by MSB in the manufacture of Biodiesel is used vegetable oil sourced from numerous restaurants in the New England area. Currently, they ship the waste glycerol to a bio-digestion plant, where it is converted to methane, ethane and other smaller fragments for utilization as fuel for heat.

A Non-disclosure agreement was established between UMass Lowell and MSB. The UMass Lowell team visited the MSB biodiesel manufacturing facility in Portland, Maine on August 11, 2014 (Figure 55). An informative tour was organized that detailed the process for conversion of used vegetable oils to biodiesel. According to MSB, the composition of the obtained crude glycerin is as follows: 45% Glycerin, 5% salts, and unspecified quantities of water, methanol and free fatty acids. Glycerin was purified in a laboratory and utilized further for the monomer synthesis.

Figure 55. UMass Lowell team at Maine Standard Biofuels.

We have performed a fractional distillation under high vacuum and tried to collect three different fractions separately on the basis of their boiling point. The collected samples are shown in Figure 56.

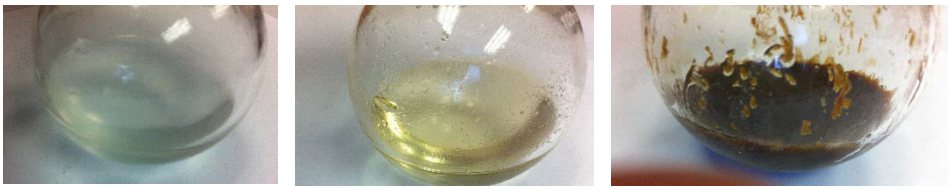


Figure 56. Isolated material during fractional distillation of the crude glycerin. (a) low boiling point material, (b) glycerin and (c) residue.

The first fraction is water, which was collected at 90-100 ºC under very mild vacuum condition. During distillation, significant foaming was observed in the flask. As a result, the higher vacuum could not be applied and water was distilled off under very mild vacuum condition. The second fraction of glycerin was collected at 195-200 ℃ under high vacuum condition. ~42.0

weight % material could not be distilled. The purity of the glycerin was determined by the 1H NMR as shown in Figure 57. ^{1H} NMR of the distilled glycerin (2nd fraction during distillation)., which showed no peaks of impurity.

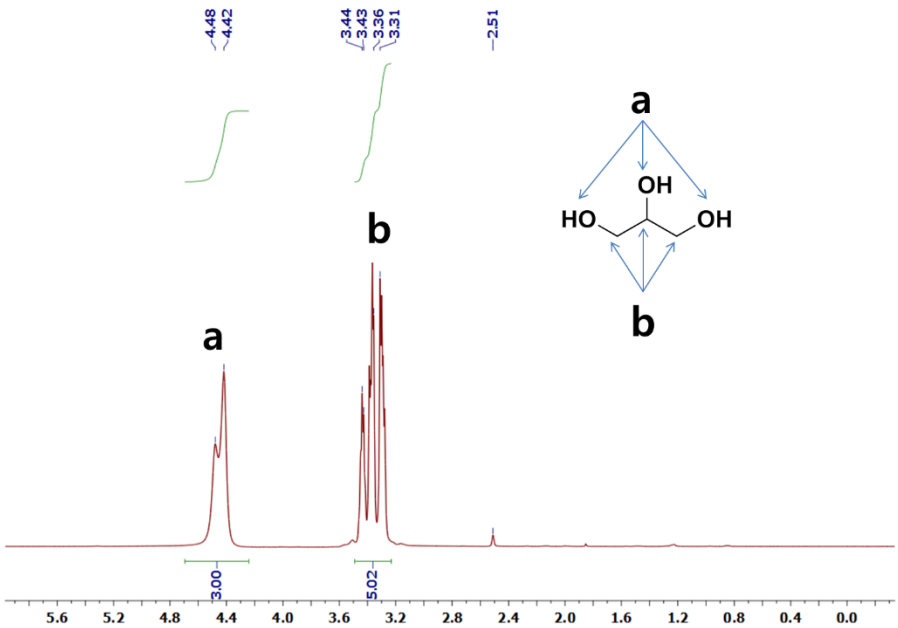


Figure 57. ^{1}H NMR of the distilled glycerin (2nd fraction during distillation).

3.2.1. Experimental Procedure

The second precursor GMA for GVER monomer was synthesized by multistep reaction of glycerin. Glycerol carbonate was synthesized from glycerin in presence of base. [8, 55-59], Glycerol carbonate was converted to glycidol in presence of sodium sulfate at high temperature. [60, 61] GMA was synthesized by transesterification of glycidol and methyl methacrylate.

3.2.2. Materials & Equipment Requirements

Magnetic stirrer hotplate with a power cord, lab jack, ring stand, mineral oil bath, thermometer, two magnetic stir bars, 100mL pear-shaped flask, 100mL four neck flask, 150mL four neck flask, assorted-size single-neck round-bottom flasks, beakers, graduated cylinders, reduced-pressure distillation glassware, aspiration and vacuum pumps, two ring stand clamps, water-cooled condenser, two pieces of plastic tubing (water in and water out), ground-glass joint grease, glass stopper, rubber septa, ground glass thermometer adapter, analytical balance, weigh boats, spatulas, TLC developing chamber, aluminum-backed TLC plates, tweezers, pencil, permanent marker, handheld UV lamp, culture tubes and rack, disposable glass Pasteur pipettes and rubber bulbs, 20mL glass scintillation vials, disposable glass capillary tubes (10uL), scissors or paper cutter, ruler.

3.2.3. Synthesis of glycidyl methacrylate

GMA was synthesized by multi-step organic reactions [62] as shown in Figure 58. All intermediate were purified either by distillation or resin treatment and analyzed by ^{1}H NMR and FT-IR.

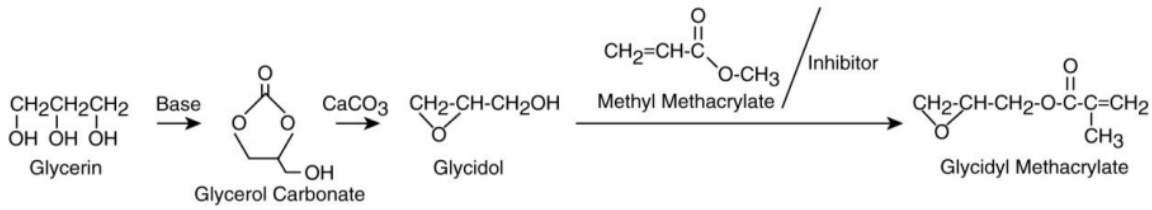


Figure 58. Conversion of glycerin to glycidol via the cyclic carbonate intermediate followed by transesterification with methyl methacrylate (MMA) to form glycidyl methacrylate (GMA)

3.2.3.1. Glycerol Carbonate from glycerin

Glycerol carbonate, which is the first intermediate during the multi-step GMA synthesis from glycerin. Glycerol carbonate is a very important material having a large number of applications such as a building block for many pharmaceutical intermediates, so we were also interested in isolation of this material with 100% purity. Glycerol carbonate was synthesized using four different methods by reactions of glycerin with (a) urea in presence of zinc oxide and magnesium sulfate at 140 ºC, (b) dimethyl carbonate in presence of molecular sieve and Novozyme 435, (c) dimethyl carbonate and sodium aluminate at 100 ºC, and (d) dimethyl carbonate and potassium carbonate at 73-75 ºC. We tried to refine our setup as much as we can in order to isolate glycerol carbonate with high purity. Among all, synthesis of glycerol carbonate by reaction with dimethyl carbonate in the presence of potassium carbonate was the most successful one.

(a) Synthesis of glycerol carbonate from glycerin and urea in presence of zinc oxide and magnesium sulfate

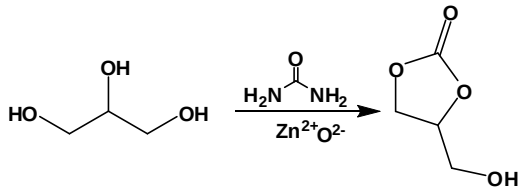


Figure 59. Synthesis of glycerol carbonate by reaction of glycerin and urea in presence of magnesium and zinc oxide

Glycerol carbonate was synthesized using glycerin and urea at 140 ºC for 18 h in presence of either $MgSO_4$ or ZnO as shown in Figure 59. The method was selected as it required glycerin and urea in 1:1 molar ratio. The reaction was performed in different set up starting from a round bottom flask equipped with water condenser to the high-pressure reaction tube.

^{1}H NMR of the glycerin from Bulk Apothecary is shown in Figure 60. The proton peak of the backbone of glycerin can be observed between 3.0-3.5 ppm. ^{1}H NMR of the reaction product mixture exhibited the presence of glycerol carbonate in the product mixture as shown in Figure 61. The presence of urea and other impurities was also observed in the product mixture along with glycerol carbonate.

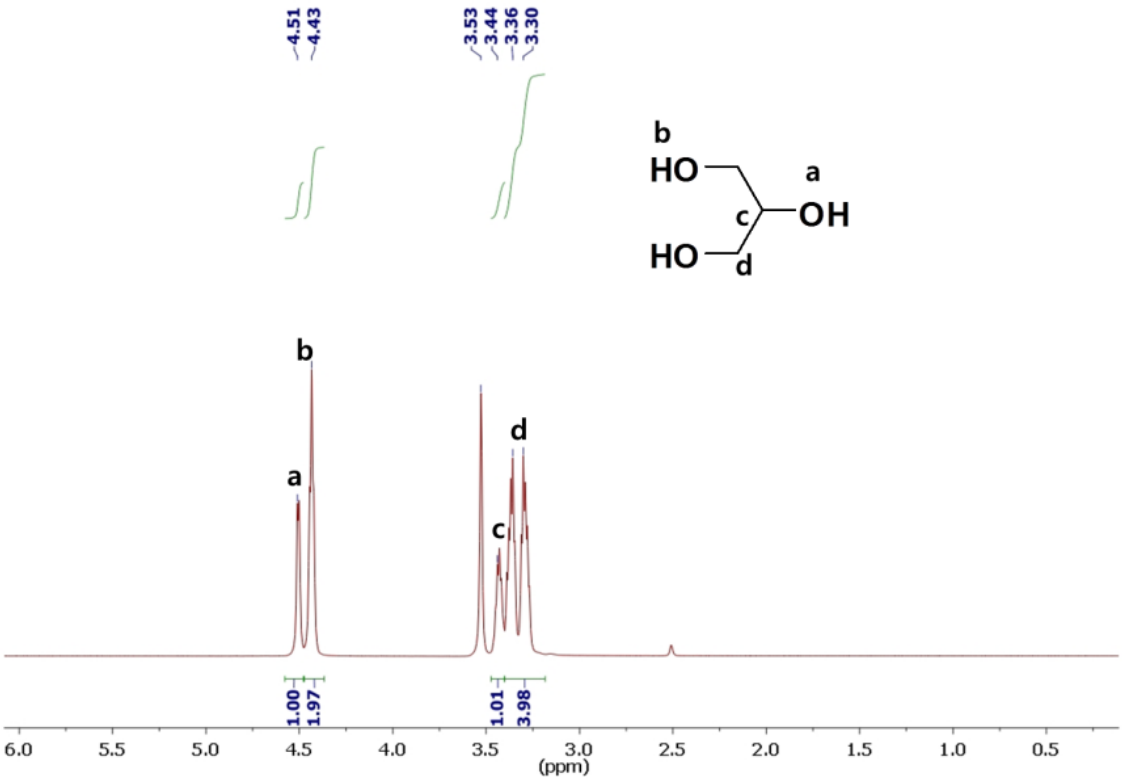


Figure 60: ^{1}H NMR of glycerin.

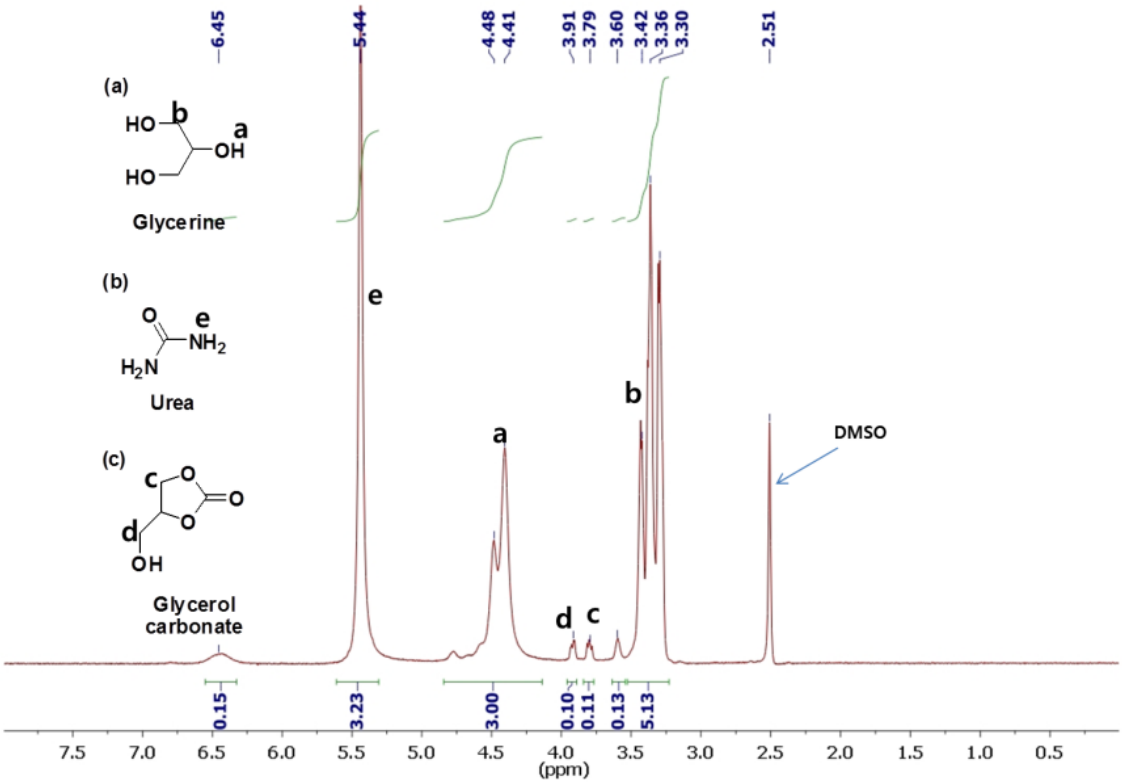


Figure 61. ^{1}H NMR of glycerin carbonates final product mixture.

During synthesis of glycerol carbonate, a small fraction of the sample was taken out to investigate conversion with respect to time. FTIR spectra of the reaction product mixture at different time interval are shown in Figure 62. The intensity of the peak of –C=O of glycerol carbonate at 1724.62 cm^{-1} increases gradually and the peak of –OH of the glycerin became broad and uniform as the reaction progresses. It suggested an increase in conversion of glycerin to glycerol carbonate as the reaction progresses.

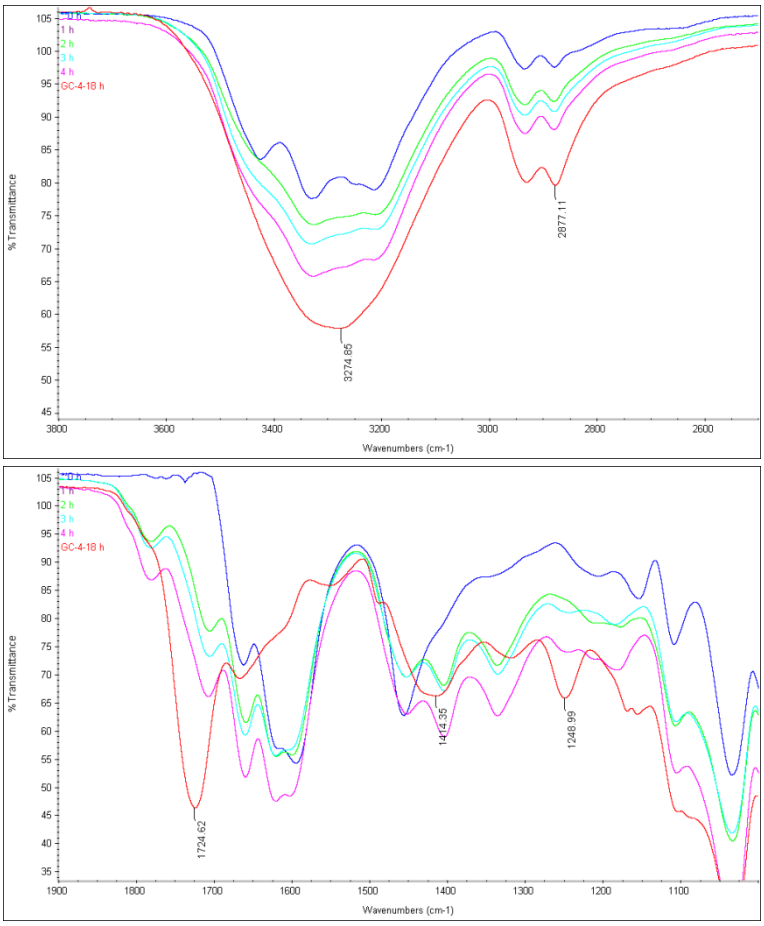


Figure 62. IR spectra of the glycerol carbonate reaction mixture at different time interval.

Glycerol carbonate was synthesized using two different setups. (a) In the first setup, a 3-neck flask with a reaction mixture was equipped with water condenser on a hot plate magnetic stirrer. As the reaction mixture attained 140 ºC, the urea started to condense over the top of the flask and at water condenser and did not remain in the reaction solution. The samples were taken out and at a periodic interval of time; the solid urea condensed over the flask was removed using a spatula and added again to the reaction flask. (b) In a second case, the reaction was performed in a high-pressure tube. Urea started to condense over the top of the reactor in the high-pressure tube also, which was again solubilized in the flask at a periodic interval of time. However, the reaction did not proceed well as significant amount of urea remained insoluble even after 72 h of reaction time.

As shown in FT-IR, a substantial conversion of glycerin to glycerol carbonate was observed, but due to sublimation of urea at the reaction temperature, it was difficult to maintain it in the system. As a result, the conversion from glycerin to glycerol carbonate was poor. We needed to investigate a different method, which is more eco-friendly and can result in a higher conversion.

(b) Glycerol carbonate from glycerin and dimethyl carbonate in presence of molecular sieves and Novozyme 435 (Sigma-Aldrich).

In a second attempt, glycerol carbonate was synthesized using glycerin and dimethyl carbonate at different temperature for 24 h in presence of Novozyme 435 and molecular sieve as shown in Figure 63. Herein, we synthesized glycerol carbonate using Novozyme catalyst in THF at different temperature for 24 h.

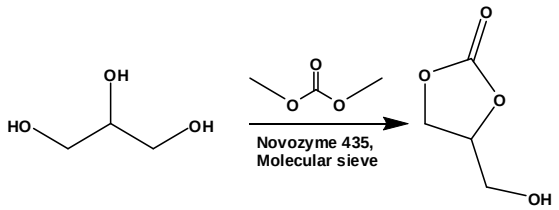


Figure 63. Synthetic of glycerol carbonate by reaction of glycerin and dimethyl carbonate in presence of Novozyme and molecular sieve.

Glycerol carbonate was synthesized using eco-friendly Novozyme 435 catalyst at three different temperatures. Firstly the reaction was performed at 40 ºC, based on the integration values; the conversion was calculated to be ~17 % as shown in Figure 64. Figure 65 and Figure 66 are the ^{1}H NMR of the glycerol carbonate synthesized at 60 ºC and 80 ºC respectively. Both NMR has many peaks; therefore, determination of the extent of conversion of glycerin on the basis of peak integration was difficult. The Novozyme based method to synthesize glycerol carbonate also did not help in improving the conversion. It was essential to explore other available approaches for the synthesis of glycerol carbonate.

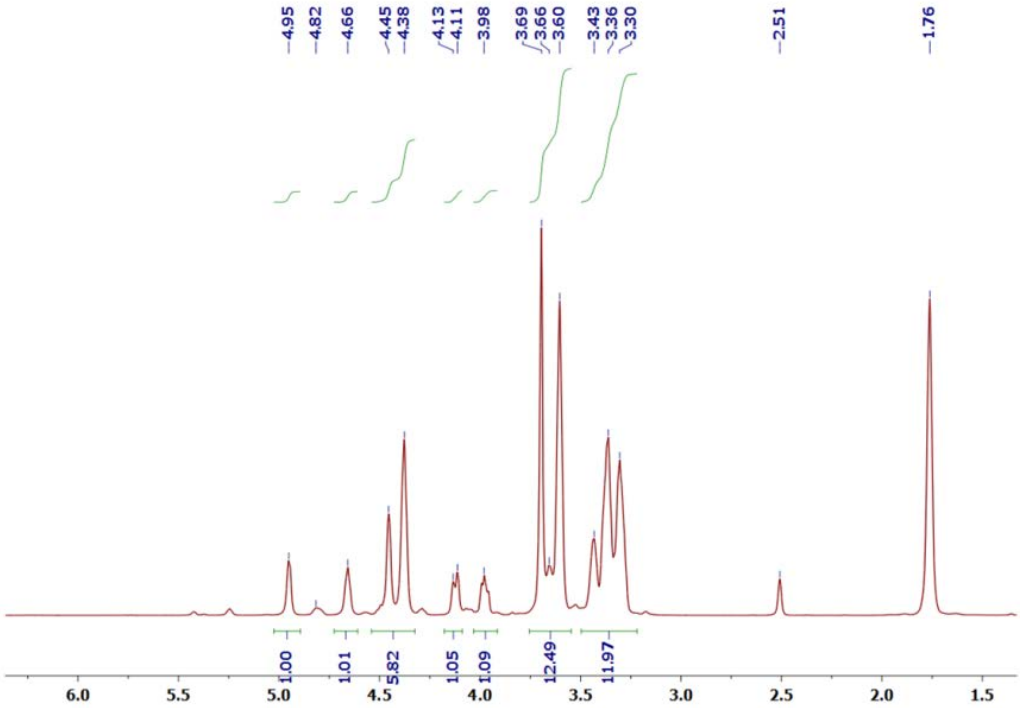


Figure 64. ^{1}H NMR of the glycerol carbonate synthesized using DMC and Novozyme 435 at 40 ºC.

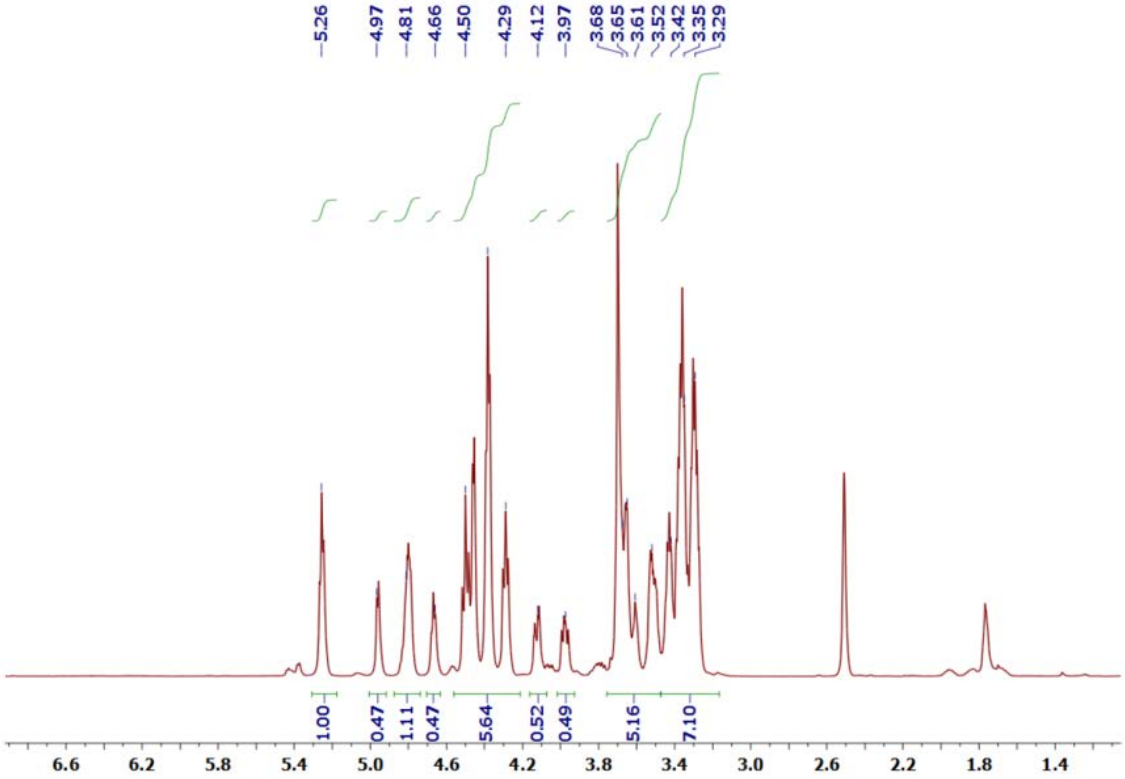


Figure 65. ^{1}H NMR of the glycerol carbonate synthesized using DMC and Novozyme 435 at 60 ºC.

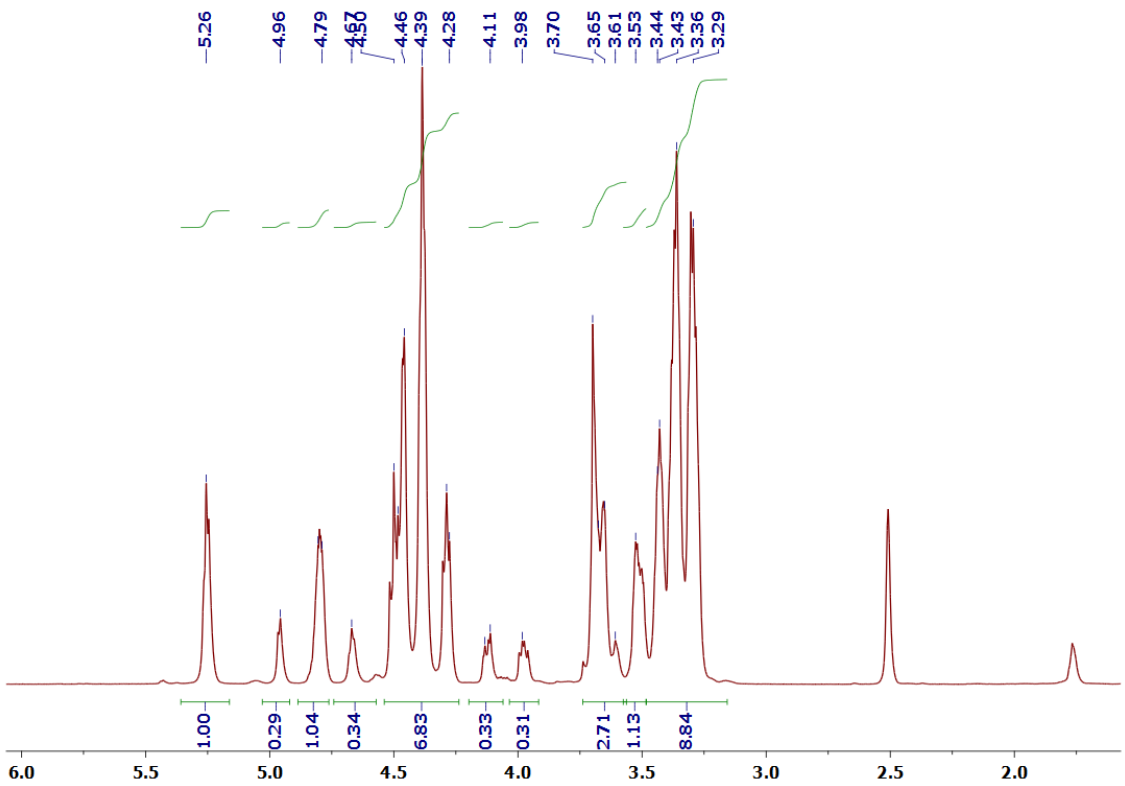


Figure 66. ^{1}H NMR of the glycerol carbonate synthesized using DMC and Novozyme 435 at 80 ºC.

(c) Synthesis of glycerol carbonate from glycerin and dimethyl carbonate in presence of sodium aluminate.

It has been reported that the reaction between glycerin and dimethyl carbonate produces glycerol carbonate in presence of various catalysts. The reaction was performed between glycerin and dimethyl carbonate at 80 ºC for 90 min in presence of sodium aluminate as shown in Figure 67. The final reaction mixture also had a small amount of unreacted glycerin.

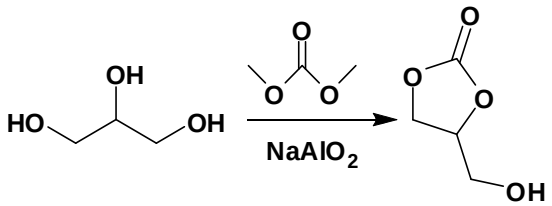


Figure 67. A synthetic scheme of glycerol carbonate using glycerin and dimethyl carbonate at in presence of sodium aluminate at 80-90 ºC for 90 min.

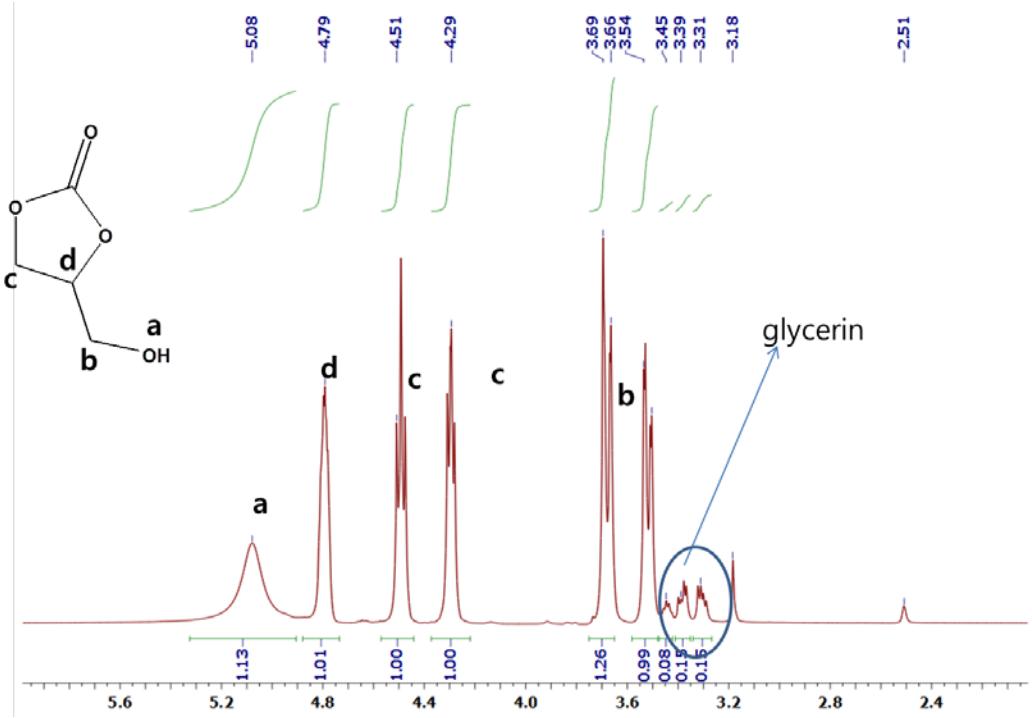


Figure 68. ^{1}H NMR of the glycerol carbonate synthesized using DMC and sodium aluminate at 80 ºC.

As can be seen in ^{1}H NMR in Figure 68, the formation of glycerol carbonate was confirmed. Secondly, FT-IR also showed a peak at ~1756 cm^{-1}, which is a strong evidence of the presence of glycerol carbonate as shown in Figure 69. Furthermore, small peaks of a proton from glycerin were observed between 3.0-3.5 ppm in ^{1}H NMR. On the basis of integration value, the conversion of glycerol carbonate was observed to be ~91.0 %.

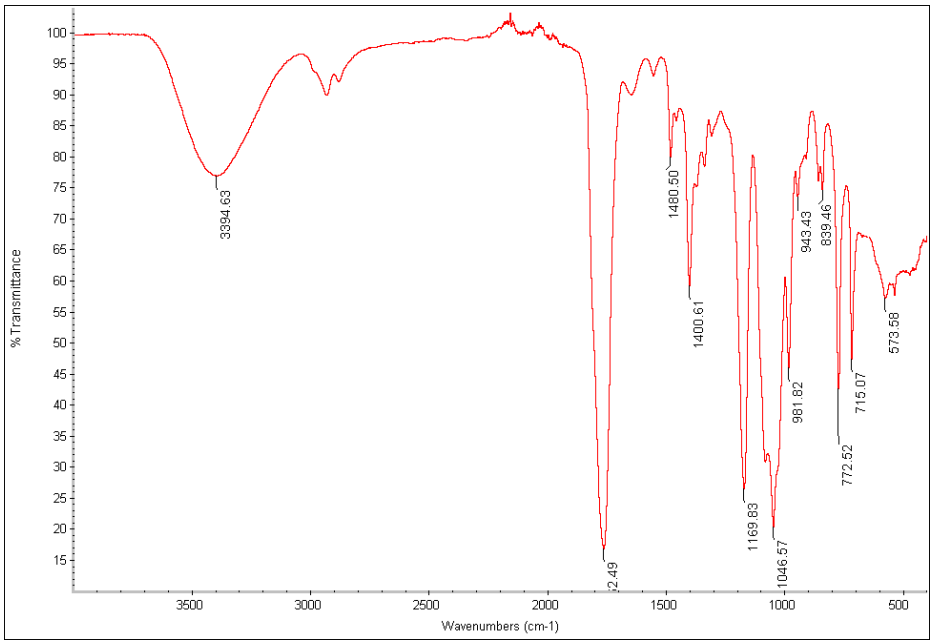


Figure 69: FT-IR of the glycerol carbonate synthesized using DMC and sodium aluminate at 80ºC.

As the glycerin and the glycerol carbonate are high boiling point liquids and their boiling point is also very close. Therefore, their purification by fraction distillation is a big challenge. Different distillation setup and conditions were used to isolate pure glycerol carbonate. However, the simple fractional distillation apparatus did not work well. The reaction mixture was also distilled using V-column but due to the length of the column and limitation of the available vacuum pump, the material could not be distilled. The material will be purified by the Kugelrohr distillation apparatus. Meanwhile, we continued to investigate new methods for efficient synthesis of glycerol carbonate.

(d) Synthesis of glycerol carbonate from glycerin and dimethyl carbonate in presence of potassium carbonate.

In a new approach, glycerol carbonate was synthesized by the reaction between glycerin and dimethyl carbonate at 100 ºC and 75 ºC and for 3 h in presence of potassium carbonate as shown in Figure 70. The method is promising, but the separation of potassium carbonate at last from the reaction mixture is a challenge as it stays soluble in the system.

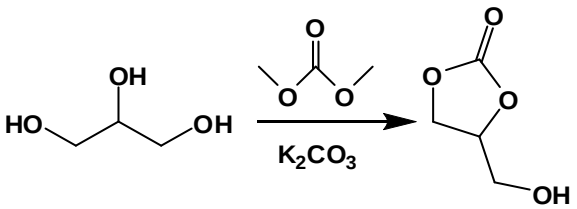


Figure 70. A synthetic scheme of glycerol carbonate using glycerin and dimethyl carbonate at in presence of potassium carbonate at 73-75 ºC for 180 min.

Firstly, the reaction was performed at 73 ºC and the glycerol carbonate was synthesized successfully. The product formation was confirmed by ^{1}H NMR as shown in Figure 71. The peak integration value suggested ~ 97.0 % conversion of glycerin to glycerol carbonate at 73 ºC. To complete the reaction to 100.0 %, the reaction temperature was gradually increased to 100 ºC; however, as the temperature increased to 100 ºC, the formation of some side product was observed and unreacted glycerin was also found in the final mixture as shown in Figure 72. The FT-IR spectra of glycerol carbonate synthesized at 73 ºC clearly showed peaks of –C=O at 1772.51 cm^{-1} and –OH at 3456.9 cm^{-1} as shown in Figure 73.

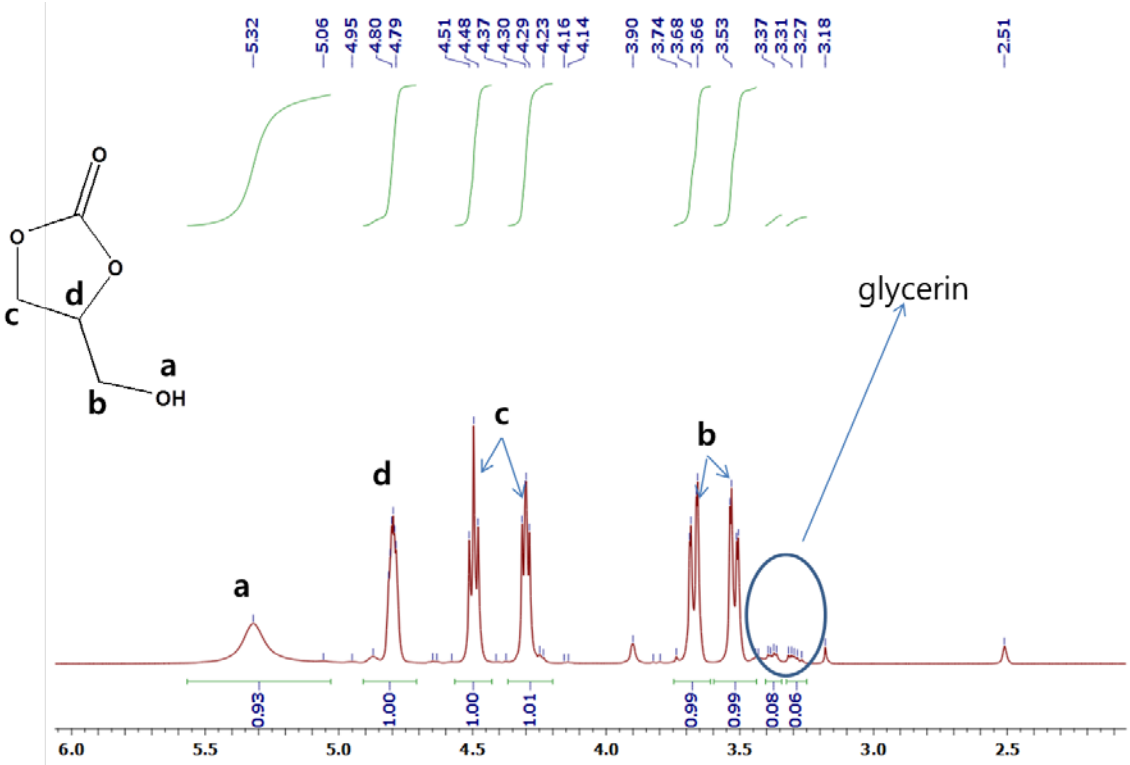


Figure 71. ^{1}H NMR of glycerol carbonate synthesized using dimethyl carbonate at 73 ºC.

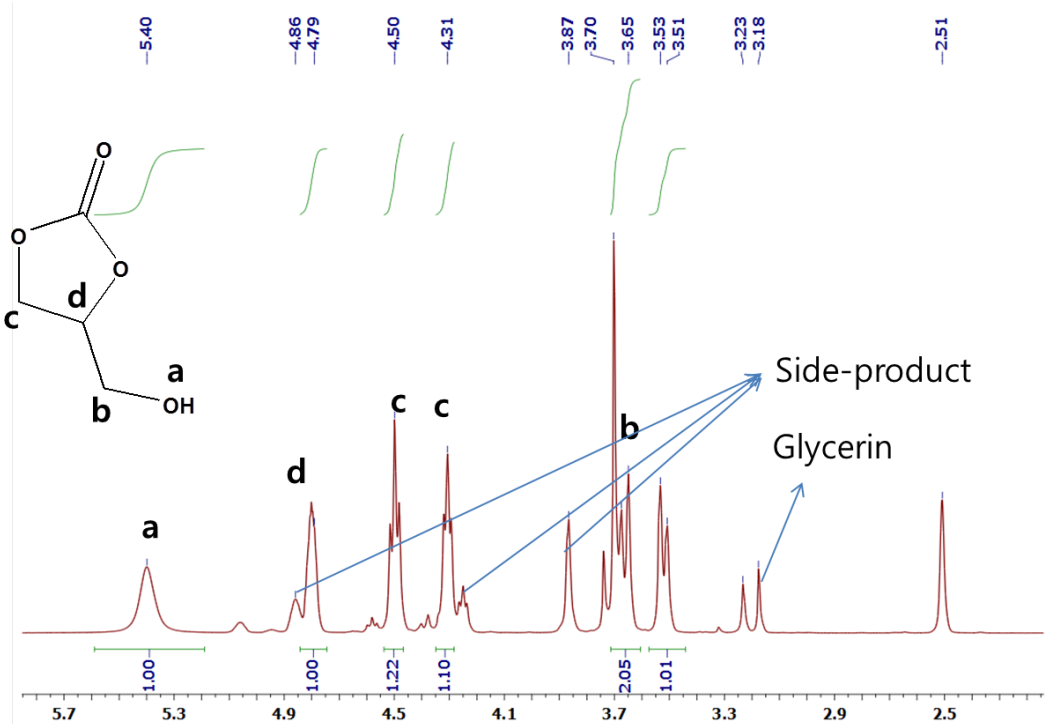


Figure 72. ^{1}H NMR of glycerol carbonate synthesized using dimethyl carbonate in presence of potassium carbonate at 100 ºC.

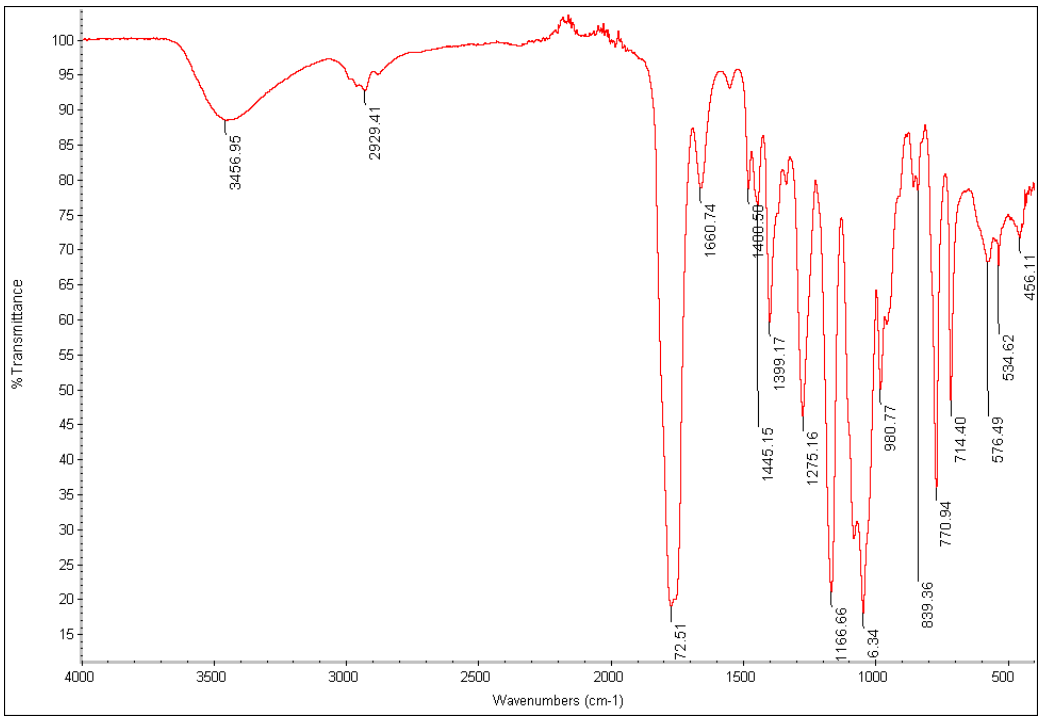


Figure 73. FT-IR of the glycerol carbonate synthesized using dimethyl carbonate in presence of potassium carbonate at 73 ºC.

In summary, four different methods for synthesis of glycerol carbonate were investigated. In the first method, the sublimation of urea at reaction temperature caused poor conversion. Secondly, usage of Novozyme 435 as a catalyst gave only 17.0 yield. Sodium aluminate as a catalyst yielded 91.0 % glycerol carbonate, but it still had ~9.0 % of unreacted glycerin. So far, usage of potassium carbonate catalyst is the most promising, as it yielded 97.0 % glycerol carbonate.

Refinement of glycerol carbonate;

The catalyst K_2CO_3 remained soluble in the glycerol carbonate and it was decomposed by passing the glycerol carbonate through Amberlite IR 120-acidic resins. During column purification, strong effervescence was observed. The rigorous effervescence is shown in Figure 74. It is presumed that after passing through the column, all potassium carbonate was decomposed by observing stopping of the effervesces.

Figure 74. Decomposition of potassium carbonate by column purification of glycerol carbonate using Amberlite IR 120-acidic resins

3.2.3.2. Glycidol from glycerol carbonate

Glycidol is the second intermediate during multi-step GMA synthesis from glycerin. Glycidol can be obtained by decarboxylation of glycerol carbonate as shown in Figure 75. In next step, transesterification will be performed between glycidol and methyl methacrylate to obtain glycidyl methacrylate. Glycidol was synthesized by simple heating of glycerol carbonate in presence of sodium sulfate.

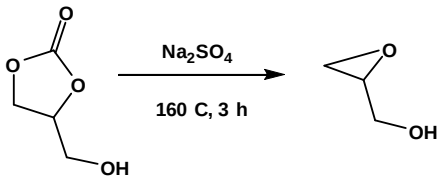


Figure 75. Synthesis of glycidol from glycerol carbonate in presence of sodium sulfate at 180 ºC for 3 h.

Materials equipment setup:

A mineral oil bath, equipped with a thermometer and a magnetic stir bar was placed on the top of the magnetic stirrer hotplate. A 100 mL round-bottom flask, equipped with a magnetic stir bar and distillation apparatus with a water condenser was placed in an oil bath using clamps. The distillation apparatus was attached to the vacuum pump. Between the distillation apparatus and vacuum pump, three acetone and dry ice based cold traps were used. A thin film of vacuum grease was applied to the male end of the distillation apparatus

Procedure:

A 100 mL round bottom flask was charged with 40.0 g of the glycerol carbonate and 4.0 g of anhydrous sodium sulfate. The reaction mixture was continuously stirred using magnetic stirrer under reduced pressure and the flask was heated to 160 °C. The glycidol was allowed to be distilled off for 3 h. The glycidol (as distillation product) was collected and transferred to a vial. The typical setup for the synthesis of glycidol is shown in Figure 76, where a distillation assembly is placed in a round bottom flask and the end of the distillation apparatus is connected to high- pressure vacuum pump. Three cold traps can also be observed between distillation apparatus and high-pressure vacuum pump.

Figure 76. Setup for the synthesis of glycidol from glycerol carbonate in presence of sodium sulfate at 160 ˚C for 3 h.

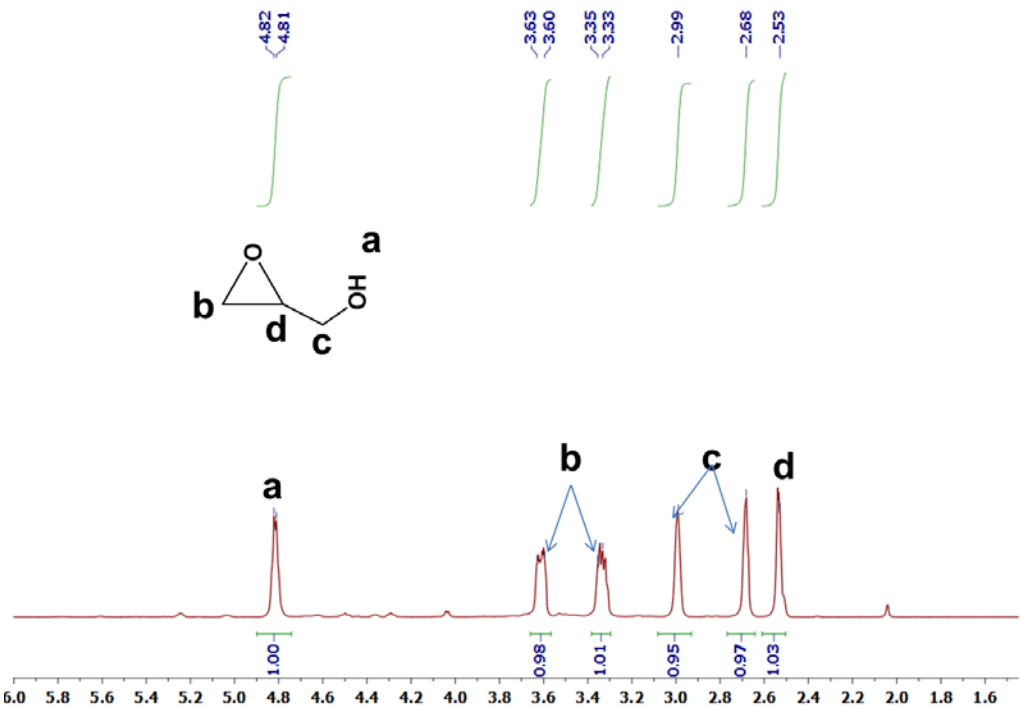


Figure 77. ^{1}H NMR of glycidol.

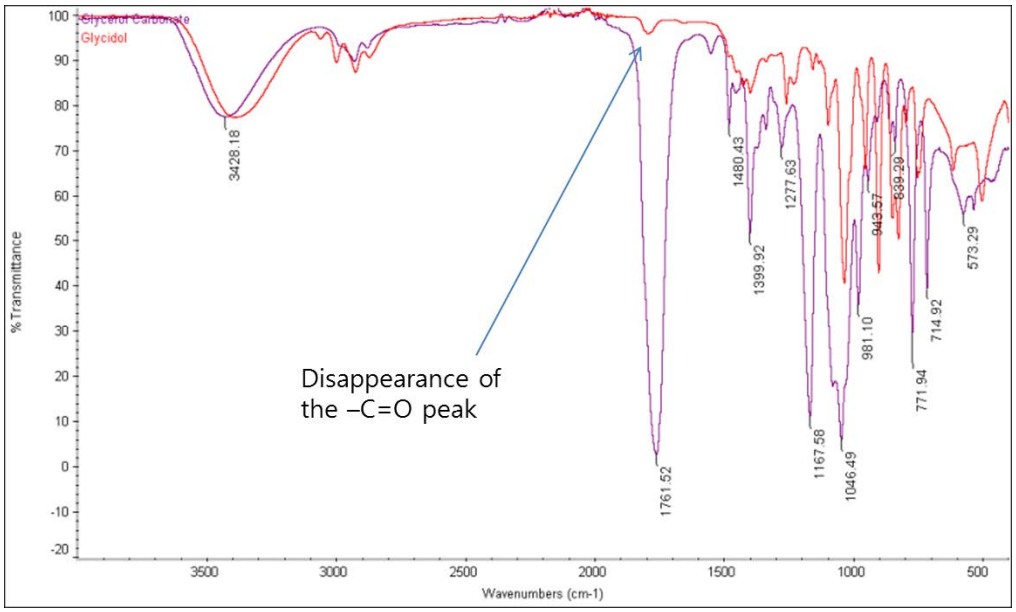


Figure 78. FTIR of glycidol

Glycidol was synthesized by simply heating the glycerol carbonate in presence of sodium sulfate at 180 ˚C for 3 h. At such a high temperature, it was not possible to collect glycidol in a flask by condensing it simply over water condenser; therefore, three cold traps were used and the synthesized glycidol is easily getting condensed in the traps. The formation of glycidol is confirmed by ^{1}H NMR by matching integration value of each proton as shown in Figure 77. In a

strong evidence, the FT-IR showed the clear disappearance of the –C=O peak at 1761 cm^{-1} as shown in Figure 78. The product was isolated with 55 % yield.

3.2.3.3. Glycidyl methacrylate from glycidol and methyl methacrylate.

Glycidyl methacrylate (GMA) is one of the precursors for the synthesis of vinyl ester resin monomer along with BPA and TBBPA. The GMA is synthesized by transesterification between methyl methacrylate and glycidol in presence of potassium cyanide as a catalyst and 2.4-dimethyl-6-tertbutylphenol as a catalyst as shown in Figure 79.

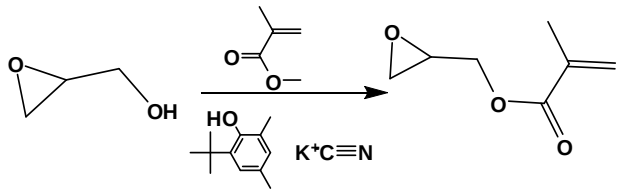


Figure 79. Synthesis of GMA from glycidol and methacrylate.

Materials and Setup:

A mineral oil bath, equipped with a thermometer and a magnetic stir bar was placed on the top of the magnetic stirrer hotplate. A 100 mL round-bottom flask, equipped with a magnetic stir bar and distillation apparatus with a water condenser was placed in an oil bath using clamps. The distillation apparatus was attached to the high-pressure vacuum pump (Edward RV5). Between the distillation apparatus and vacuum pump acetone and dry ice based cold traps was used. A thin film of vacuum grease was applied to the male end of the distillation apparatus.

Procedure

A round bottom flask was set up on an oil bath with magnetic stirring with distillation apparatus over it. A flask was charged with 50.0 g (0.5 moles) of methyl methacrylate and 7.4 g (0.1 mole) of glycidol, 0.05 grams of 2,4-dimethyl-6-tert butyl phenol. Then there was added 0.055 g (0.85 mmole) of potassium cyanide and the mixture heated to 70 ℃to 80 °C for 2 h. They were immediately vacuum distilled and two fractions were collected. Firstly, the temperature was reduced in the reaction flask, and the temperature was raised to 70 ˚C. The temperature of 70 ˚C was maintained for 2 h, and after that unreacted methyl methacrylate and methanol were distilled off. In the second fraction, unreacted glycidol was collected and in the last fraction, GMA was obtained. The structure of GMA was confirmed by ^{1}H NMR as shown in Figure 80. The GMA was isolated with 26.1 % yield.

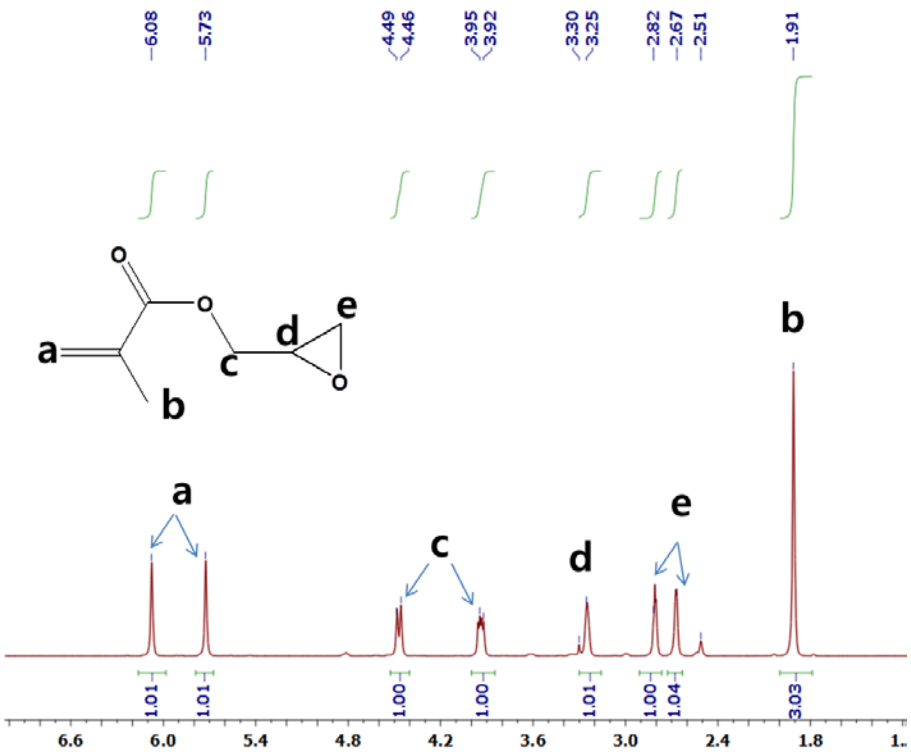


Figure 80. ^{1}H NMR of the distilled glycidyl methacrylate.

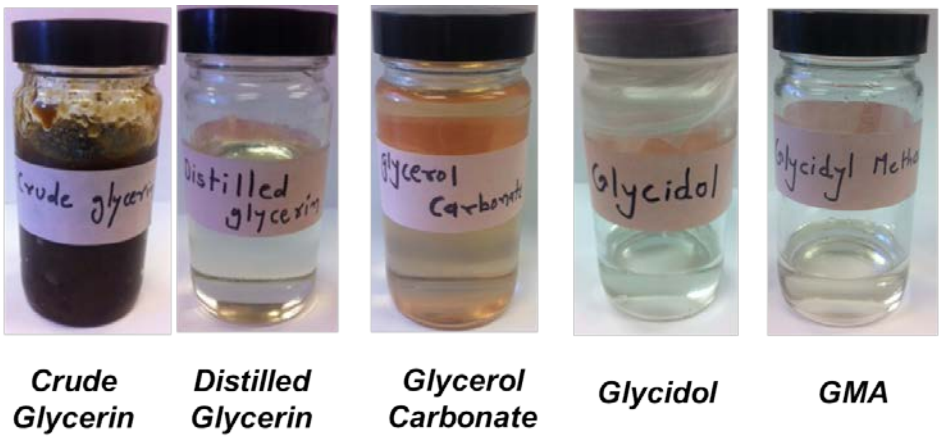


Figure 81. All product and intermediate starting from biodiesel glycerin to glycidyl methacrylate.

All products and their intermediate on the synthetic route of glycidyl methacrylate are shown in Figure 81.

3.3. Task 3 - Scale Up Resin Processing

In Task 1 and Task 2, we have demonstrated synthesis of precursors such as bisphenol A and glycidyl methacrylate from the biowaste materials of lignin and biodiesel glycerin,

respectively. In Task 3, we will demonstrate synthesis and purification of the vinyl ester resin using bioderived precursors exploring various synthetic routes.

3.3.1. Synthesis of BPA-based VER monomer

BPA based vinyl ester resin (VER) monomer was synthesized using BPA and glycidyl methacrylate as a precursor using tertiary amine based catalyst under an inert condition at 70 ºC for 6 h as shown in Figure 82.

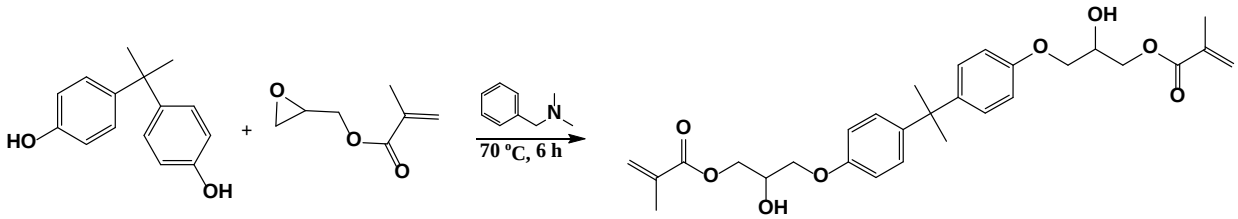


Figure 82. VER monomer synthesis using BPA and GMA

3.3.1.1. Materials and Setup for Synthesis of Vinyl Ester Resin Monomer

A mineral oil bath, equipped with a thermometer and a magnetic stir bar, was placed on the top of the magnetic stirrer hotplate. A 250 mL round-bottom flask, equipped with a mechanical stirrer and rubber septa, was placed in an oil bath using clamps. Argon was flushed continuously into the reaction flask by maintaining positive pressure.

3.3.1.2. Procedure

A 25 mL round-bottom flask was charged with bisphenol A (22.829 g, 0.10 mol), glycidyl methacrylate (28.4 g, 0.20 mol) and N, N-dimethyl benzylamine (0.13 g, 1.0 mmol). The flask had a continuous flow of argon, and the temperature was raised to 70 ºC, which was maintained for 6 h. After the reaction, the highly viscous liquid was transferred to a glass vial, and the product was analyzed by TLC, ^{1}H NMR, and FT-IR.

3.3.1.3. Results

The vinyl ester monomer was synthesized by simple one pot reaction between BPA and GMA in the presence of a tert-amine catalyst. The reaction was performed at 70 ℃ using a mechanical stirrer. After the reaction, the highly viscous product was transferred to the scintillation vial, and the resultant product was completely transparent. As can be seen in ^{1}H NMR, the peak of –OH of the BPA disappeared completely, so it was presumed that the reaction was 100 %. However, the integration value is not matched precisely as shown in Figure 83. The TLC showed three spots. The integration values in ^{1}H NMR and a higher number of spots in TLC confirmed the presence of product in the reaction mixture. The three spots could be due to the presence of unreacted BPA, monofunctionalized BPA, and difunctionalized BPA (product). Secondly, as can be seen in FT-IR, the peak of –OH of the BPA was appeared to be at 3318 cm^{-1}, which shifted to 3324 cm^{-1} in VER monomer. The shift in the peak of –OH, clearly indicate the consumption of

aromatic hydroxy and generation of the aliphatic hydroxy group. In other observation, a clear peak of –C=O was observed ~1760 cm^{-1}, which should be due to either mono or difunctionalized BPA as shown in Figure 84.

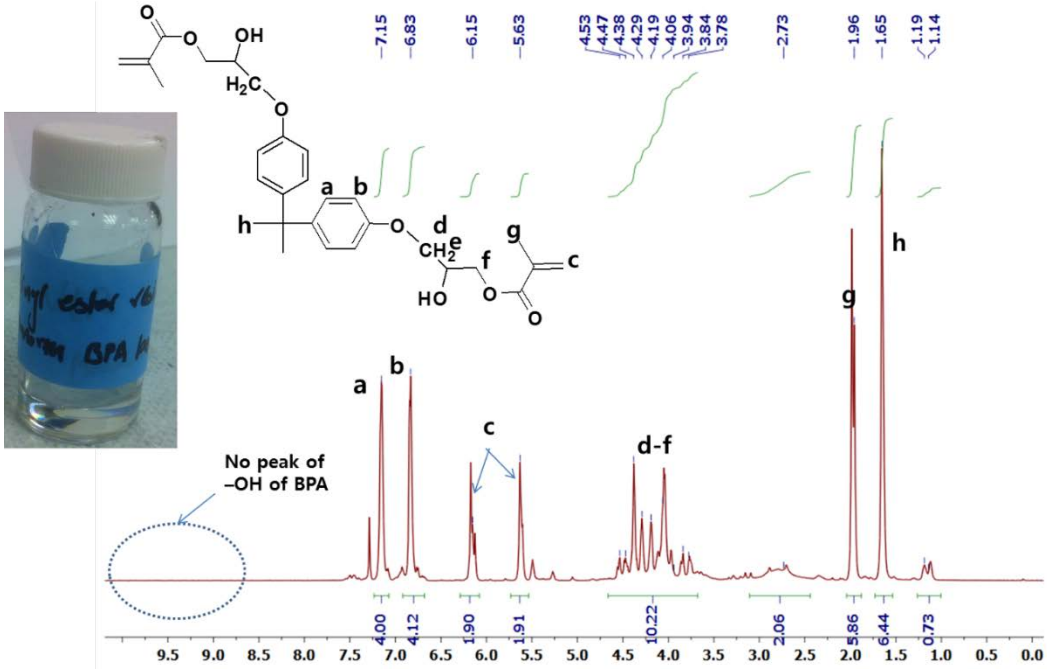


Figure 83. ^{1}H NMR and image of vinyl ester monomer synthesized using bisphenol A.

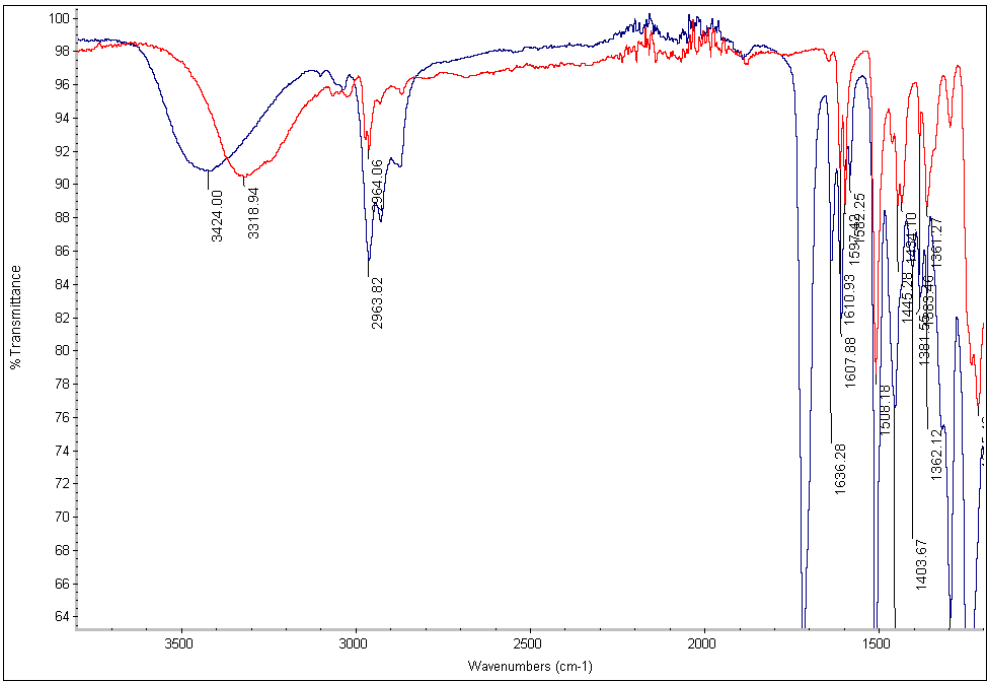


Figure 84. FT-IR and image of vinyl ester monomer synthesized using bisphenol A.

3.3.1.4. Separation of VER

The VER monomer was separated by column chromatography, in which silica gel was used as a packing material and ethyl acetate-hexane was used in 3:7 (v/v) as shown in Figure 85. The ^{1}H NMR of each fraction confirmed the presence of non-, mono-, and di-functional BPA in the product mixture. Figure 86 is the ^{1}H NMR of the first fraction during column, which clearly confirmed that BPA was the first eluted material. In a second fraction, monofunctionalized BPA, BPA with GMA substitution at only one –OH group, was observed as shown in Figure 87. The monofunctional product can easily be confirmed by peak integration and four aromatic proton peak of equal intensity. In a third fraction, VER oligomer, disubstituted BPA was observed as shown in Figure 88.

As the reaction did not reach to completion at 70˚C during 4 h, it was necessary to determine the optimum condition to attain the maximum amount of di-functional BPA. The parameter, such as temperature, reaction time and the molar ratio of GMA:TBBPA was varied. However, to quantify the amount of each fraction precisely, a development of HPLC method was highly desirable. Each fraction was analyzed using UV spectroscopy to investigate their detection range in UV detector as shown in Figure 89.

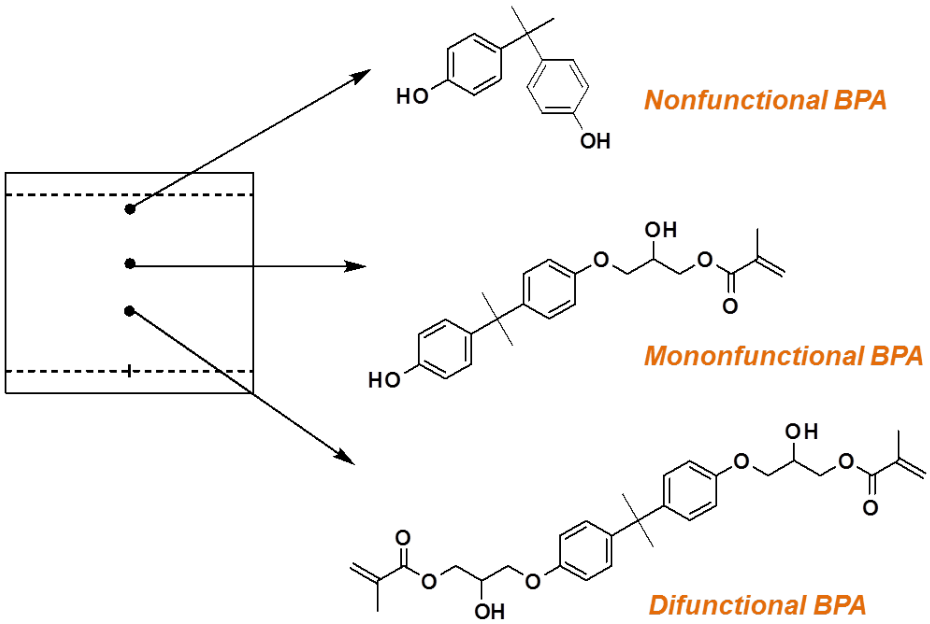


Figure 85. TLC of vinyl ester resin using Ethyl acetate: Hexane in 3:7 ratio.

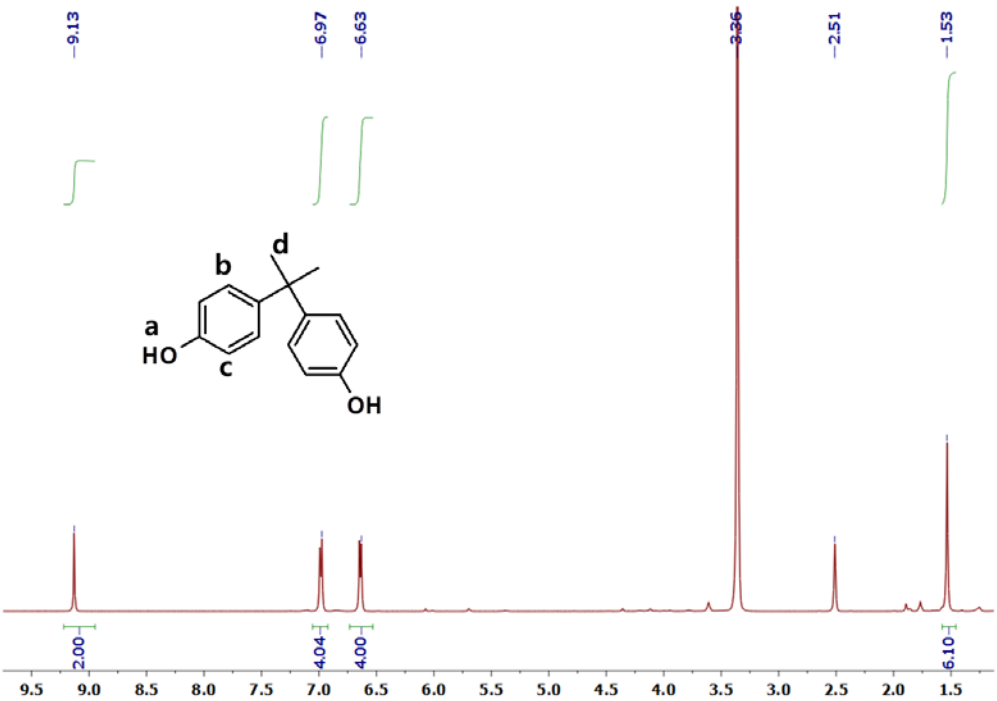


Figure 86. ^{1}H NMR of the first fraction of material isolated during column chromatography.

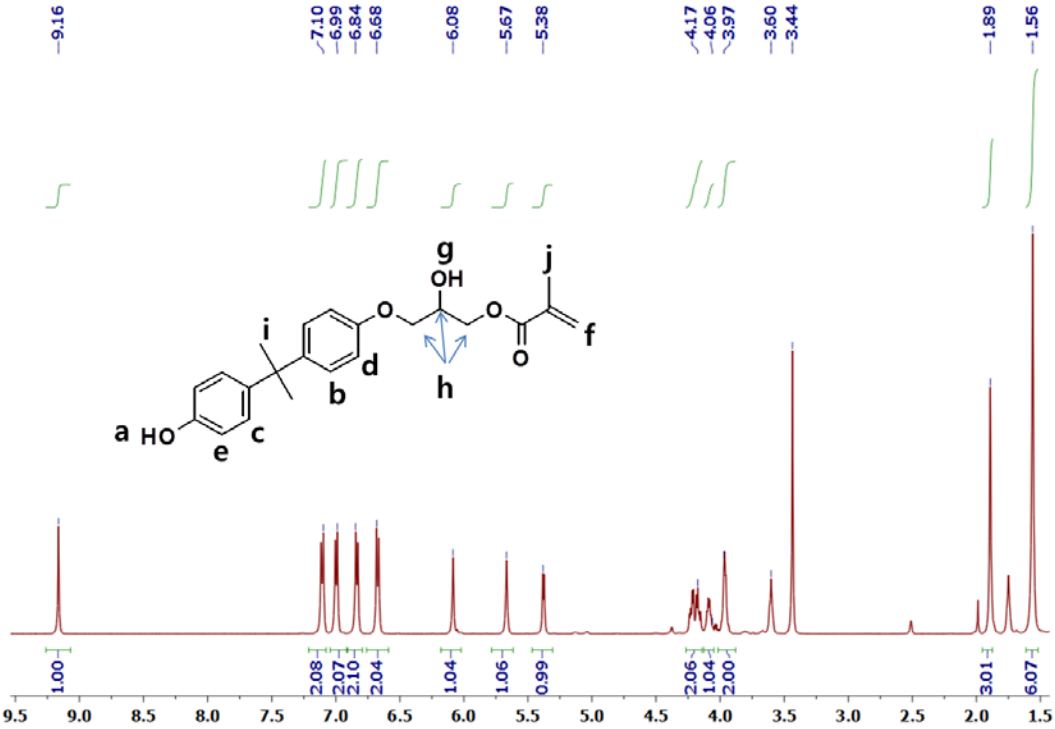


Figure 87. ^{1}H NMR of the second fraction of material isolated during column chromatography.

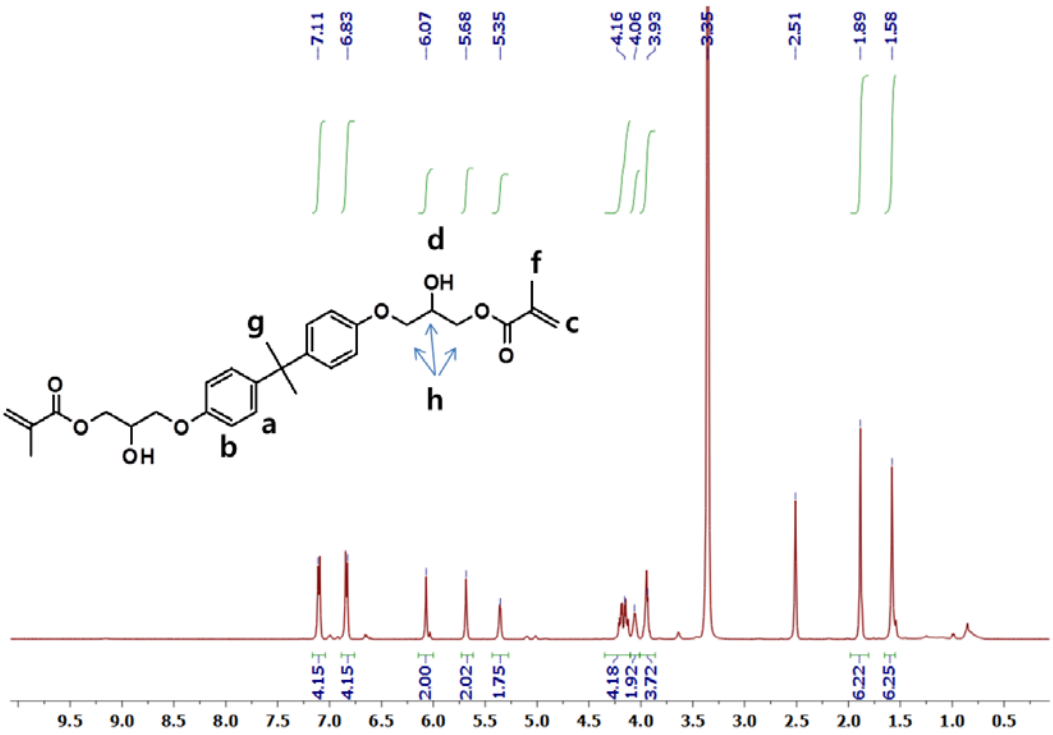


Figure 88. ^{1}H NMR of the third fraction of material isolated during column chromatography.

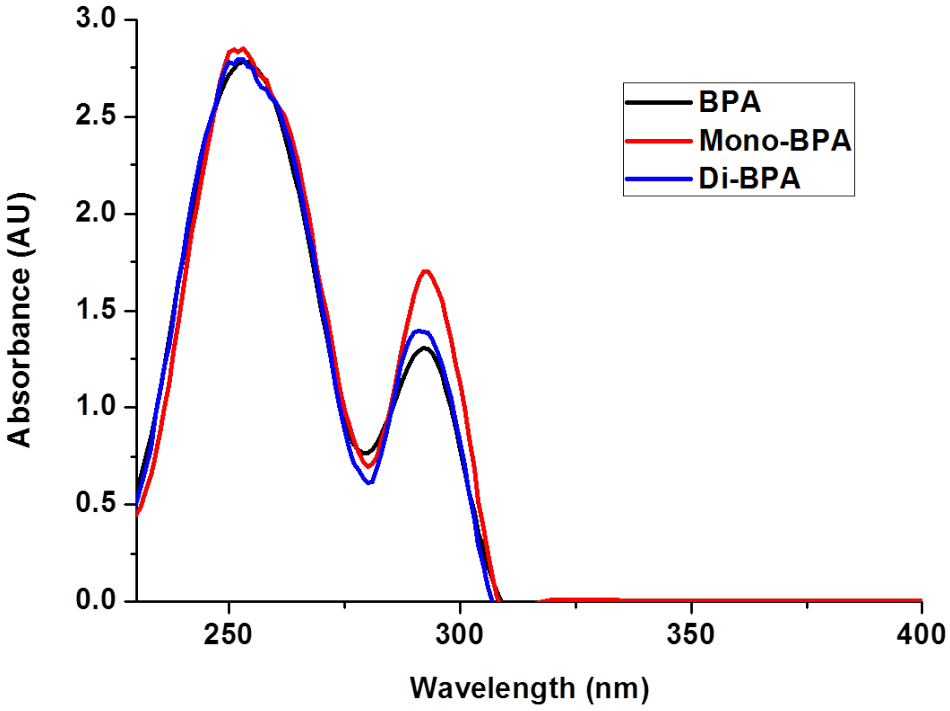


Figure 89. UV spectra of nonfunctional, monofunctional, and difunctional bisphenol-A obtained after column chromatographic separation of VER product mixture.

Preliminary work was conducted to develop a high-performance liquid chromatographic (HPLC) method for the separation and determination of BPA and reaction products in the synthesis of a vinyl ester monomer or VER from GMA with the goal is to separate di-functionalized BPA from non-functional and mono-functional BPA and determine their concentrations in a reaction mixture.

Chromatographic system: The liquid chromatograph (Water's Alliance system model 2695 HPLC system) is equipped with a photodiode array (PDA) detector (Water's model 2996) monitored at 277 nm and a 4.6 mm × 15 cm column that contains 3-µm packing (Polar - Diol). The column temperature is maintained at 25C with a flow rate of 1.0 mL/min and an injection volume of 1 uL. The system was run isocratic with a 70:30 mixture of hexane and ethyl acetate. Samples were injected without dilution.

Chromatograms showed in Figure 90 clearly demonstrate that the 3 compounds have very different retention times on the diol column with 70:30 hexanes: ethyl acetate and should be easily separated and determined in a reaction mixture. As shown in Figure 90(a), the first fraction eluted with a retention time of 5.218 min clearly confirmed that nonfunctional BPA was the first eluted material. Figure 90(b) is the chromatogram of the second fraction, mono-functionalized (MF) BPA, which eluted at 7.946 min. In a third fraction, VER oligomer, disubstituted (DF) BPA was observed as shown in Figure 90(c) and eluted at 13.686 min.

In order to determine the kinetics of the reaction, the quantification of NF, MF, and DF in the reaction mixture is very essential. Such quantification can be obtained by HPLC separation of the mixture. Therefore, preliminary work was conducted to develop an HPLC method for the separation and determination of the BPA and reaction products in the synthesis of a VER. The goal was to separate each fraction without overlapping retention time.

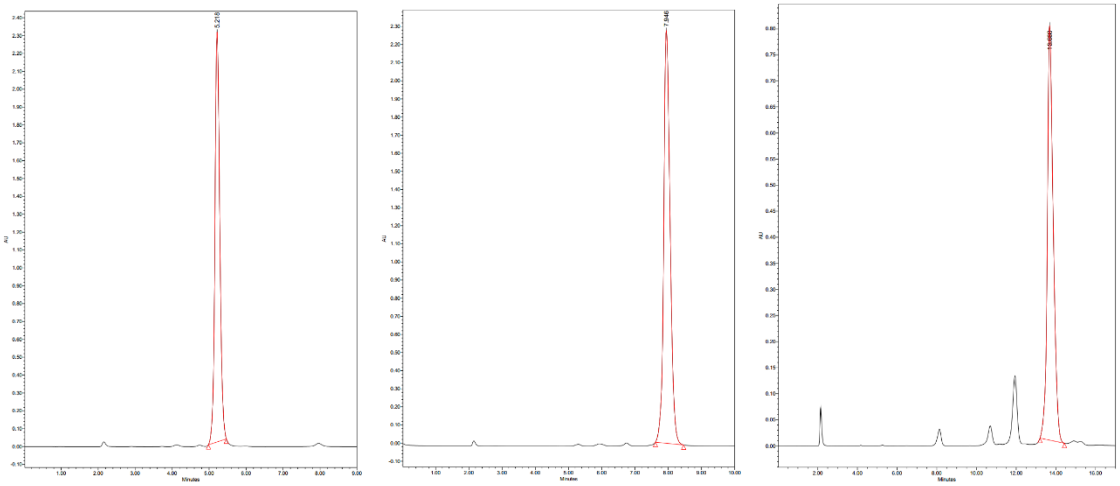


Figure 90. Chromatogram of (a) first fraction (b) second fraction, and (c) third fraction isolated during column purification of the VER-monomer.

Table 19. Percentage of various components in VER-reaction mixture at different time intervals.

Reaction time (h)	Different functional BPA		
	Non	Mono	Di
2h	32.00	49.24	18.76
3h	20.79	46.28	32.93
4h	14.13	40.63	45.23
5h	13.38	28.27	58.34
6h	12.70	18.05	69.26

In order to determine the optimum conditions, we performed one VER synthesis at 70 ºC using BPA:GMA in 1:4 molar ratio. We quantified the nonfunctional, monofunctional, and difunctional BPA by calculating and comparing the area under the peak of the chromatogram obtained at different time intervals as shown in Table 19. The results suggested that reaction proceeds well as time progresses. However, it did not attain completion at 6 h, 69.26 % of the VER monomer was obtained, and prolonged reaction time was causing crosslinking and further side reaction, in which the secondary -OH group of VER monomer was participating in the ring opening of the other GMA molecules.

3.3.2. Various Synthesis routes of VER Monomer by reaction of glycerin and BPA

Performing reactions in one-pot are promising as the purification of intermediates is averted. This results in a higher atom economy and a significantly greener synthetic protocol. With these aims, we pursued the one-pot synthesis of the VER monomer.

It was recently reported that glycerin can selectively be converted to aryloxy propanediol's in a one-pot reaction, through in situ formed glycerol carbonate, under benign and solvent-free conditions. The reaction occurs through the intermediate glycerol carbonate (GC), which is a non-toxic reagent. The reaction proceeded through nucleophilic attack of phenol on the in situ formed intermediate GC. The base played a dual role; it catalyzed both the formation of GC through carbonatation of glycerin by the dialkyl carbonate and the subsequent nucleophilic attack of the phenol.

3.3.2.1. One pot synthesis of VER by the reaction of glycerin and BPA.

Extending these concept initial investigations were performed for the one-pot synthesis of bisphenol-A diglycidyl ether (BADGE) and VER monomer. As shown in the reaction schematic Figure 91, BPA. Glycerin and dimethyl carbonate were allowed to react at 90 ºC in the presence of potassium carbonate After the reaction, methyl methacrylic acid was added to the reaction mixture. The product was purified using column chromatography using same protocol followed previously.

The catalyst (potassium carbonate) utilized for the two reactions reported above is the same and it is used in same concentrations. Hence, the above two reactions can be combined to obtain VER.

Materials. Bisphenol A, diethylene carbonate, potassium carbonate, and methyl methacrylate were procured from Sigma-Aldrich and utilized without further purification. Crude glycerin as a bio-waste was procured from Maine Standard Biofuels. Glycerin in pure from was obtained using vacuum distillation.

Procedure. In a single necked round bottom flask bisphenol A (1 g, 4.38 mmol), glycerin (2.42 g, 26.28 mmol), diethyl carbonate (1.552 g, 1.314 mmol) and potassium carbonate (300 mg, 2.17 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 110 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethyl carbonate, glycerol, and ethanol byproduct. To the crude reaction mixture, 5 mL of dimethyl sulfoxide was added to reduce the viscosity of the reaction mixture and 3 mL of methyl methacrylate was added. The transesterification reaction was performed at 110 °C with the application of mild vacuum to remove the azeotrope formed by methanol and methyl methacrylate. After 12 hours the vacuum was increased to remove any unreacted methyl methacrylate and methanol byproduct. The crude reaction mixture in dimethyl sulfoxide was then introduced into 1:8 mixture of methanol: deionized water to precipitate the product and centrifuged to obtain a viscous precipitate. The precipitate was washed 3 times with 1:8 mixture of methanol: deionized water to remove any trapped methyl methacrylate and glycerol derivative. The resulting product was analyzed by proton NMR as shown in Figure 92. ^{1H} NMR of the single pot VER reaction product in DMSO-d6. A 75 % conversion was obtained as seen from the NMR. The purification of the product is underway.

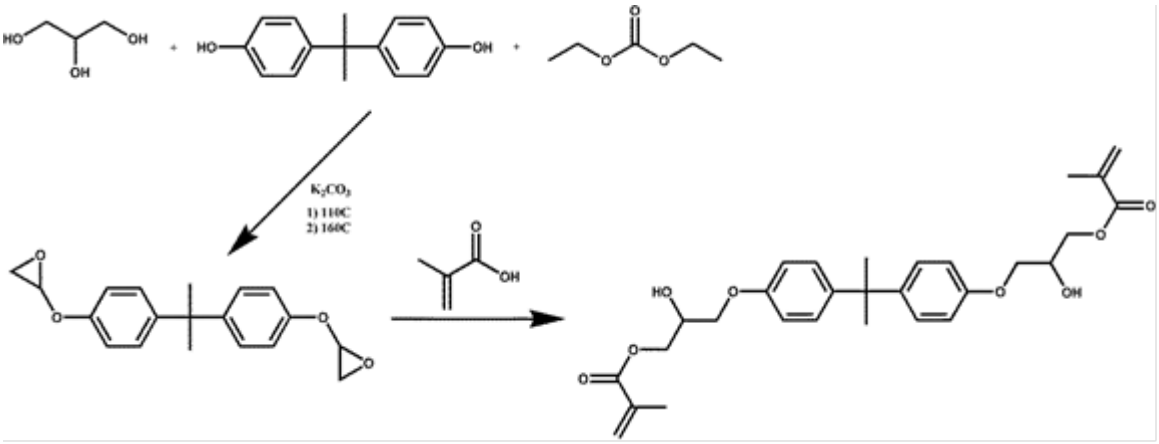


Figure 91. Reaction scheme for the one-pot synthesis of BADGE and VER monomer.

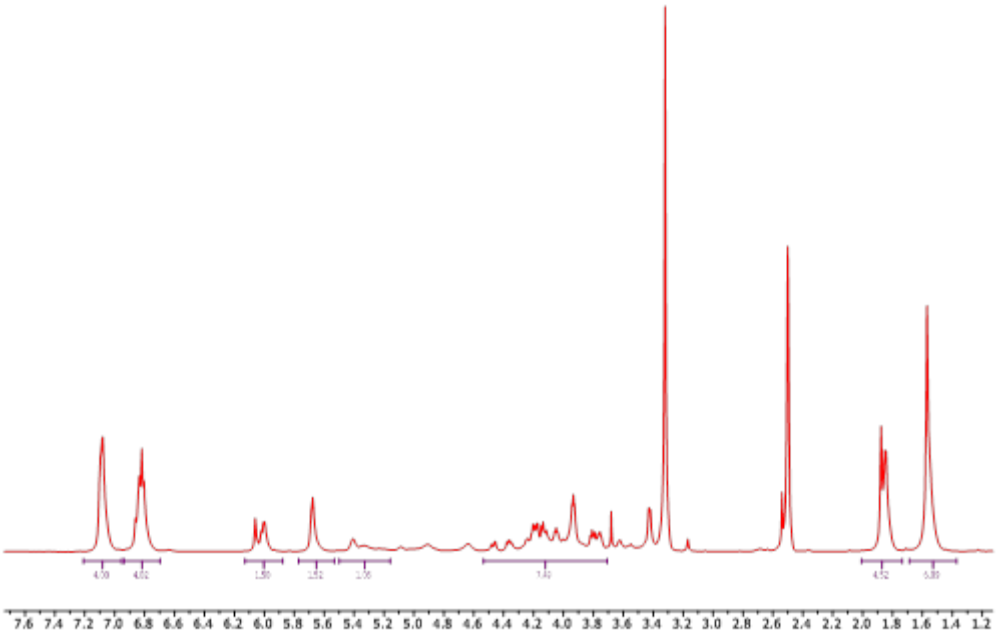


Figure 92. ^{1}H NMR of the single pot VER reaction product in DMSO-d6.

3.3.2.2. One pot synthesis of intermediate Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE)

As in one pot method described in the previous section, the yield of the final VER monomer was very low. In order to improve the yield further, we tried two-step synthesis of VER. In this method, a Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE) intermediate was first synthesized by the reaction of glycerin with BPA using diethyl carbonate in presence of potassium carbonate.

Materials. Bisphenol A, diethylene carbonate and potassium carbonate were procured from Sigma-Aldrich and utilized without further purification. Crude glycerol as a bio-waste was procured from Maine Standard Biofuels. Glycerol in pure form was obtained using vacuum distillation**.**

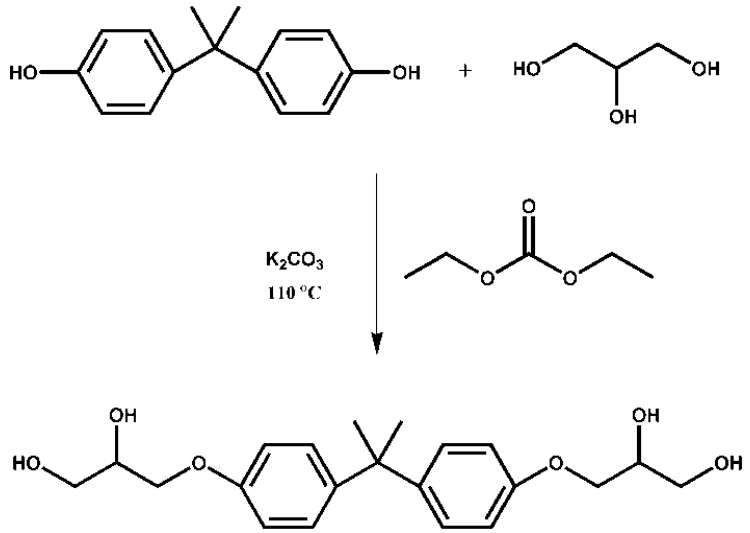


Figure 93. Reaction scheme for the synthesis of Bisphenol A bis(2,3-dihydroxypropyl)-ether (BABDHPE).

Procedure. In a single necked round bottom flask bisphenol A (10 g, 43.80 mmol), glycerin (24.20 g, 262.82 mmol), diethyl carbonate (15.52 g, 131.4 mmol) and potassium carbonate (3 g, 21.70 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 110 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethyl ether and the ethanol byproduct. The hot reaction mixture was then added to a beaker containing 500 mL deionized water. A viscous reaction product was allowed to settle over time and the supernatant water removed. The crude reaction product was washed twice with 500 mL deionized water to remove any unreacted glycerol. The 99 % pure Bisphenol A bis(2,3-dihydroxypropyl)ether (Figure 93) was isolated in quantitative yields. The purity of the reaction product was determined using proton NMR as shown in Figure 94 &Figure 95. This solvent-free reaction occurs through in-situ formation of glycerol carbonate as described in the literature[63]. The reaction can also be performed using commercially available glycerol carbonate instead of glycerol and diethyl carbonate.

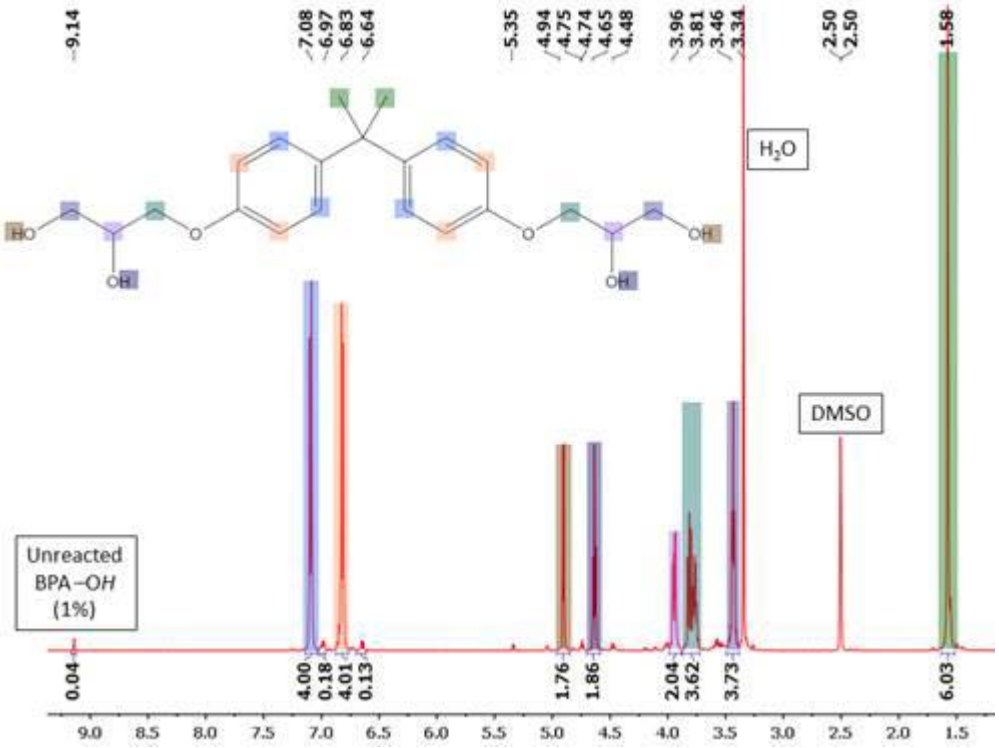


Figure 94. Proton NMR of Bisphenol A bis(2,3-dihydroxypropyl)-ether (BABDHPE)

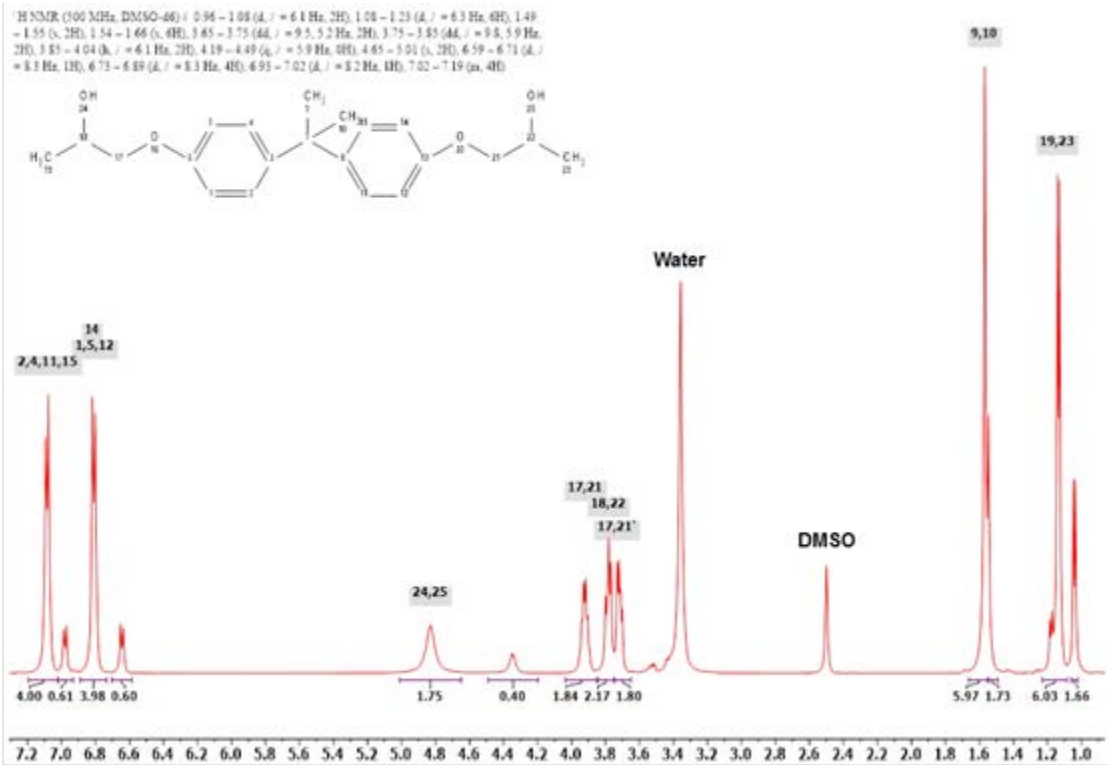


Figure 95. Proton NMR of BABHPE in DMSO-d6.

3.3.2.3. Synthesis of VER through BABDHAP route.

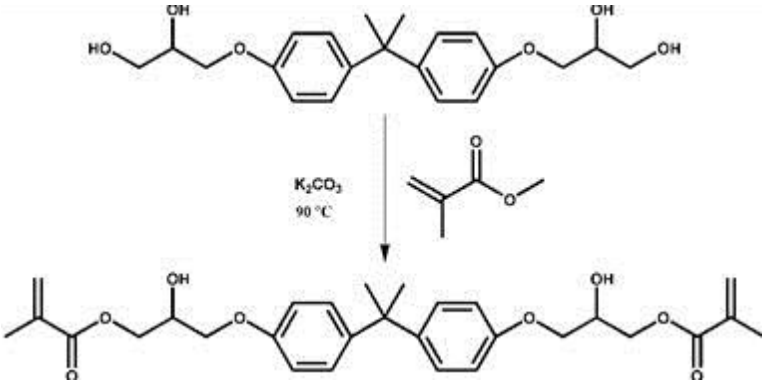


Figure 96. Reaction scheme for the synthesis of VER by transesterification of BABDHPE.

Once we have purified Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE), it was allowed to react with methyl methacrylate (MMA) by transesterification reaction to produce VER as shown in Figure 96. Reaction scheme for the synthesis of VER by transesterification of BABDHPE.

Materials. Methyl methacrylate and Potassium Carbonate were procured from Sigma-Aldrich and utilized without further purification. The isolated BABDHPE was utilized for the reaction (Figure 96).

Procedure. In a single necked round bottom flask bisphenol A bis(2,3-dihydroxypropyl)ether (1 g, 2.65 mmol), as received methyl methacrylate (1.32 g, 13.28 mmol) and potassium carbonate (300 mg, 2.17 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 90 °C. After 18 h the reaction was stopped by applying vacuum to remove any unreacted methyl methacrylate and the methanol byproduct. The resulting product was analyzed by proton NMR as shown Figure 97.

Transesterification is a well know reaction which can be performed using a variety of catalysts. Potassium carbonate was selected as an example here to demonstrate the feasibility of the reaction protocol. Further investigations are underway to improve the conversion of the reaction and will be included here. A 25 % conversion was obtained in the current reaction protocol as evidenced by the presence of vinyl protons around 6.04 and 5.61 ppm.

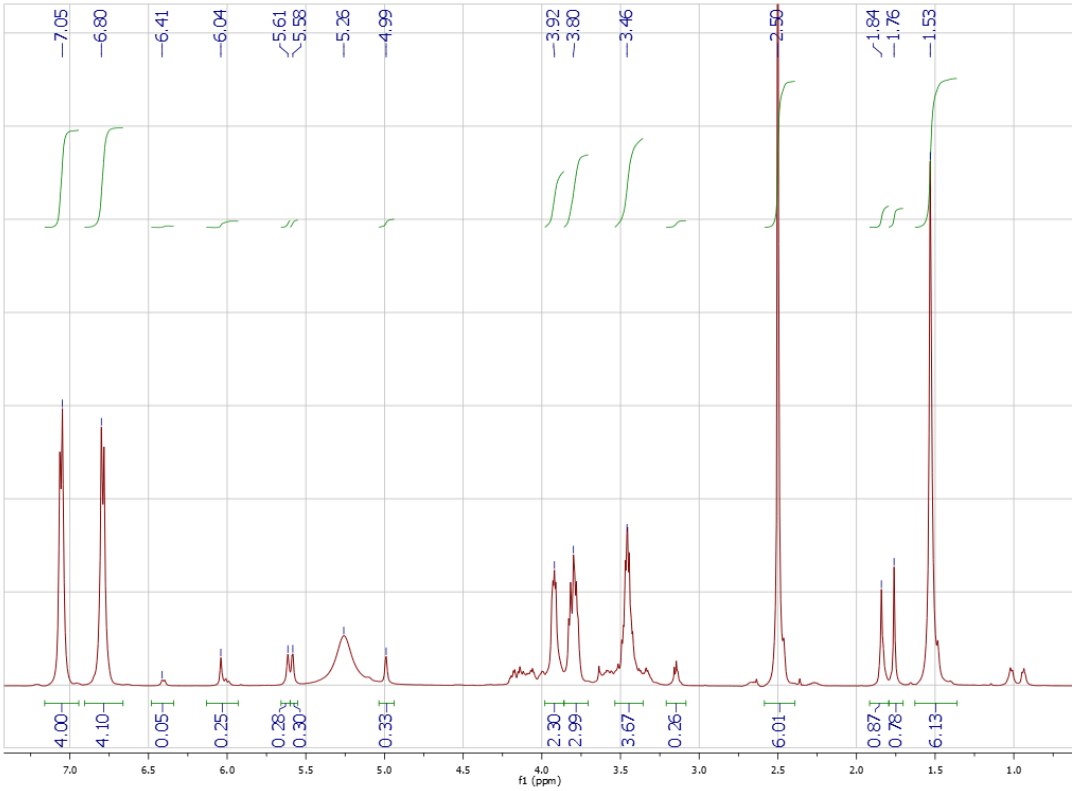


Figure 97. Proton NMR of the reaction product in DMSO-d6.

3.3.2.4. Synthesis of GVER by the reaction of the GCMA and BPA.

In this section, synthesis of green vinyl ester resin (GVER) from biowaste generated by biodiesel industries was demonstrated. We have synthesized vinyl ester resin using BPA or TBBPA as one of the precursor and glycerol carbonate methacrylate (GCMA) as another precursor. We have used crude glycerin obtained during manufacturing of the biodiesel in the preparation of GCMA. Conversion of glycerin to GCMA required a two-step synthesis. Firstly, glycerol carbonate (GC) was synthesized from glycerin and dimethyl carbonate under basic conditions. GCMA was synthesized by reaction of GC with methyl methacrylate in presence of zirconium acetylacetonate[64] as shown in Figure 98.

There has been a considerable dearth of literature pertaining to systemic studies on the use of functional vinyl monomers such as GMA [65], which is a versatile bidentate monomer capable of imparting oxirane functionality to VER containing styrene or other vinyl monomers. A significant literature has been reported in VER without showing concern for the manufacturing on the environment. We have also published an article on the synthesis of VER using GMA and BPA [66]. In this section, we focused on the synthesis of the GVER from waste glycerin via synthesis of GCMA.

In the present work, we report for the first time the following:

- A simple two-step synthesis of glycerol carbonate methacrylate (GCMA) from glycerin has been proposed for the first time. In the synthesis, glycerin generated at biodiesel manufacturing plant was used.
- The first intermediate on the synthetic route, glycerol carbonate was synthesized with ~98.5 % purity using waste glycerin for the first time. Secondly, the product was made catalyst-free by simply passing over acidic resin. Glycerol carbonate possesses a large number of applications in many diverse fields, which can potentially expand the market scope for proposed methodology.
- The GCMA was synthesized with 81.0 % yield. The green GCMA will be very useful not only as a precursor in VER but also many other resins.
- Green vinyl ester resins were successfully synthesized from BPA or TBBPA and GCMA at 90 °C using potassium carbonate as catalysts.
- The synthetic method consists of four steps and uses renewable biowaste as starting materials, whose disposal is a big problem as by 2020 the production of glycerin will be six times higher than its demand.
- Moreover, in the previous literature of green vinyl ester resin, we have used glycidol as one of the intermediates for the production of GVER. Glycidol is a potential carcinogen and its production is an extremely energy intensive process as the decarboxylation from glycerol carbonate to glycidol is performed at 140 to 160 °C. In current proposed plan, we have eliminated a step for formation of glycidol as one of the intermediate.
- In previous synthetic route of vinyl ester resin from biowaste, we had used potassium cyanide as a catalyst for the transesterification between glycidol and methyl methacrylate. In current work, we have used zirconium acetylacetonate as a catalyst for transesterification between glycerol carbonate and methyl methacrylate. Using current synthetic route, we have eliminated the use of toxic potassium cyanide.

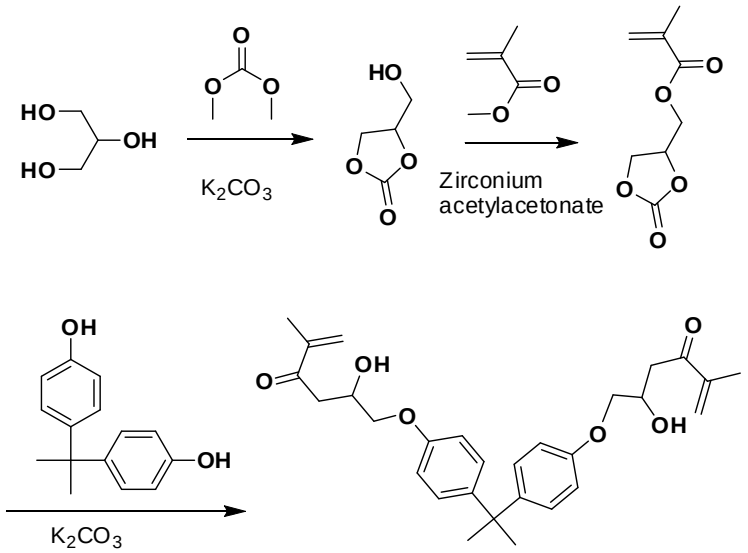


Figure 98. Synthesis of vinyl ester oligomer from phenol and glycerin.

1) **Experimental.**

*Materials***.** Glycerin (Maine Standard Biofuels), potassium carbonate (99 % Sigma-Aldrich), dimethyl carbonate (99 % Alfa-Aesar), sodium sulfate (99.9 % Alfa-Aesar), methyl methacrylate (99.9 % Alfa-Aesar), potassium cyanide (Sigma-Aldrich), 2,4,-dimethyl,6-tert-butyl phenol (Alfa-Aesar), and N,N-dimethylbenzylamine, lignin (Flambeau River Paper and Sigma-Aldrich).

Characterization. ^{1}H NMR spectra of the synthesized materials were recorded at 25 °C on a Bruker 500 MHz spectrometer using DMSO (Cambridge Isotope Lab., Inc.) as the solvent and tetramethylsilane (TMS) as the internal reference (δ H 0.00).

Refine Glycerol Carbonate Methacrylate (GMA) from Glycerin

The GCMA was synthesized by a two-step organic synthesis. The first intermediate, glycerol carbonate, was synthesized from glycerin and dimethyl carbonate under basic condition. GCMA was synthesized by reaction of glycerol carbonate and methyl methacrylate using zirconium acetylacetonate as described in Figure 98. Here, we will discuss the synthetic procedure of each intermediate.

Glycerol carbonate. In a typical setup, a 250 mL flask equipped with a magnetic stirrer, condenser and thermometer were charged with glycerin (40.05 g, 0.435 mol), dimethyl carbonate (117.45 g, 1.305 mol) and K_2CO_3 (1.8 g, 13.05 mmol). The reaction mixture was refluxed (73–75 °C) for 3 h. After completion of the reaction, methanol and the excess of dimethyl carbonate were distilled off at 40 °C under reduced pressure. The remaining glycerol carbonate was analyzed by ^{1}H NMR and FT-IR spectroscopy.

Glycerol Carbonate Methacrylate. An RB flask was placed in an oil bath with magnetic stirring with a distillation apparatus over it. A flask was charged with 11.8 g (0.1 mol) of glycerol carbonate and 60.0 g (0.6 mol) of methyl methacrylate and 1.8 g of zirconium acetylacetonate and the mixture heated to 90 °C for 48 h. The reaction was terminated by removing the catalyst by addition of dilute phosphoric acid and removed by centrifugation. The organic layer was then washed with water to remove unreacted glycerol carbonate. The remaining methyl methacrylate was removed at a rotary evaporator, and the product was confirmed by ^{1}H NMR and ^{13}C NMR.

Synthesis of vinyl ester resins (VER). A 25 mL RB flask was charged with BPA (1.14 g, 5 mmol), GCMA (1.86 g, 10 mmol) and potassium carbonate (0.030 g). The flask had a continuous flow of argon, and the temperature was raised to 90 °C, which was maintained for 18 h. After the reaction, the highly viscous liquid was transferred to a glass vial, and the product was analyzed by TLC, ^{1}H NMR, and FT-IR.

Herein, we have demonstrated the feasibility of the sustainable, environmentally safe, 'green' vinyl ester resin (GVER) technology using renewable biowaste. The GVER structures will be made predominantly from biowaste, namely lignin, recovered from wood wastes, and glycerin, recovered from biodiesel wastes. These source materials are renewable, low-cost, and are

becoming increasingly abundant and thus will eliminate dependence on imported oil. Figure 98 shows the sequence of reactions leading from lignin and/or wood wastes to GVER monomer.

Synthesis of glycerol carbonate methacrylate from glycerin (GCMA)

GCMA was synthesized using glycerin as the main precursor. Glycerin is a side-product of the transesterification of triglyceride in the manufacturing of biodiesel or the hydrolysis of triglyceride during saponification. We obtained vegetable glycerin from a local vendor Bulkapothecary (Streetsboro, OH).

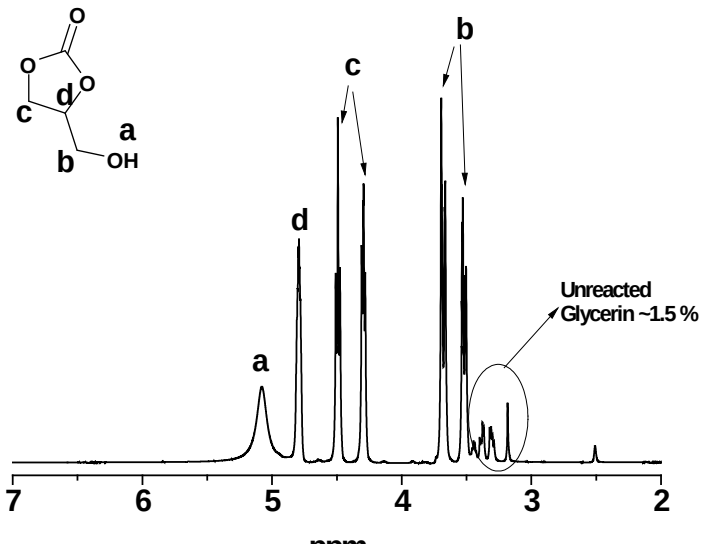


Figure 99. ^{1}H NMR of glycerol carbonate.

GC, a first intermediate in the synthetic route to GCMA from glycerin, is a very important material having a large number of applications in various fields. We have also developed a tremendous interest in isolation of this material with 100 % purity. Various approaches had been adopted by different groups for the synthesis of the GC; such as using (a) Novozyme 435 catalyst and dimethyl carbonate as a precursor [59], and (b) metal oxide as a catalyst and urea as a precursor [67]. In a new approach, GC was synthesized by the reaction between glycerin and dimethyl carbonate at 73 °C for 3 h in the presence of potassium carbonate [68]. The method is promising, with several challenges, for example, the separation of potassium carbonate from the reaction mixture. Firstly, the reaction was performed at 73 °C and the GC was synthesized successfully. The product formation was confirmed by ^{1}H NMR as shown in Figure 99. The peak integration value suggested ~ 98.5 % conversion of glycerin to GC at 73 °C. In order to complete the reaction to 100.0 %, the reaction temperature was increased to 100 °C; however, as the temperature increased to 100 °C, the formation of some side product was observed and unreacted glycerin was also found in the final mixture.

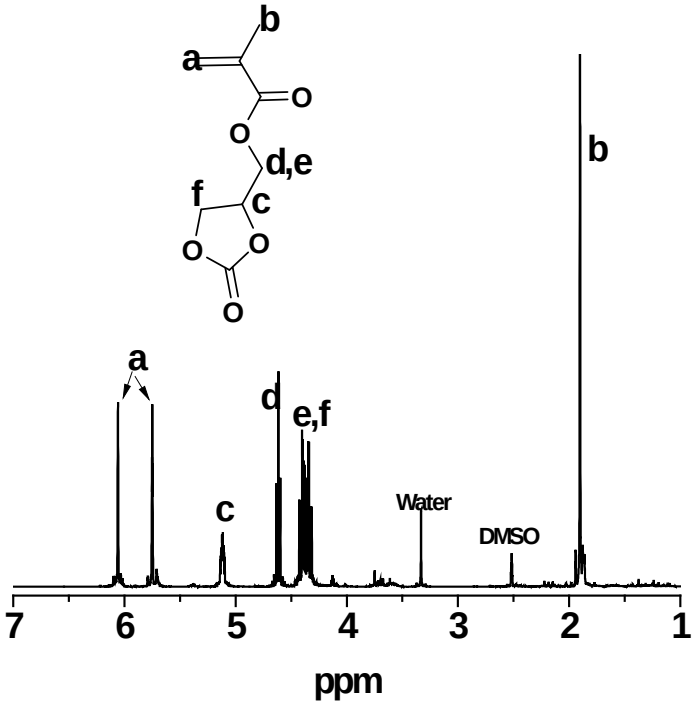


Figure 100. ^{1}H NMR of glycerol carbonate methacrylate.

GCMA is one of the precursors for the synthesis of vinyl ester resin monomer along with BPA and TBBPA. The GCMA is synthesized by transesterification between methyl methacrylate and glycerol carbonate in the presence of zirconium acetylacetonate as a catalyst as mentioned previously. Firstly, the temperature was maintained in the reaction flask to 70 °C and then it was raised to 100 °C over the period of 48 h. The catalyst was neutralized by hydrolysis with dilute phosphoric acid and removed by centrifugation. The remaining liquid was decanted in the flask and water was added to the reaction mixture. The organic layer was taken out and the excess of methyl methacrylate was removed at rotary evaporator. The structure of GCMA was confirmed by ^{1}H NMR as shown in Figure 100. The GCMA was isolated with 81.0 % yield.

Synthesis of vinyl ester resin (VER) monomer:

The VER monomer was synthesized by a one-pot reaction between BPA and GCMA in the presence of potassium carbonate as a catalyst. The reaction was performed at 90 °C using a magnetic stirrer. The ^{1}H NMR did not exhibit the –OH peak of the BPA, so it was presumed that the reaction was 100 % complete as shown in Figure 101. The product was purified by initially dissolving in acetone and later precipitation in water. VER settled down in the acetone-water mixture and later isolated and dried under vacuum at room temperature.

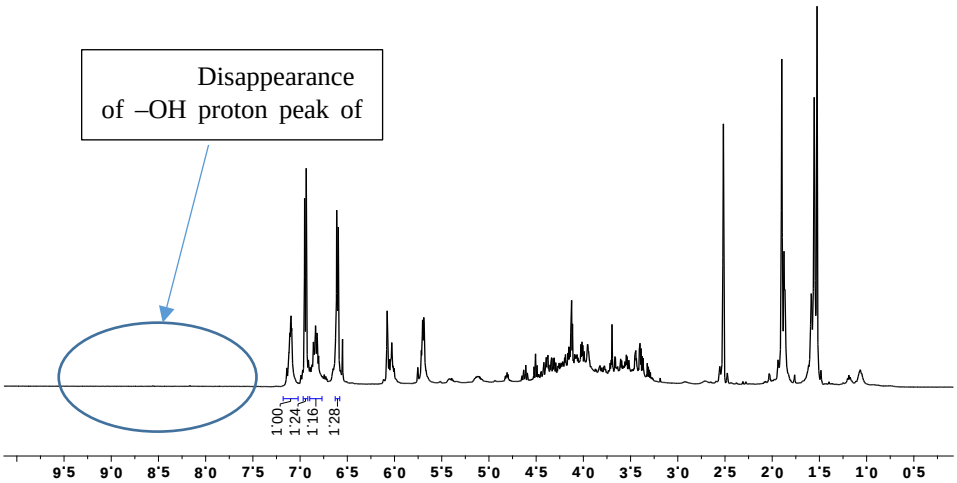


Figure 101. ^{1}H NMR of the Vinyl Ester Resin synthesized by reaction of GCMA and BPA.

3.3.3. Synthesis of brominated GVER by the reaction of TBBPA and GMA

The brominated vinyl ester monomer was synthesized by the reaction between TBBPA[69] and GMA in presence of tert-amine catalyst as shown in Figure 102. The reaction was performed at 70 ºC using a mechanical stirrer.

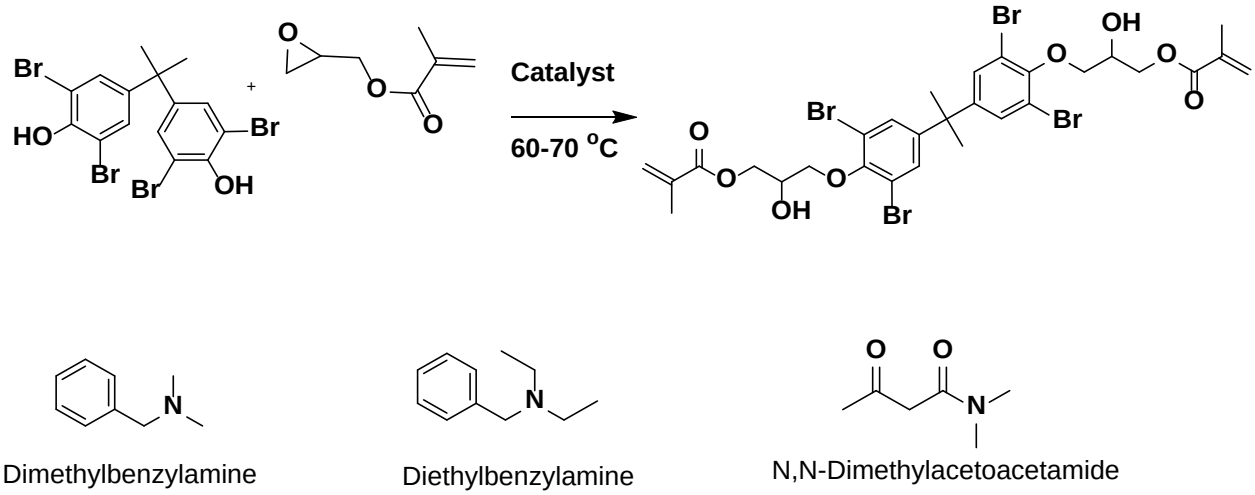


Figure 102: VER monomer synthesis using TBBPA and GMA

3.3.3.1. Material and Setup for Synthesis of Brominated Vinyl Ester Resin Monomer.

A mineral oil bath, equipped with a thermometer and a magnetic stir bar, was placed on the top of the magnetic stirrer hotplate. A 250 mL round-bottom flask, equipped with a mechanical

stirrer, was placed in an oil bath using clamps. Argon was flushed continuously into the reaction flask using a needle in septa.

3.3.3.2. Procedure.

A 250 mL round-bottom flask was charged with TBBPA (27.2 g, 50 mmol), glycidyl methacrylate (14.2 g, 100 mmol) and N,N-dimethyl benzylamine (0.065 g, 0.5 mmol). The flask had a continuous flow of argon, and the temperature was raised to 70 ºC, which was maintained for 2 h. After the reaction, the highly viscous liquid was transferred to a glass vial, and the product was analyzed by TLC, ^{1}H NMR, and FT-IR.

3.3.3.3. Results

The brominated vinyl ester monomer was synthesized by one-pot reaction between TBBPA and GMA in presence of tert-amine catalyst. The reaction was simply performed at 70 ºC using a mechanical stirrer.

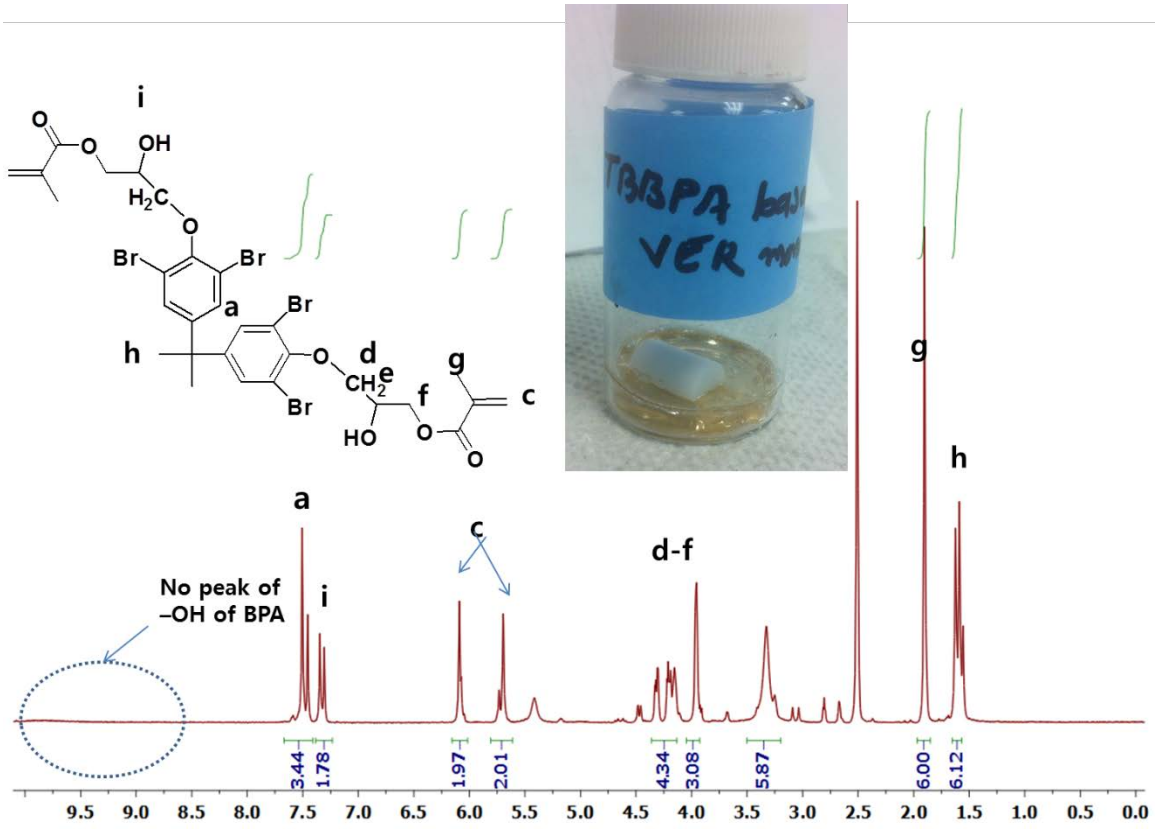


Figure 103. ^{1}H NMR of VER monomer synthesis using TBBPA and GMA

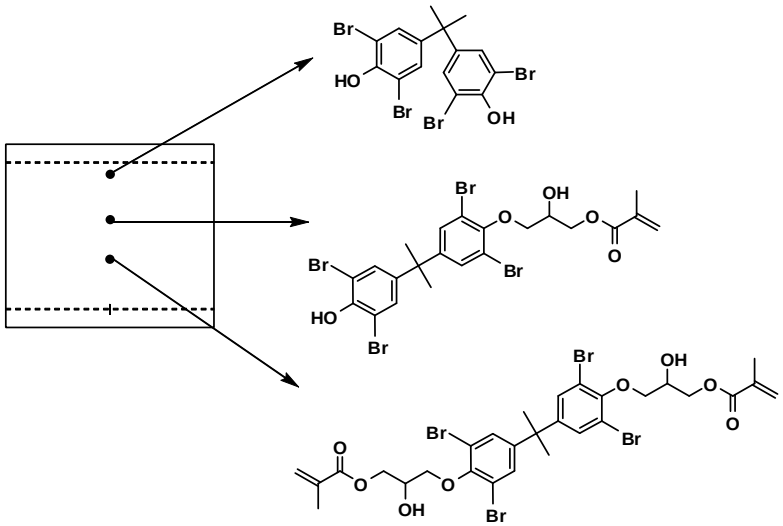


Figure 104. Separation of brominated vinyl ester resin monomer using THF/Hexane 3/7.

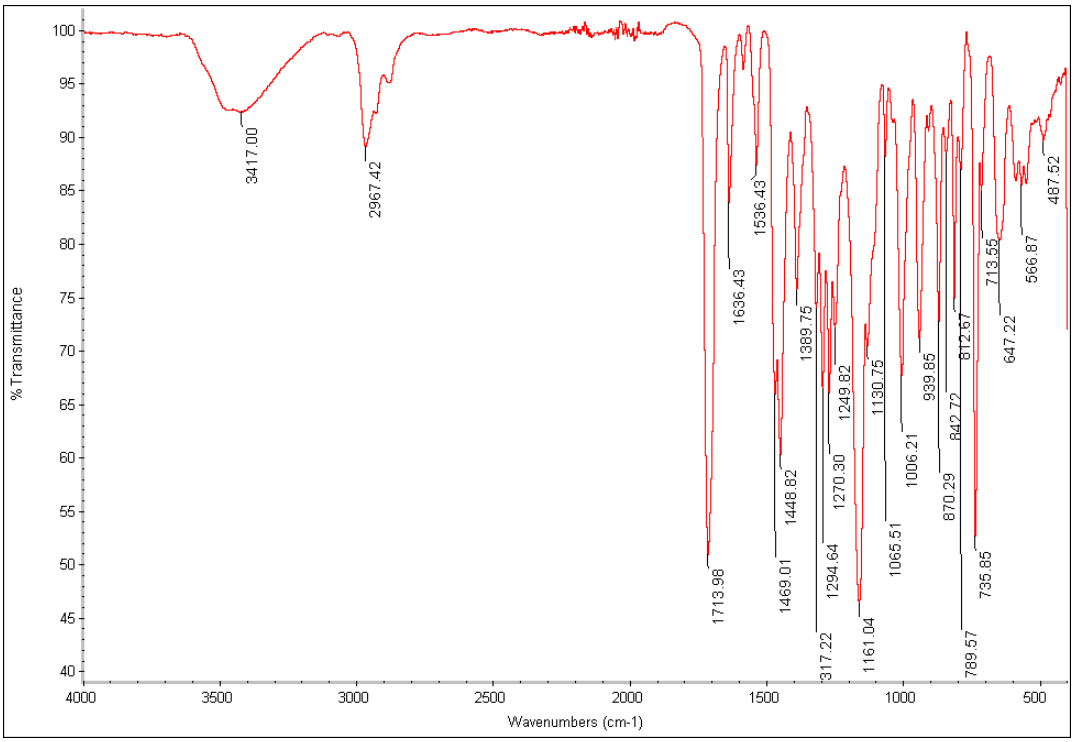


Figure 105. FT-IR of VER monomer synthesis using TBBPA and GMA

The product was slightly yellowish in color. As can be seen in ^{1}H NMR, the peak of –OH of the bisphenol A disappeared completely as shown in Figure 103. So it was presumed that the reaction was 100 % but the integration value is not matching precisely. The TLC showed three spots. The integration values in ^{1}H NMR and a higher number of spots in TLC confirmed the presence of product in the reaction mixture as shown in Figure 103 and Figure 104. The four spot could be due to the presence of unreacted TBBPA, monofunctionalzied TBBPA, and

difunctionalzied TBBPA (product). Secondly, as can be seen in FT-IR of TBBPA in Figure 105, the peak of –OH was very sharp and appeared at of the BPA was appeared to be at 3473 cm^{-1}, which shifted to 3417 cm^{-1} in VER monomer. The shift in the peak of –OH, clearly indicate the disappearance of aromatic hydroxy and generation of the aliphatic hydroxy group. In other observation, a clear peak of –C=O was observed ~1713 cm^{-1}, which should be due to either mono or difunctionalized TBBPA.

In order to investigate the kinetics of the reactions by varying parameter at the different condition, there was a necessary to develop a method of HPLC by separating each fraction and quantifying the amount by evaluating area under the peak. Each fraction obtained during column separation was characterized by UV spectroscopy as shown in Figure 106. It will develop the idea of condition selection of UV detector during HPLC analysis. HPLC of the column purified sample was performed using Waters Alliance system equipped with a photodiode array (PDA) detector (monitored at 277 nm) and a 4.6-mm × 15-cm column that contains 3-µm packing (Polar - Diol). The column temperature was maintained at 25 ºC, and the flow rate is 1.0 mL per minute. The injection volume was 1uL. Hexane and THF (70:30) was used as a mobile phase.

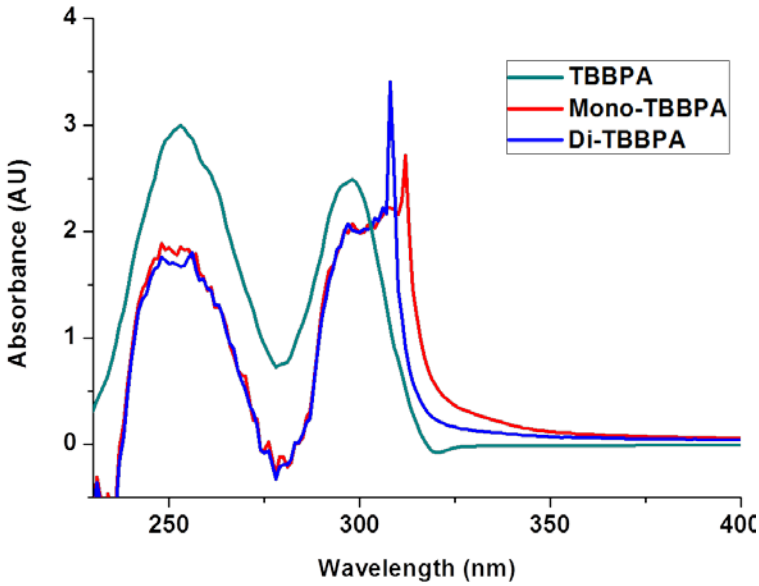


Figure 106. UV spectra of non, mono and di-functional tetrabromobisphenol-A obtained after column chromatographic separation of Br-VER product mixture.

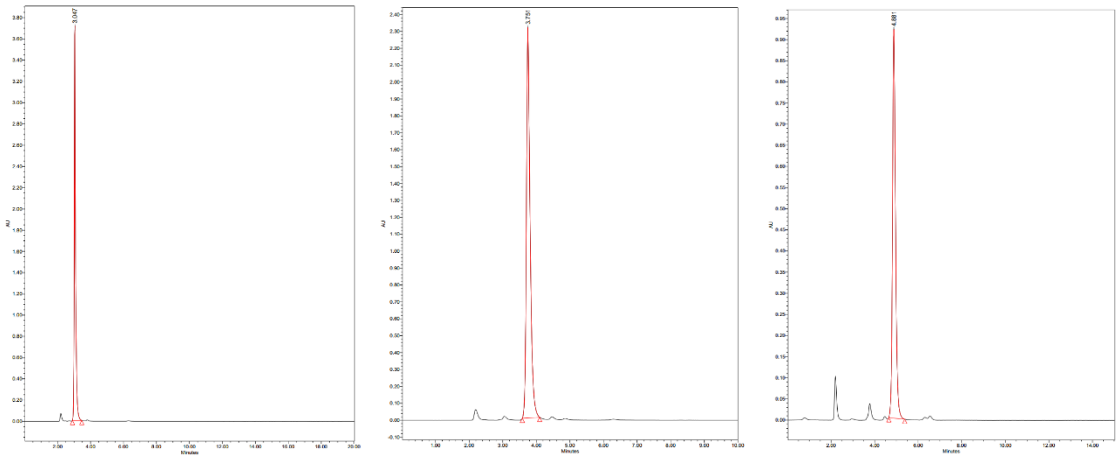


Figure 107. Chromatogram of (a) Nonfunctional-TBBPA (1st fraction), (b) monofunctional – TBBPA (2nd fraction), and (c) difunctional-TBBPA (3rd fraction).

The retention time of the non-functional TBBPA was 3.047 min, of mono-functional TBBPA was 3.751, and difunctional TBBPA was 4.881 as shown in Figure 107. Using the proposed method, kinetics of several Br-VER will be determined and their synthesis will be attempted under various conditions.

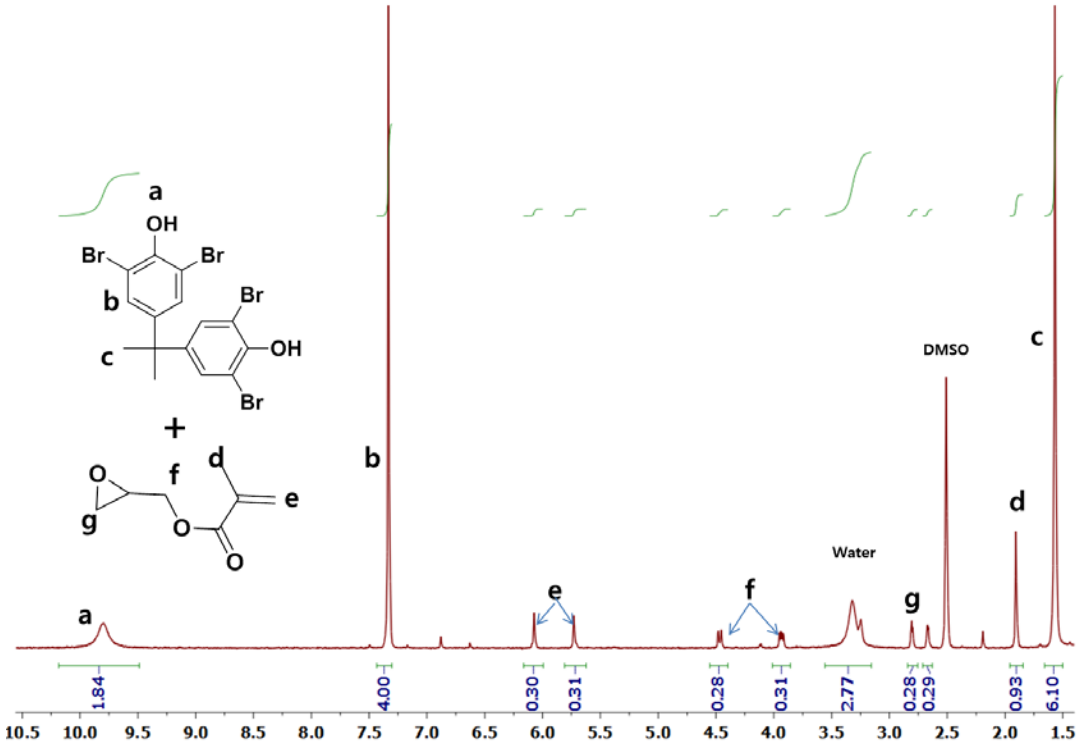


Figure 108: ^{1}H NMR of the first fraction of material isolated during column chromatography.

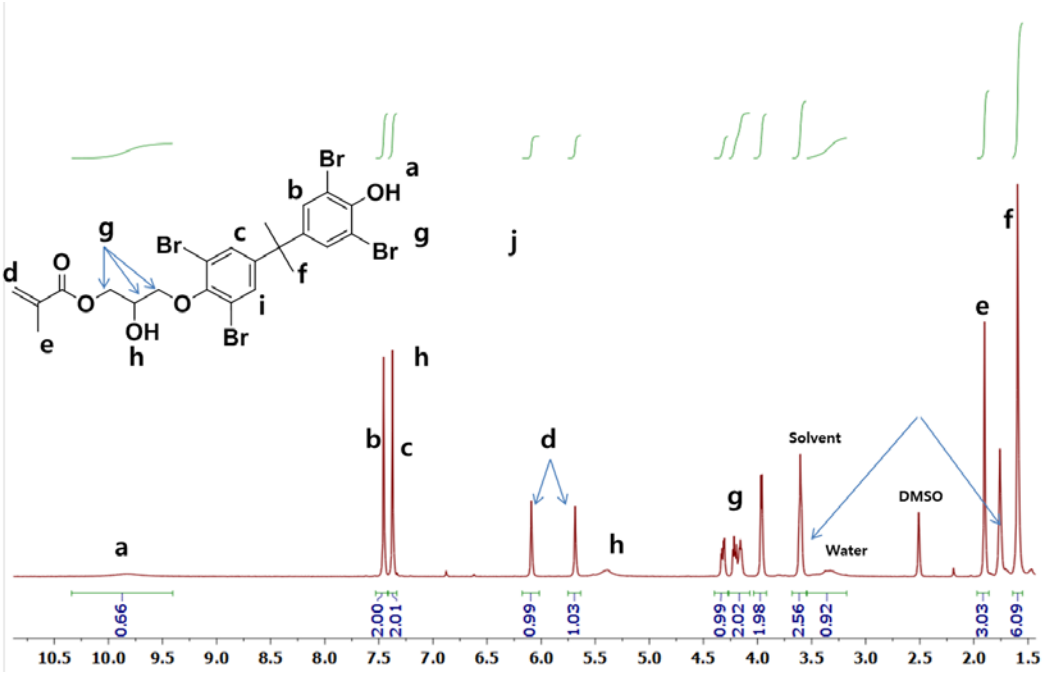


Figure 109. ^{1}H NMR of the second fraction of material isolated during column chromatography.

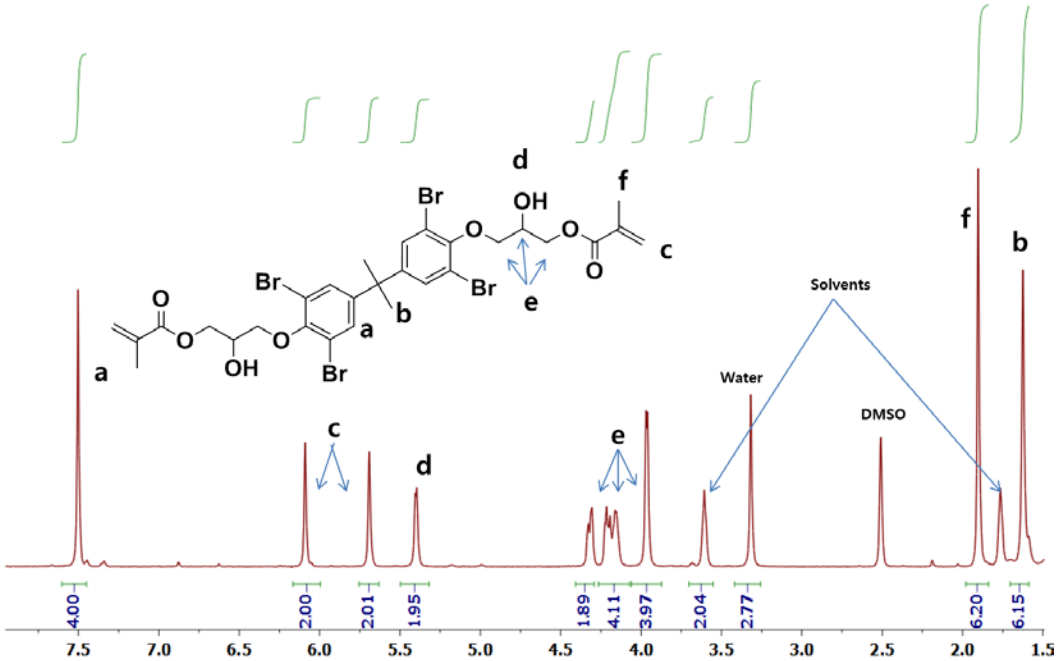


Figure 110. ^{1}H NMR of the third fraction of material isolated during column chromatography.

The brominated vinyl ester resin was separated by column chromatography, in which silica-gel was used as a packing material and tetrahydrofuran (THF): hexane was used in 3:7 (v/v). Figure 108 is the ^{1}H NMR of the first fraction during column, which clearly confirmed that TBBPA was the first eluted material. In a second fraction, monofunctionalized TBBPA, TBBPA with GMA substitution at only one –OH group was observed as shown in Figure 109. The

monofunctional product can easily be confirmed by peak integration and four aromatic proton peak of equal intensity. In a third fraction, VER oligomer, disubstituted TBBPA was observed as shown in Figure 110.

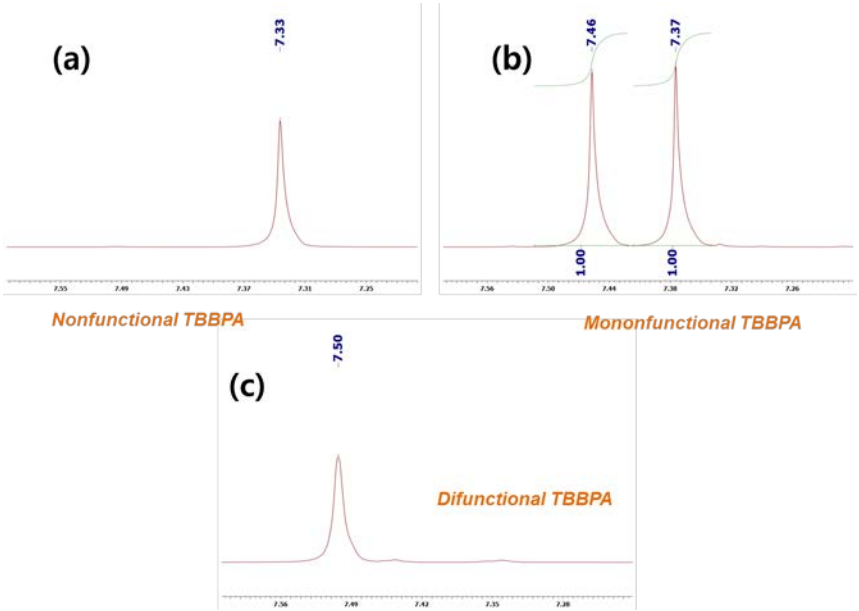


Figure 111. ^{1}H NMR of the aromatic proton peaks of each fraction obtained during column separation.

In order to optimize reaction condition, it is essential to determine the fraction of nonfunctionalized TBBPA, monofunctionalized TBBPA, and difunctionalized TBBPA. We have already proposed a plausible method with feasible condition using normal phase separation on high-performance liquid chromatography. Interestingly each separated fraction had a very distinct aromatic proton peaks as shown in Figure 111. The aromatic proton peak can be observed in nonfunctionalized TBBPA at 7.33 ppm, monofunctionalized TBBPA at 7.36 and 7.46 ppm, and difunctionalized TBBPA at 7.50 ppm. We have used aromatic proton peak integration to quantify each fraction.

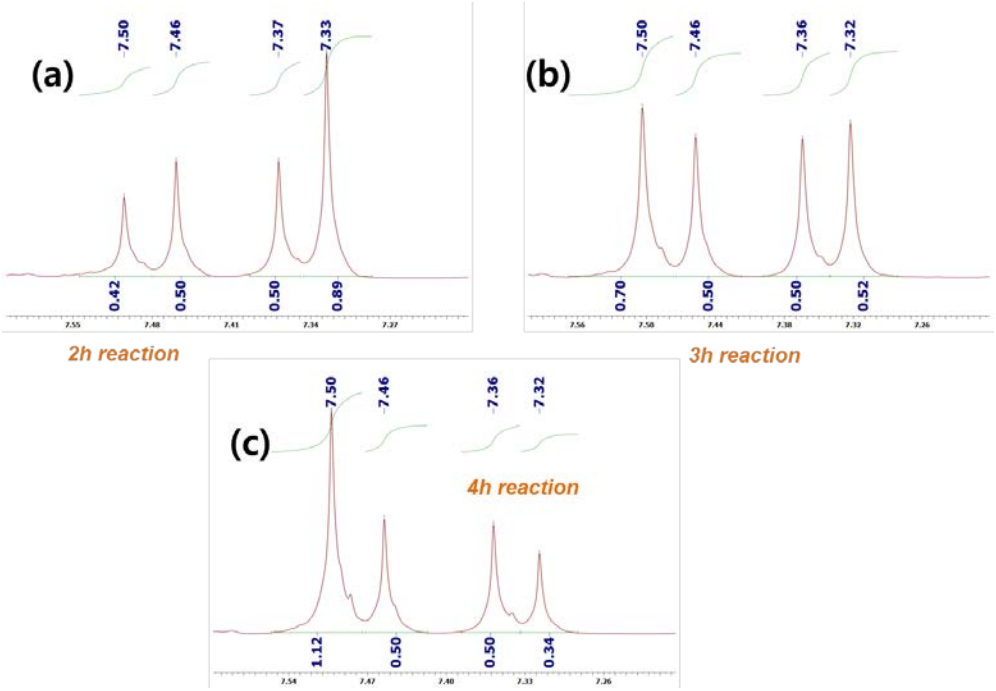


Figure 112. ^{1}H NMR of the different time interval in the Br-VER synthesis using GMA:TBBPA in 2:1 molar ratio.

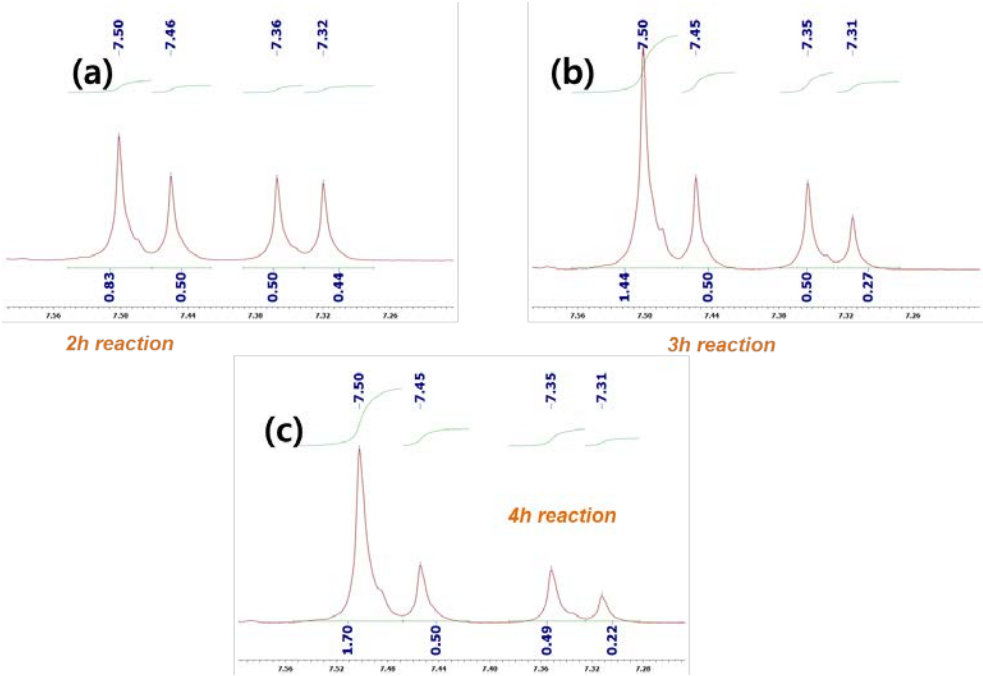


Figure 113. ^{1}H NMR of the different time interval in the Br-VER synthesis using GMA:TBBPA in 3:1 molar ratio.

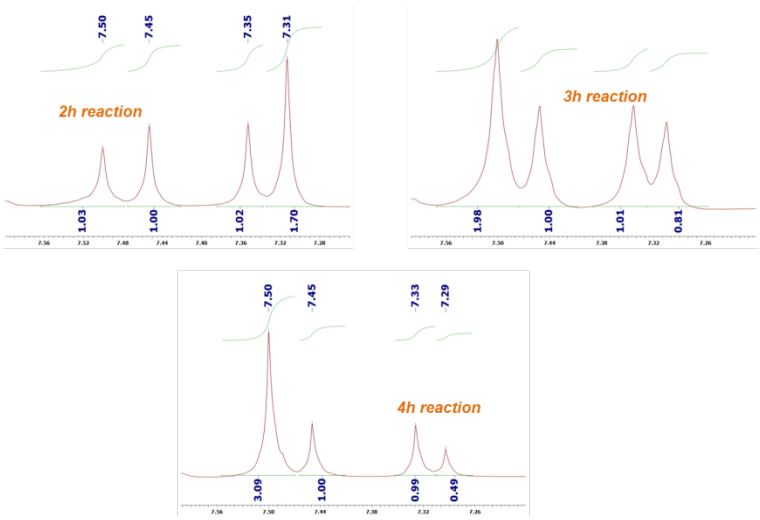


Figure 114. ^{1}H NMR of ArH of Br-VER synthesized in 4:1 molar ratio of GMA:TBBPA at 60C.

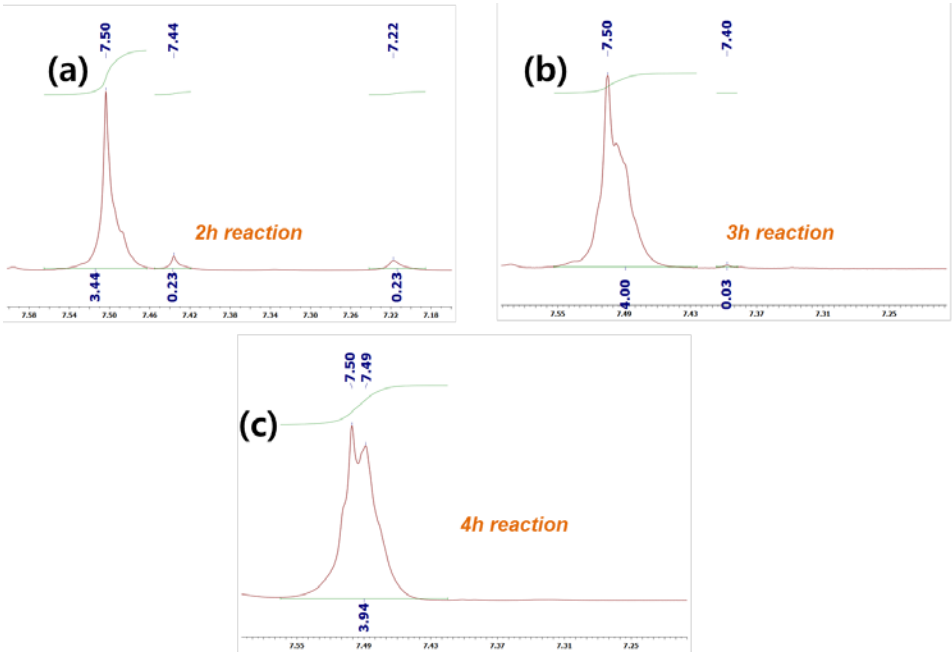


Figure 115. ^{1}H NMR of the different time interval in the Br-VER synthesis using GMA:TBBPA in 5:1 molar ratio.

Brominated vinyl ester resin was synthesized using a different molar ratio of GMA and TBBPA and the reactions were monitored at different time interval. Firstly, the reaction was performed with GMA:TBBPA in 2:1 molar ratio as shown in Figure 112. After 4 h, 13.8% non-, 40.7% mono- and 45.5% di-functional TBBPA remained in the system. As even after 4 h ~13.0 % unreacted TBBPA remained, so the ratio of GMA:TBBPA was increased to 3:1 as shown in Figure 113. In this case, after 4 h, 7.5% non-, 34.4% mono- and 58.1% difunctional TBBPA was observed (Figure 114). Still the unreacted BPA was high, so the ratio of GMA:TBBPA was increased to 5:1.

In this case, a complete conversion was observed at 3 h of reaction time as shown in Figure 115. All these data are summarized in Table 20.

Table 20. Different product formation at a different time interval during synthesis of brominated vinyl ester resin.

GMA:TBBPA Molar ratio	Reaction time (h)	Type of functionality of BPA		
		Non	Mono	Di
2:1	2	38.5	43.3	18.2
	3	23.4	45.1	31.5
	4	13.8	40.7	45.5
3:1	2	19.4	44.0	36.6
	3	9.90	36.9	53.2
	4	7.50	34.4	58.1
4:1	1	32.5	42.2	25.3
	2	9.80	36.4	53.8
	3	2.05	21.5	76.3
	4	0	0	100
4:1 (60 ºC)	2	32.9	42.6	21.8
	3	16.9	41.8	41.3
	4	8.8	35.8	55.4

Table 21. Synthesis of Br-VER using TBBPA:GMA (1:3) molar ratio and dimethyl benzyl amine in different weight %.

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
(0.05 wt. %) 60 ºC	2	3.22	3.90	4.84	8.23	42.3	49.5
	3	3.20	3.89	4.84	1.82	27.5	70.7
	4	-	3.76	4.82	-	28.7	71.3
(0.01 wt. %) 70 ºC	1	3.10	3.79	4.81	64.9	30.2	4.90
	2	3.13	3.80	4.82	23.0	48.5	28.5
	3	3.03	3.69	4.72	8.82	45.6	45.6
	4	3.08	3.76	4.77	4.90	25.9	69.2
(0.005 wt. %) 70 ºC	2	3.17	3.86	4.82	52.5	35.5	12.0
	3	3.17	3.85	4.82	40.7	43.6	15.7
	4	3.17	3.85	4.82	29.5	47.6	22.9
	5	3.15	3.84	4.80	24.0	44.8	31.2
	6	3.16	3.84	4.81	14.3	46.1	39.6

Several experiments were performed using TBBPA:GMA in 1:3 molar ratio and dimethylbenzylamine as a catalyst. Firstly, the catalyst concentration was taken to be ~0.05 weight percentage of the total. Such high concentration resulted in very fast reaction and 4 h, all nonfunctional TBBPA was consumed and 28.7 % of the monofunctional TBBPA remained in the system as shown in Table 21. The reaction mixture turned into a solid gel upon prolonged reaction time.

Secondly, the reaction catalyst concentration was decreased to 0.01 weight percent, where the rate of reaction decreased significantly and at 4.0 h of reaction time, unreacted TBBPA was found in the product mixture. Upon prolonged reaction time, the material formed a gel.

Table 22. Synthesis of Br-VER using TBBPA:GMA (1:3) molar ratio and diethylbenzylmine.

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
(0.005 wt. %) 70 ºC	2	3.12	3.80	4.69	96.1	2.31	1.10
	3	3.12	3.69	4.69	93.4	2.88	3.62
	4	3.13	3.69	4.70	87.4	7.29	5.30

We have tried diethybenzylamine as another catalyst. Only one reaction was performed using 0.005 weight % catalyst and the reaction was slower compared with dimethylbenzylamine as shown in Table 22.

Table 23. Synthesis of Br-VER using TBBPA:GMA (1:3) molar and N, N-Dimethylacetoacetamide

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
(0.005 wt. %) 70 ºC	2	3.14	-	-	100	-	-
	3	3.12	-	-	100	-	-
	4	3.13	3.69	4.70	92.2	4.80	3.02
	48	3.12	3.81	4.64	57.1	31.0	11.9
	72	3.12	3.79	4.81	40.6	40.0	19.4

We have tried one aliphatic catalyst N, N-dimethylacetoacetamide, which has a very slow rate of reaction. 40.6 % of unreacted TBBPA was found in the system even after 72 h of the reaction time as shown in Table 23.

Table 24. Synthesis of Br-VER using TBBPA:GMA (1:5) and N, N- dimethylbenzylamine

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
(0.01 wt. %) 70 ºC	1	3.04	3.67	4.70	61.2	32.5	6.30
	2	3.00	3.66	4.71	30.0	50.5	19.5
	3	3.00	3.65	4.70	17.5	52.0	30.5
	4	2.99	3.66	4.71	3.55	49.7	46.7

(0.005 wt. %) 70 ºC	1	2.99	3.65	4.62	60.4	27.3	12.3
	2	3.00	3.63	4.69	45.2	47.2	7.60
	3	2.99	3.66	4.70	31.9	50.3	17.8
	4	3.00	3.66	4.71	20.9	53.2	25.9
	5	3.00	3.66	4.71	12.9	51.4	31.7
	6	2.99	3.66	4.71	3.60	49.6	46.8
	7	2.99	3.65	4.69	1.93	38.5	59.6

With the intention to decreasing the possibility of the crosslinking upon prolonged reaction time and increase the chances of getting the difunctional TBBPA faster, the TBBPA:GMA ratio was changed to 1: 5 as shown in Table 24. Upon attempt of completing the reaction, the material turned in to gel.

Table 25. Synthesis of Br-VER using 0.01 wt. % dimethyl benzyl amine catalyst at 70 ℃

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
TBBPA:GMA (1:2.1) 40 wt. % styrene	2	3.03	3.69	4.60	68.3	21.1	10.6
	3	3.02	3.67	4.59	60.7	24.7	14.6
	4	3.03	3.67	4.59	40.9	34.2	29.9
TBBPA:GMA (1:4)	1	3.02	3.67	4.59	65.1	22.0	12.9
	2	3.01	3.67	4.59	43.8	37.2	19.0
	3	3.01	3.66	4.69	28.5	48.0	23.4
	4	3.01	3.67	4.69	11.3	49.0	39.7
	5	3.01	3.66	4.69	3.20	40.1	56.7
	6	3.00	3.65	4.69	0.20	27.4	72.4
	7	-	3.54	4.69	-	14.8	85.2
	8	-	3.52	4.59	-	18.1	81.9

We performed a Br-VER synthesis by adding 40 weight % of styrene at the beginning of the reaction. However, the dilution decreased the rate of reaction and as the reaction time increased in order to complete the reaction; the reaction turned into a gel.

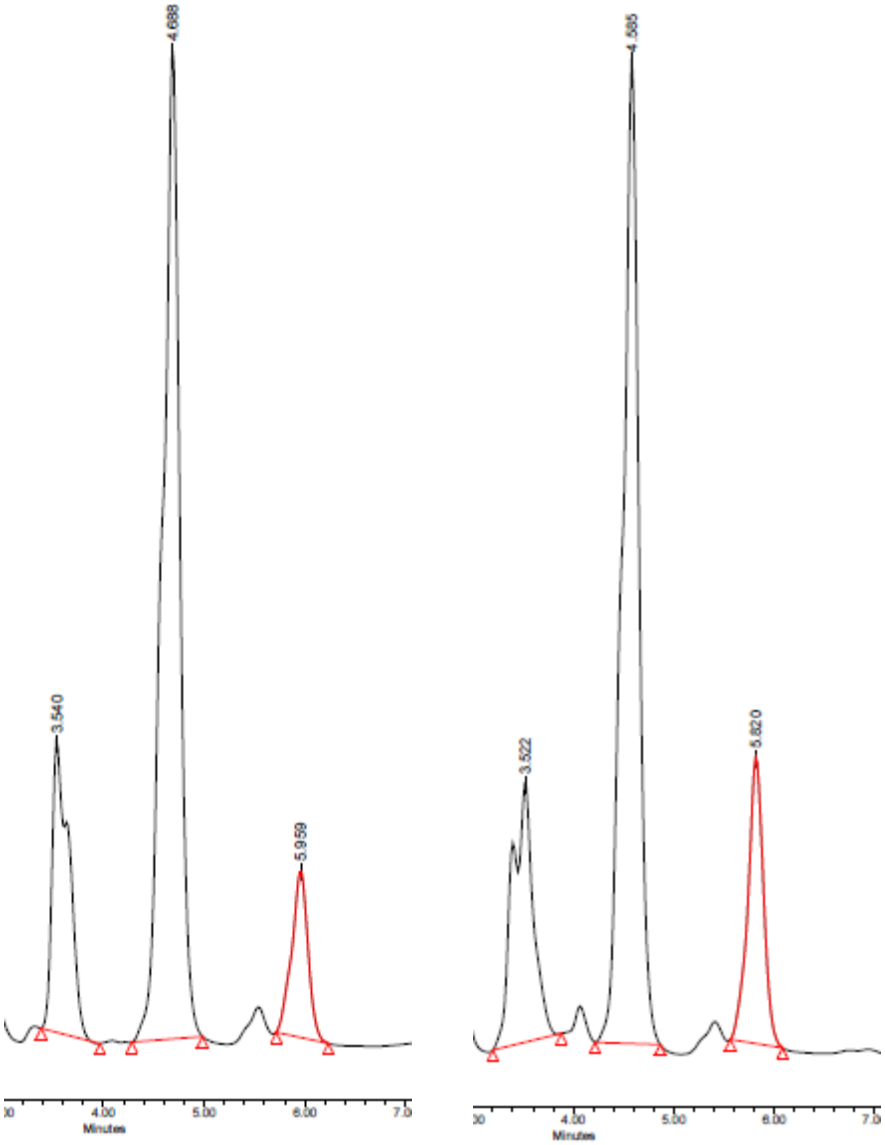


Figure 116. Chromatogram of product mixture at (a) 7 h and (b) 8 h.

There is a great possibility that the secondary –OH of Br-VER can participate in the ring opening of the epoxy and can create a TBBPA with the substitution of three GMA molecules on it. As mentioned in Table 25 and Figure 116, after 7 h of reaction time such side reaction increases.

The pure fraction of VER was isolated by column chromatography and further used for characterization of green monomer. We have previously reported that the secondary hydroxy of the functionalized GMA also participates in the ring opening reaction of the unreacted GMA. As a result, some side-product formation was observed, which are presumed to be $(GMA)_2$-TBBPA and $(GMA)_2$-TBBPA-(GMA). We have synthesized VER using different methods. In one of our approach, TBBPA was taken in a three neck flask and stirred continuously using mechanical stirrer at 70 °C, and GMA was added drop-wise to the flask. After complete addition, the first sample

was taken as shown in Table 26, then 40 wt. % of styrene was added and the reaction was continued for 18 hours. The significant presence of unreacted TBBPA was found in the reaction mixture even after 18 h as shown in Figure 117 &Figure 118.

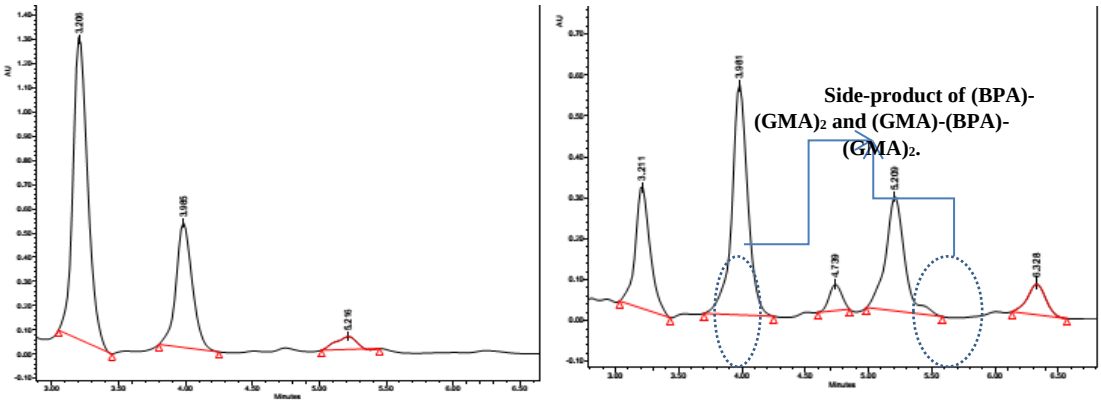


Figure 117. Chromatogram of Br-VER of (a) after completion of slow addition of GMA during two hours and (b) after 18 h of the reaction.

Table 26. Synthesis of Br-VER using 0.01 wt. % dimethylbenzyl amine catalyst at 70 ˚C.

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
TBBPA:GMA (1:2.1)	0	3.21	3.99	5.22	65.4	30.4	4.20
40 wt % styrene	18	3.21	3.98	5.21	23.2	46.8	30.0

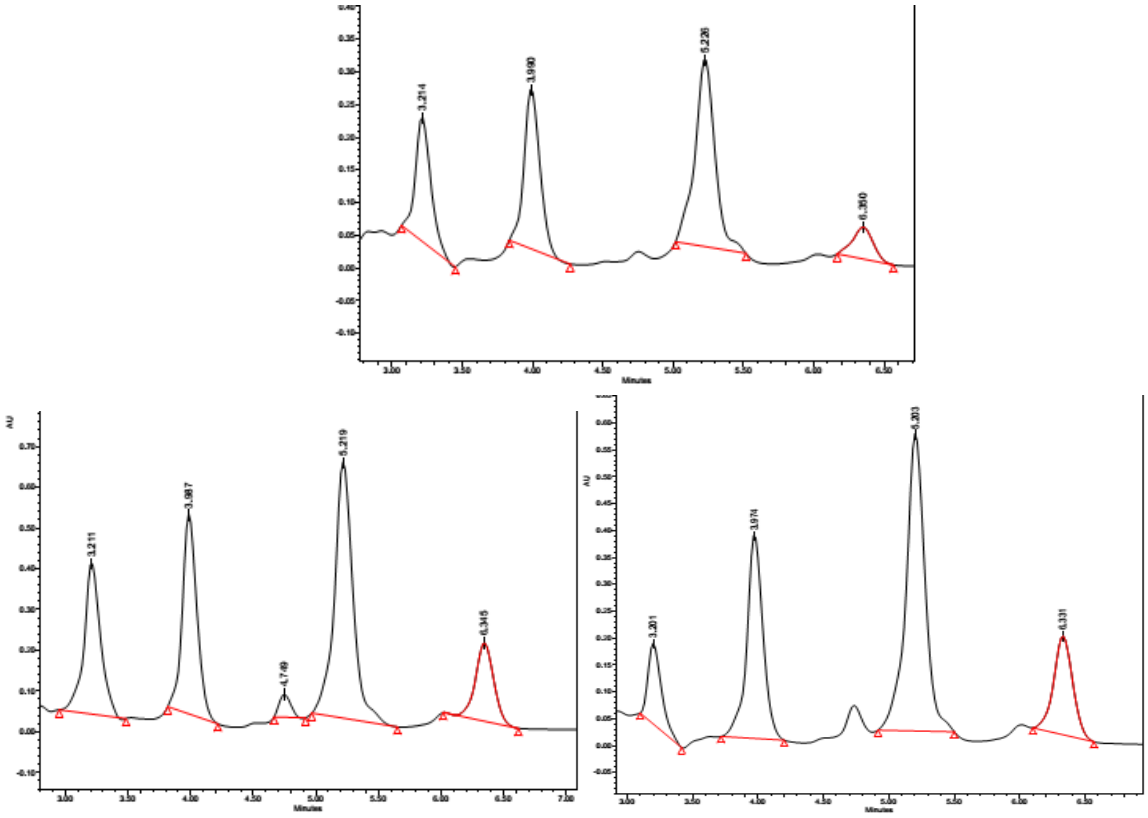


Figure 118. Chromatogram of Br-VER of (a) after completion of slow addition of GMA during two hours and last addition of styrene (b) after 18 h of the reaction and (c) after 36 h of the reaction.

Table 27. Synthesis of Br-VER using 0.01 wt. % dimethylbenzyl amine catalyst at 70 ºC.

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
TBBPA:GMA (1:2.1) 40 wt. % styrene	0	3.21	3.99	5.23	22.3	31.2	46.5
	18	3.21	3.98	5.22	24.3	30.0	45.7
	60	3.20	3.97	5.20	10.8	32.8	56.4

As the addition of the styrene in the second stage of the reaction did not help in reducing the side-product formation; we have performed one reaction by adding styrene from the beginning of the reaction. 10.8 % of the TBBPA remained unreacted even after 60 h of the reaction as shown in Table 27. After 60 h, the amount of side product formation increased more compared with the consumption of TBBPA.

The high amount of side-product were observed in VER synthesized at 70 ºC, so we have performed some reaction at a lower temperature. One reaction was performed at 60 ºC, where almost half of the TBBPA remained unreacted after 18 h of reaction time. The second reaction was performed at 65 ºC and after 18 h of reaction time; ~ 17 % of the TBBPA remained unreacted but higher amount of ide product formation was observed as shown in Table 28.

Table 28. Synthesis of Br-VER using TBBPA:GMA (1:2) molar ratio and diethylbenzylmine and styrene at a different temperature.

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
60 ºC	18	3.19	3.94	5.14	46.7	42.6	10.7
65 ºC	18	3.19	3.93	5.10	17.2	36.2	46.6

Table 29. Synthesis of Br-VER using TBBPA:GMA (1:4) molar ratio and dimethyl benzyl amine at a different temperature.

Catalyst and Temperature	Reaction time (h)	Retention time (min)			Type of functionality of BPA		
		Non	Mono	Di	Non	Mono	Di
60 °C	18	2.80	3.64	5.20	39.1	40.4	20.5
65 °C	18	2.80	3.64	5.20	39.4	34.9	25.7

The lower temperature did not help and allowed the reaction to be completed. Instead of completion of the reaction, an intense peak started to appear at ~6.20 min, which is TBBPA with more than two substitutions of GMA. We have changed the ratio of TBBPA: GMA from 1: 2.1 to 1:4 and performed the reactions in 40 wt. % of styrene. At both 60 °C and 65 °C, ~ 40 % of TBBPA remained unreacted even after 18 h of the reaction time. It suggested that lower temperature or diluted condition at low temperature was not favoring Br-VER synthesis.

3.3.4. Vinyl Hydroxyl Ether Resin (VHER) monomer derived from Waste Glycerin

Here we report a new class of resin material, namely Vinyl Hydroxyl Ether Resin (VHER), which retains the hydroxyl group and eliminates the less stable ester linkages in the Glycidyl Methacrylate (GMA) based VER, derived from waste glycerin.

I) a completely new class of resins, namely, Vinyl Hydroxy Ether Resin (VHER)
II) An environmentally benign "green" methodology for the synthesis of VHER
III) A novel single step synthetic protocol for its synthesis.

Following is the detailed one step protocol used for the synthesis of a model compound Bisphenol A bis (2-hydroxypropyl) ether (BABHPE). Based on the model reaction, the following procedure also outlines the concept for the synthesis of VHER in a single step using two different strategies. Investigations are currently underway for demonstrating the synthesis of VHER and will be included in this invention disclosure

The model reaction procedure given above establishes the synthetic procedure for VHER. As in-situ formation of the cyclic carbonate occurs, two different synthesis strategies can be used as presented below (Figure 119 and Figure 121). The reactions thus performed will be a single step and single pot procedures. Investigations on these concepts are underway and the results will be included here. By changing the length of the alkyl segments (e.g. hexyl, octyl etc.) used the viscosity and other properties of the final product can be tailored. The use of longer alkyl chains would also provide the non-allylic product. This can be performed by using longer chain 1,2-diols, for example by using 5-hexene-(1,2-diol), as a reactant with bisphenol A.

Materials: Bisphenol A, Vinyl ethylene carbonate, and Potassium Carbonate were procured from Sigma-Aldrich and utilized without further purification.

Procedure: In a single necked round bottom flask bisphenol A (1 g), as received vinyl ethylene carbonate (1.5 mL) and potassium carbonate (300 mg) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 115 °C. After 18 h the reaction was stopped by applying vacuum to remove any unreacted vinyl ethylene carbonate. The obtained product was dissolved in 3 mL of dimethyl sulfoxide and added dropwise to 40 mL deionized water. The isolated precipitate, in quantitative yield, was analyzed using proton NMR (Figure 120). As seen in the NMR a quantitative conversion of BPA to VHER was obtained.

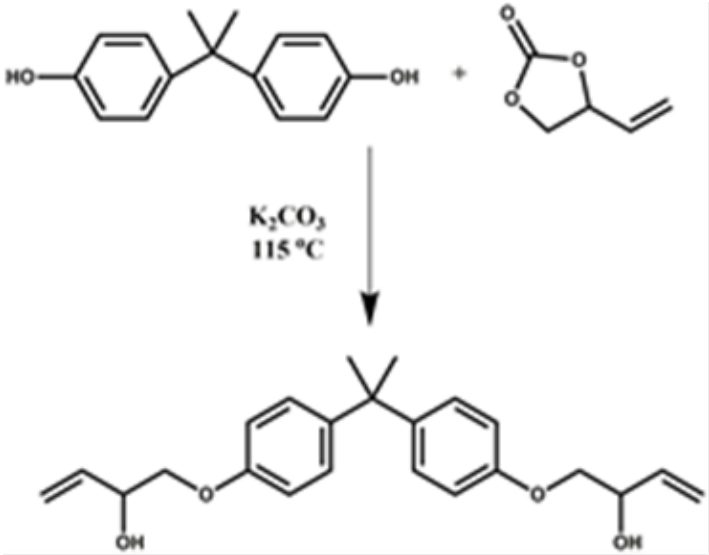


Figure 119. Reaction scheme for the synthesis of VHER by employing vinyl ethylene carbonate.

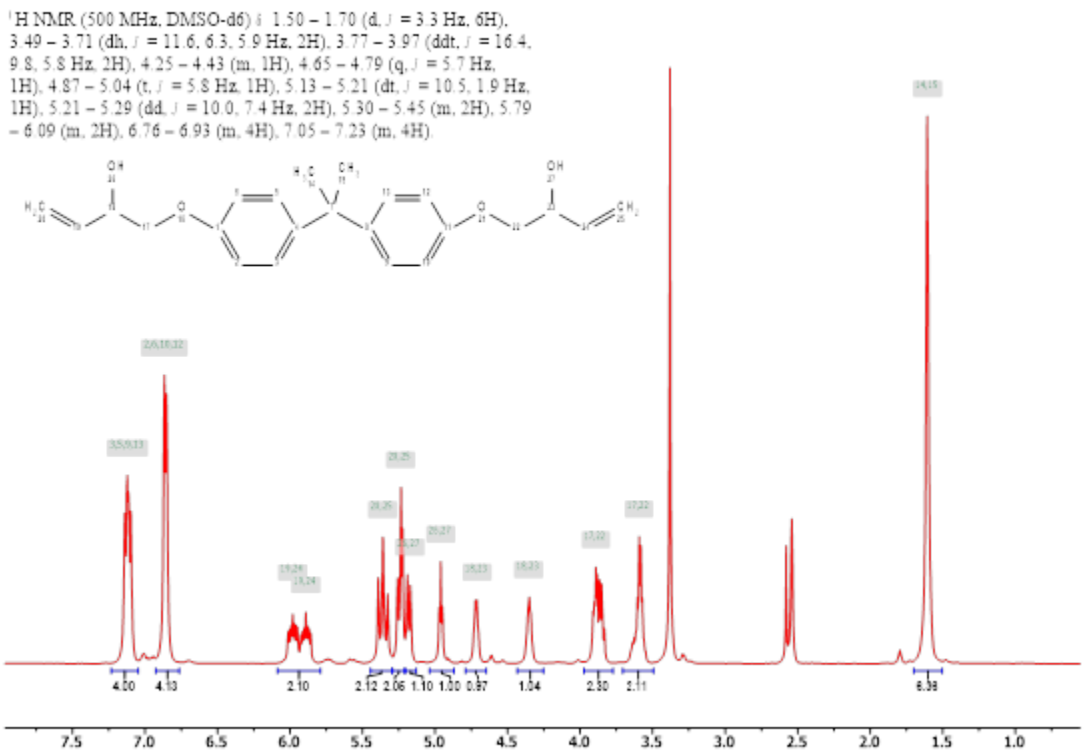


Figure 120. Proton NMR of VHER in DMSO d6.

Using the reaction procedure shown above for BABHPE, VHER can also be synthesized using 3-butene-(1, 2-diol) according to the reaction scheme presented in Figure 121.

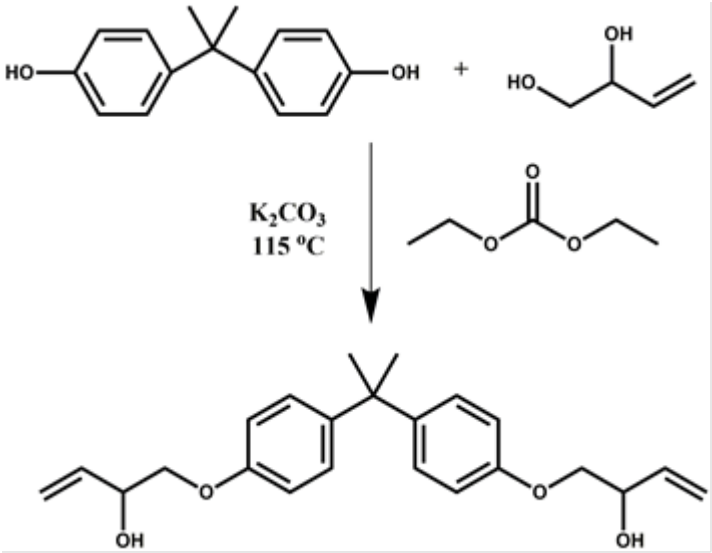


Figure 121. Reaction scheme for the synthesis of VHER by employing 3-butene-(1,2-diol).

VHER Formulations and Characterization.

The synthesized VHER was mixed with 20, 33 and 40 wt. % styrene to give formulations analogous to commercially available Derakane VERs. These mixtures were stored at room temperature in a dark location, and were stable under these conditions for over 6 months, with no gelation or precipitation. The synthesized VHER was mixed with 33 wt. % styrene, which is similar to the commercially available Derakane 441-400. For curing, 1.5 phr methyl ethyl ketone peroxide (MEKP, Norox MEKP-925H) was used as the initiator and 0.2 phr cobalt naphthenate (6.0 % in mineral spirits, Sigma-Aldrich) was used as the accelerator. In a typical formulation step, the MEKP was first added to the VHER solution in styrene and mixed at 1000 rpm for 1 min using a FlackTek Speedmixer. The accelerator was then introduced to the formulation and mixed at 1000 rpm for 1 min using a FlackTek Speedmixer. The formulation was then cured at 60 °C for 16 hours followed by post curing at 110 °C for 4 hours. In order to reduce the cure time of this formulation, 0.15 phr of dimethyl aniline (DMA) was added to the above VHER formulation as a secondary accelerator and mixed at 1000 rpm for 1 min using a FlackTek Speedmixer. In order to reduce the curing time, 0.15 phr dimethyl aniline was added to the above described VHER formulation as an accelerator. The resulting formulation was then cured at 60 °C for 10 hours followed by post curing at 110 °C for 1 hour. At the end of which a stiff non-tacky cured VER sample was obtained Figure 122. The Derakane 411-400 formulations were obtained using same procedure used for VHER and contained the same amounts of initiator and accelerator. The Derakane formulations were then cured at 60 °C for 3 hours followed by post curing at 110°C for 1 hour.

Figure 122. Comparison between Derakane and VHER

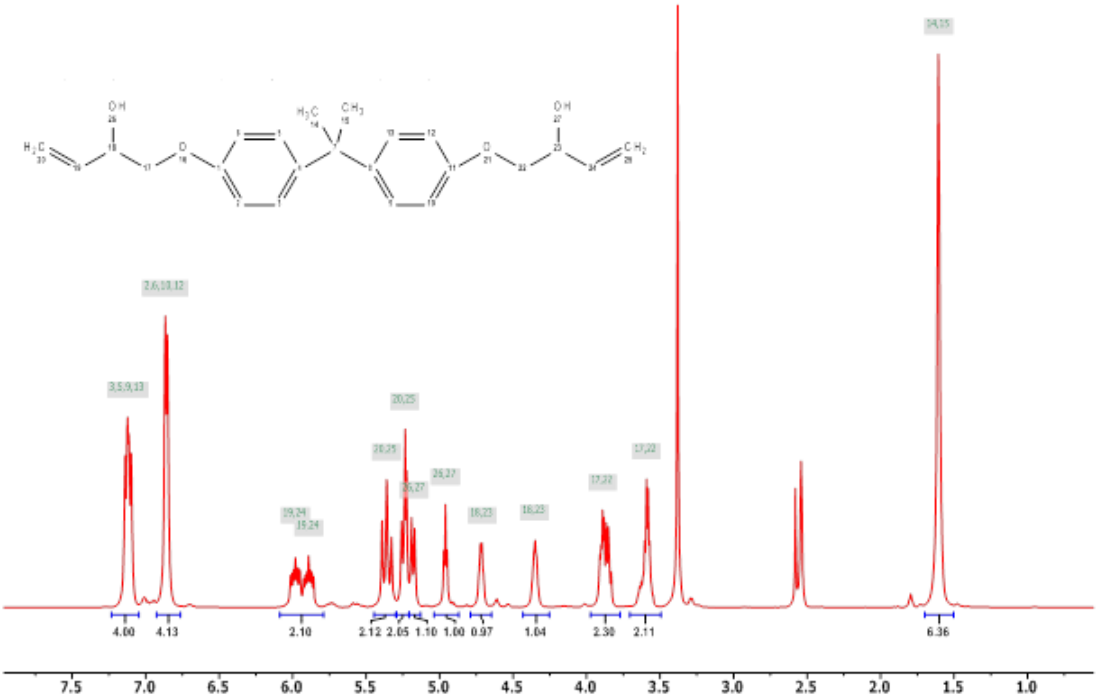


Figure 123. 1H NMR of VHER monomer

3.4. Task 4 - Formulate with Derakane Vinyl Ester

The green vinyl ester resin was successfully developed as mentioned in Task 3. After purifying the resin by column chromatography, its various formulations were prepared. In order to determine the structural equivalence with commercial resin, various formulations have been prepared and their composites were prepared.

Resins were prepared in kg scale and their composites following this protocol.

- Preparation of various formulations of GVER.
- Determine curing condition of the neat GVER.
- Fabrication of neat GVER and carbon fiber reinforced composite coupons.
- Mix GVER with Ashland material in different compositions and fabricate coupons and evaluate their performances.

3.4.1. Preparation of various formulations of GVER.

The green VER, both brominated and non-brominated were mixed in different ratios with Derakane 510A-40 and Derakane Momentum 411-350, respectively. The various formula was prepared as shown in Table 30 and Figure 124.

Table 30. Formulations of Bio-derived Vinyl Ester Resin Investigated

Name[a]	Prepolymer (wt. %)[b]	Styrene (wt. %)
Green Vinyl Ester Resin		
CVER	60 [0/100]	40
FVER-1	60 [20/80]	40
FVER-2	60 [50/50]	40
FVER-3	60 [80/20]	40
FVER-4	60 [100/0]	40
FVER-5	70 [100/0]	30
FVER-6	80 [100/0]	20
Brominated **Green Vinyl Ester Resin**		
Br-CVER	60 [0/100]	40
FVER-7	60 [20/80]	40
FVER-8	60 [50/50]	40
FVER-9	60 [80/20]	40
FVER-10	60 [100/0]	40
FVER-11	70 [100/0]	30
FVER-12	80 [100/0]	20

[a] CVER-Commercial Vinyl Ester Resin, FVER-Formulated Vinyl Ester Resin, [b] in parenthesis, the ratio of the prepolymer was mentioned, in the case of GVER, it is the ratio of GVER/Derakane Momentum resin, and in the case of brominated GVER, it is the ratio of Br-GVER/Derakane 510 40a.

Both, the brominated and nonbrominated vinyl ester prepolymer was mixed with 40 wt. % styrene to obtain the baseline brominated bio-derived resin. This resin was then blended with the commercial resin, Derakane 510-40A, in ratios of 20 to 80 wt. % to investigate the performance of blends of bio-sourced and traditional petroleum-based materials. In addition, two other formulations with lower styrene content (20 wt. % and 30 wt. %) were also prepared. Derakane 510-40A was chosen because it is presently the most widely used vinyl ester resin for naval vessels and the target goal of this project was to be able to develop and characterize a lower viscosity resin that could be used as a direct substitute for 510-40A.

Due to variations in molecular weight and styrene content, all resin formulations of brominated and nonbrominated have different cure times. The curing of these resins occurs through free radical polymerization and the rate of this polymerization can be altered through the addition of promoters such as cobalt salts (naphthenate, octoate, and hexanoate). These salts act alongside the initiator to increase the free radical production rate. Concurrently, the presence of a retarder can slow the rate of polymerization in cases where a longer gel time is desired. The experimental cure conditions for all formulations were: 0.2 wt. % cobalt naphthenate as a promoter, 0.3 wt % acetylacetone as a retarder and 1 wt. % cumene hydroperoxide as an initiator. These amounts were chosen in accordance with desired cure times for vacuum infusion as reported in the manufacturer's technical data sheet. The formulations used for thermo-mechanical characterization are listed in Table 30.

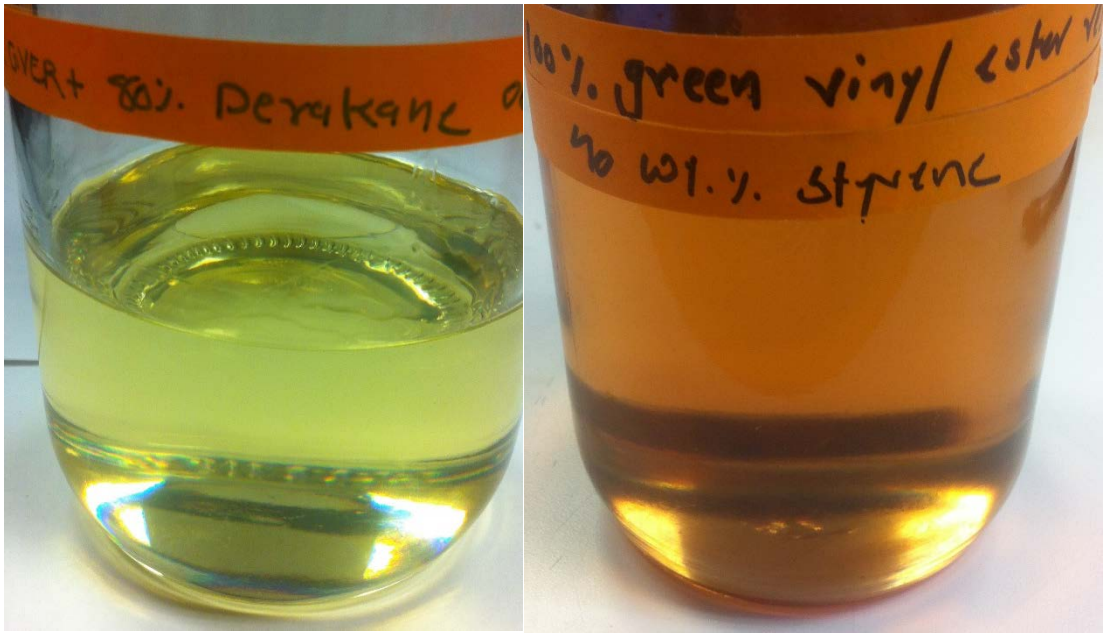


Figure 124. GVER resins prepared on kilogram scales (a) Formulated Resin with 20 % GVER and 80 % Derakane, and (b) GVER with 40 wt. % of Styrene.

The high amount of resin is required to prepare coupons for flammability testing as shown in Figure 124. Some representative formulated resin describing all compositions of nonbrominated GVER are shown in Figure 125.

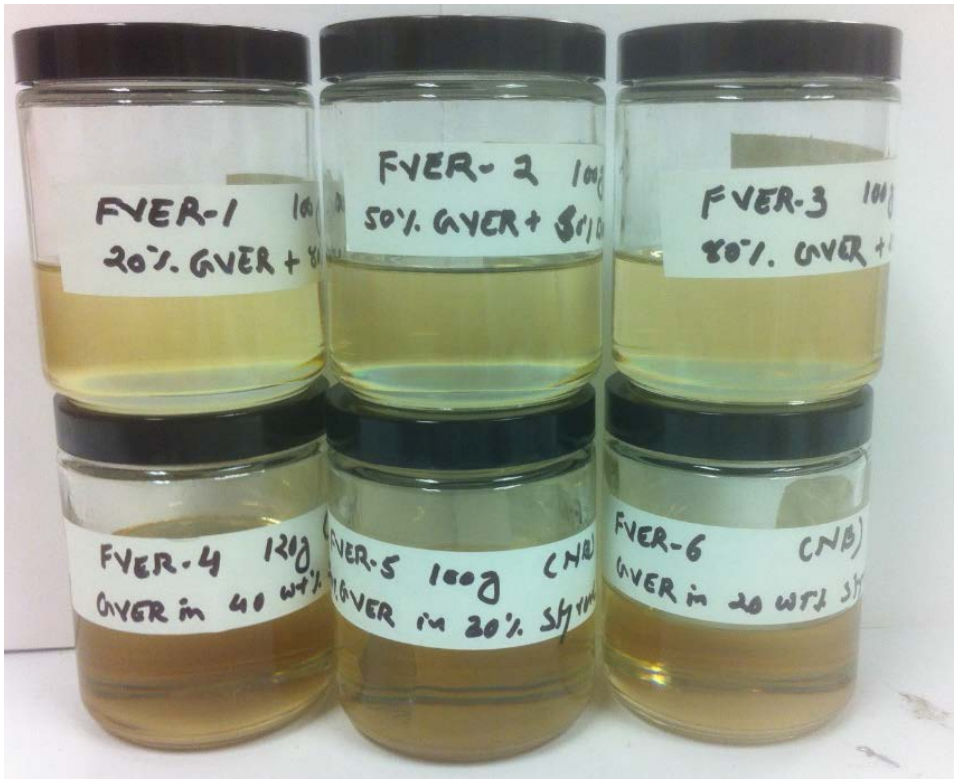


Figure 125. Representative Formulated Resin with Different Amount of Styrene and Commercial Derakane Resin.

3.4.2. Determine curing condition of the neat GVER

We analyzed rheological properties of resin using a parallel-plate rheometer (ARES-G2, TA Instruments) equipped with 25 mm diameter stainless steel parallel disks. Start-up measurements of steady shear were performed at a shear rate (γ) of 0.1 s^{-1} to avoid edge rupture during the test.

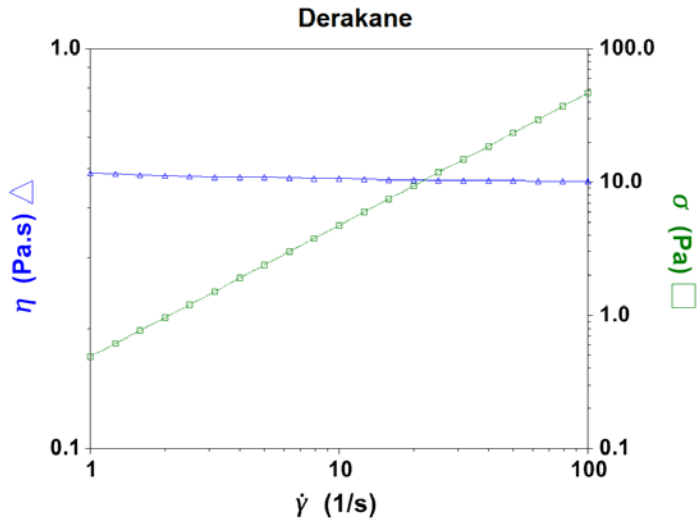


Figure 126. Shear rate vs rheology plot for Derakane Momentum 411-350.

As can be seen in Figure 126, the Derakane Momentum 411-350 (CVER) has a viscosity of 458 cps. Low viscosity increases ease of resin handling and making it more favorable for infusion during VARTM.

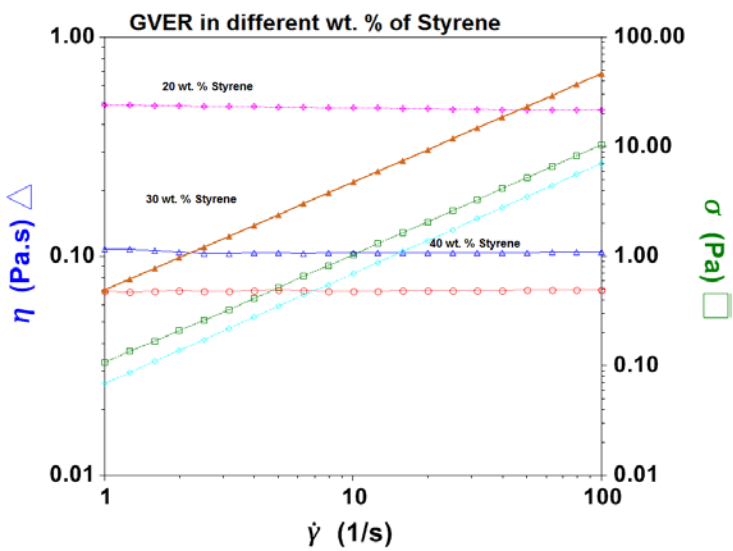


Figure 127. Shear rate vs rheology plot for GVER in different wt. % of styrene.

We have prepared a solution of GVER in 40, 30 and 20 wt. % of styrene (FVER-4, FVER-5, and FVER-6), which has a viscosity of 68, 108, and 427 cps, respectively. Clearly, higher the styrene, lower the viscosity and vice-versa as shown in Figure 127.

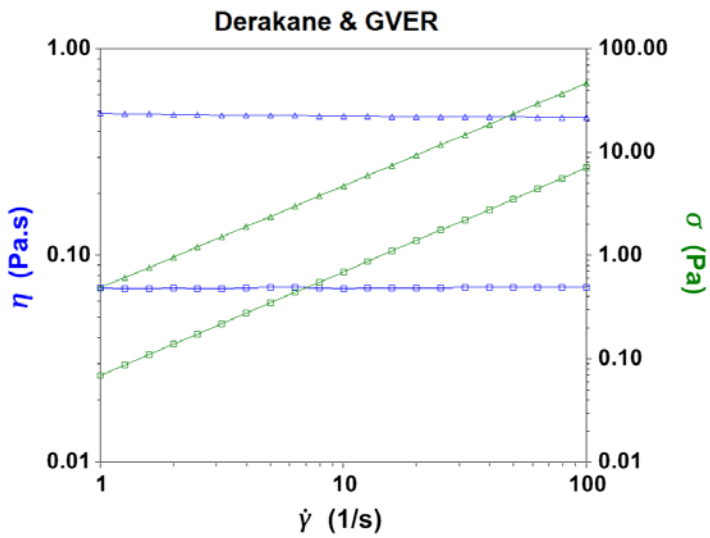


Figure 128. Viscosity comparison between Derakane and GVER with same styrene content.

Figure 128 gives a clear comparison of viscosity between commercial resin and GVER. GVER with 40 wt. % of styrene has a viscosity of 68 cps, whereas Derakane has 458 cps. GVER with 20 wt. % of styrene has a viscosity of 427 cps. Using GVER 20 wt. % styrene same viscosity can be achieved as Derakane with 40 wt. % styrene. The usage of reactive diluent can be reduced significantly using GVER.

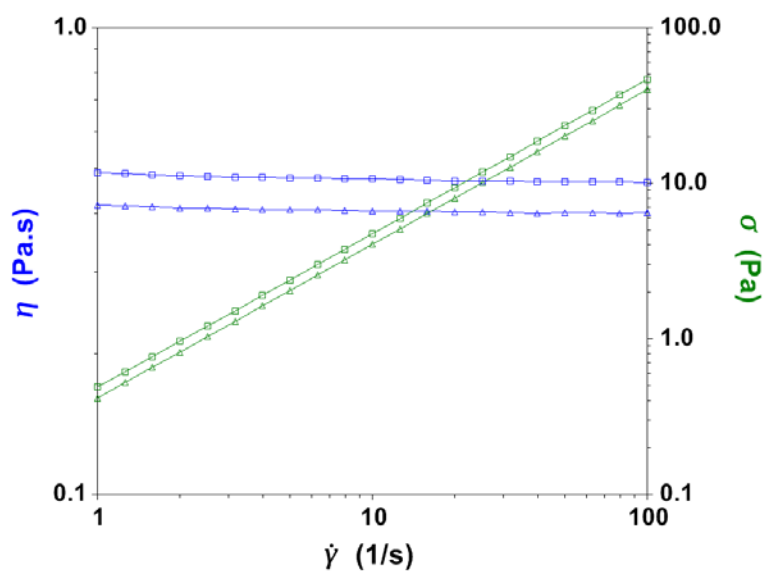


Figure 129. Viscosity comparison of formulated resin with 20 wt. % of GVER with original Derakane resin.

We have formulated resin with 80 wt. % of Derakane Momentum 411-350 and 20 wt. % of GVER (with 40 wt. % of styrene). As shown in Figure 129, the viscosity decreased significantly using 20 wt. % of GVER only.

Resin infusion processing of fiber-reinforced composites depends upon the chemorheological behavior of the resin formulation. The initial viscosity, η_0, dictates the initial infusion rate. Figure 130 shows that as the fraction of GVER in the resin formulation increases progressively, the viscosity decreases. This trend is due to the lower molecular weight of the synthesized vinyl ester monomer fraction as compared to the commercial vinyl ester. Previous work has shown that the viscosity of vinyl ester resins with the same styrene content can be controlled by adjusting the molecular weight of the vinyl ester monomer[70]. The trend across FVER-4 to FVER-6 indicates that as the styrene fraction is decreased, the viscosity increases significantly. Styrene acts as a reactive diluent and reduces the interactions such as hydrogen bonding and entanglements among vinyl ester, allowing these larger molecules to more easily slide past one another [70-72].

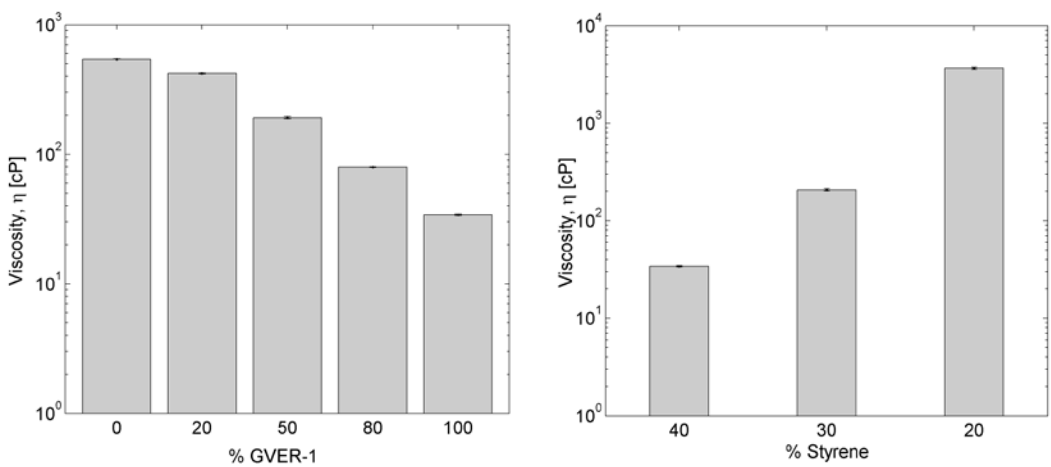


Figure 130. Zero shear viscosity of the resins as a function of GVER and styrene content.

The rheology of formulations as they cure were also examined. During the cure cycle, the viscosity dynamically increases the formation of polymer networks. The time to gelation is a critical processing parameter, as resin infusion slows dramatically near the gel point and ceases above the gel network formation. However, excessive gel times the slow throughput of the manufacturing and inefficiently use mold time. Hence, manufacturers value a resin cure that offers a gel point minimally longer than the anticipated infusion time; typical industrial infusion times range from 30 minutes to 2 hours.

The time to gelation for formulations composed of CVER and GVER or “comprising” mixtures were investigated. The formulation gel points are measured by oscillatory rheology and the crossover between the storage modulus (G') and loss modulus (G'') is used to approximate the gel point. The time varying rheology measured at room temperature is shown in Figure 131. The

G′/ G″ crossover times for the CVER, FVER-2, and GVER are 110, 379, and 550 minutes, respectively. The gel time for the FVER-2 formulation of equal parts CVER and GVER are three times that of the neat CVER while the FVER-4 gel time is excessively long at ~9 hours. This significantly higher gel time is due to the presence of added inhibitor (hydroquinone), leading to a higher concentration in the FVER-4 as compared to the CVER.

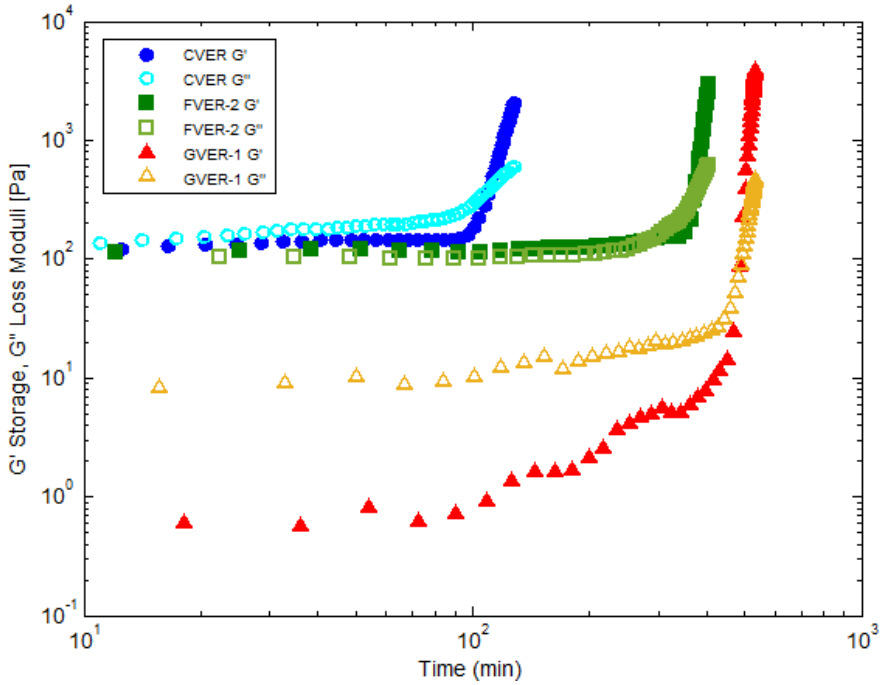


Figure 131. *G′* storage modulus and *G″* loss modulus for commercial resin (CVER), 50 wt% commercial and 50 wt. % bio-derived vinyl ester resin (FVER-2), and neat bio-derived vinyl ester resin (FVER-4) as a function of cure time.

Increases in initiator or promoter concentrations were not investigated but offer future avenues to further reduce the gel time by activator concentration modifications [73, 74].

3.4.2.1. Cure Kinetics of GVER

As we are developing this material with complete or in part substitution of the commercial Derakane resin; the curing conditions selected for the green VER was same as the one described in the literature published by Ashland, which was kept constant through the study of all formulations. We have prepared samples for cure kinetics of VER using 1.0 wt. % of cumene hydroperoxide (CHP), 0.2 wt. % of cobalt naphthenate (Co-Naph) and 0.3 wt. % of acetylacetone (AA). CHP is an initiator, which forms a free radical and starts the chain polymerization and crosslinking reaction, Co-Naph acts as a promoter and acetylacetone is a gel retarder.

The material was mixed and then put in the parallel plate for characterization. We have analyzed its storage modulus G’, which describes elastic properties and loss modulus G” describing viscous properties. We have also monitored viscosity of the curing sample constantly.

The graph of shear vs time for the commercial Derakane Momentum is shown in Figure 132. In the first 10 min after adding all curing agent the viscosity increases significantly and then it starts to stabilize. It again starts to increase from 55 min, at ~65 min, the values of storage modulus crosses the loss modulus, which can be termed as a gel point for the resin.

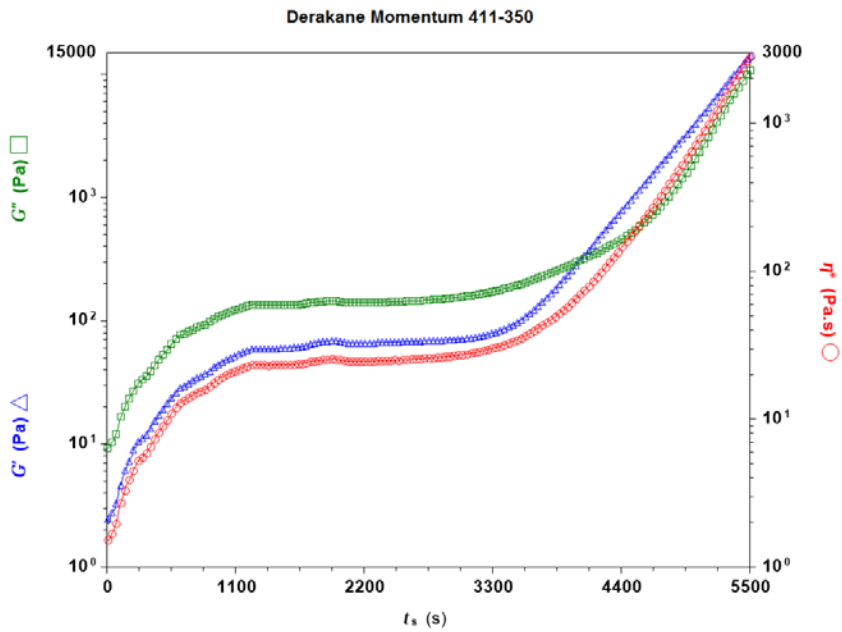


Figure 132. Shear vs Time Plot for Derakane Momentum 411-350.

We investigated gel point values of various formulated VER. Firstly, as can be seen in Figure 133, GVER with 40 wt. % of styrene (FVER-1) was mixed with all curing material and then its shear value vs time was plotted. It has taken a longer time compared with commercial resin to achieve gel point. The GVER with 40 wt. % styrene (FVER-4) has taken almost 11 h to achieve its gel point. Such longer time can be reduced by using less amount of gel retarder or increasing the amount of promoter. The FVER-4 has extremely low viscosity compared with commercial resin, which provides a scope to reduce its styrene content and making it environmentally less hazardous.

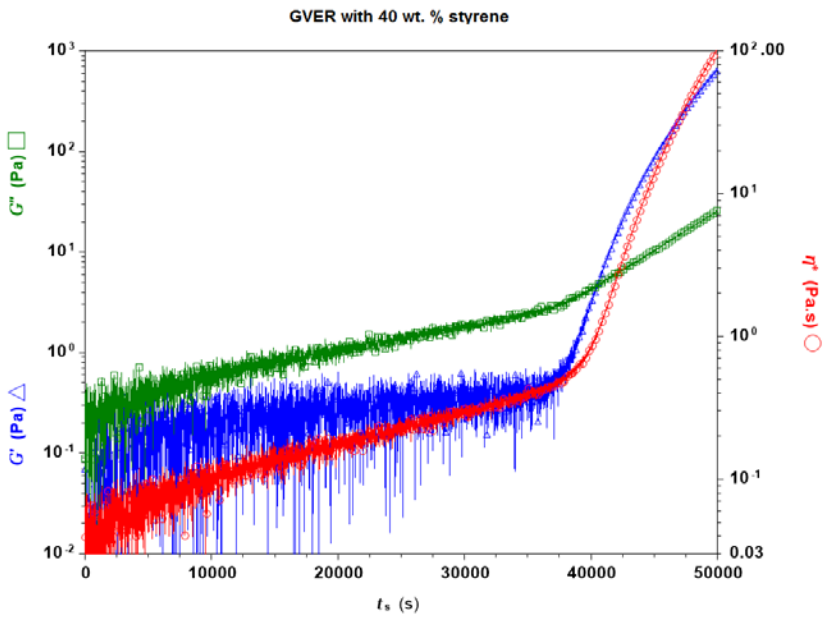


Figure 133. Shear vs Time Plot for FVER-4 with 40 wt. % of Styrene.

The second sample was GVER with 30 wt. % of styrene (FVER-5). As can be seen in Figure 134, the gel time for this material was achieved in ~6 hours. Due to a technical problem, the first three-hour data were collected.

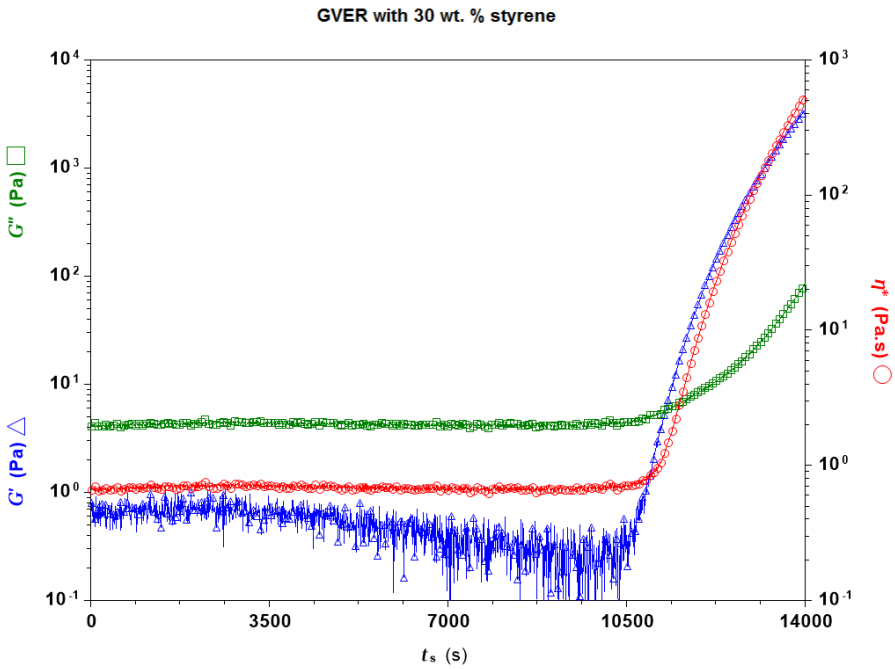


Figure 134. Shear vs Time Plot for FVER-5 with 30 wt. % of Styrene.

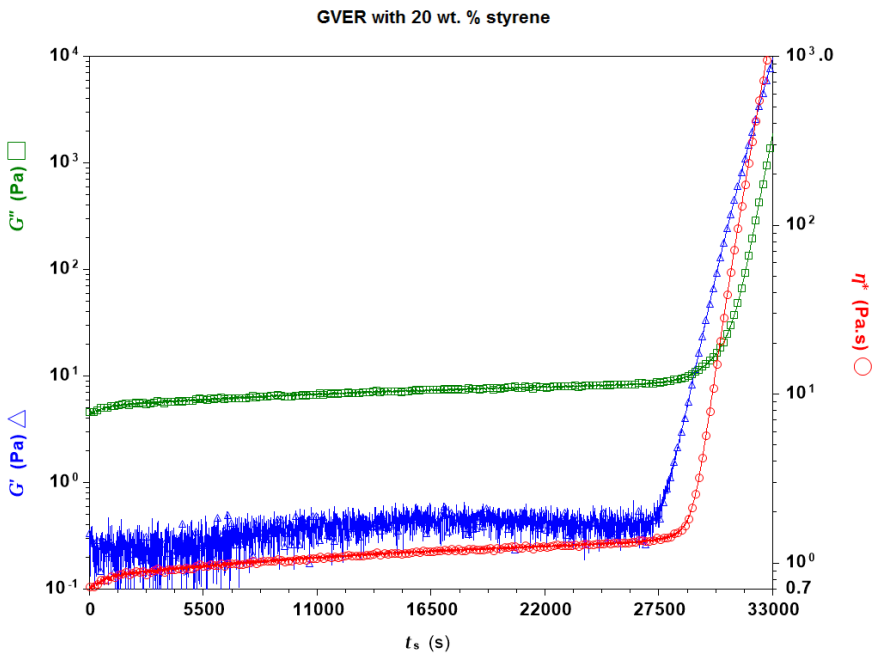


Figure 135. Shear vs Time Plot for FVER-6 in 20 wt. % of Styrene.

Figure 135 shows shear vs time plot of GVER with 20 wt. % of styrene (FVER-6). We can see a slight increase in the viscosity as the time increases. The gel time was achieved at ~7 h. In commercial resin, the microgel formation becomes dominant immediately after the addition of the catalyst and a sudden increase in the viscosity can be observed. However, as in the GVER, such microgel formation does not cause a significant increase in the viscosity and the material is getting cured.

The fractional double bond conversion of both the styrene and methacrylate groups provides insight into the rate of polymerization as well as the degree of cure of the vinyl ester resin. Previous studies have demonstrated the efficacy of isothermal FTIR in determining the double bond conversion as well as the in situ rate of polymerization. It has been shown that the initial rate of conversion of vinyl ester double bonds is significantly faster than that of the styrene double bonds. This behavior has been attributed to the higher reactivity of the acrylate free radicals as compared to the styrene free radicals during the early stages of the reaction. However, it was also observed that the final conversion of methacrylate double bonds was lower than that of the styrene double bonds. This result has been reasoned to be due to the formation of a microgel network during the polymerization process, thereby inhibiting the access of the vinyl ester double bonds to the active free radicals within the system. In addition to the decreasing reactivity of the vinyl ester as the reaction progresses, homopolymerization of styrene to form linear polystyrene chains continues to occur even towards the end of the reaction, further adding to the significant difference in double bond fractional conversion of styrene relative to the vinyl ester.

FTIR studies were conducted on the seven resin formulations to determine the fractional conversion of the styrene and vinyl ester double bonds as separate populations, as well as the overall double bond conversion. Conversion rates were determined by comparing the peaks in the FTIR spectra for the neat resin compositions to the FTIR spectra of specimens cured for 24 hours at 25 °C followed by a post-cure for 2 hours at 120 °C. Figure 136 shows an example spectra for FVER-4 from 650 cm^{-1} to 1000 cm^{-1}.

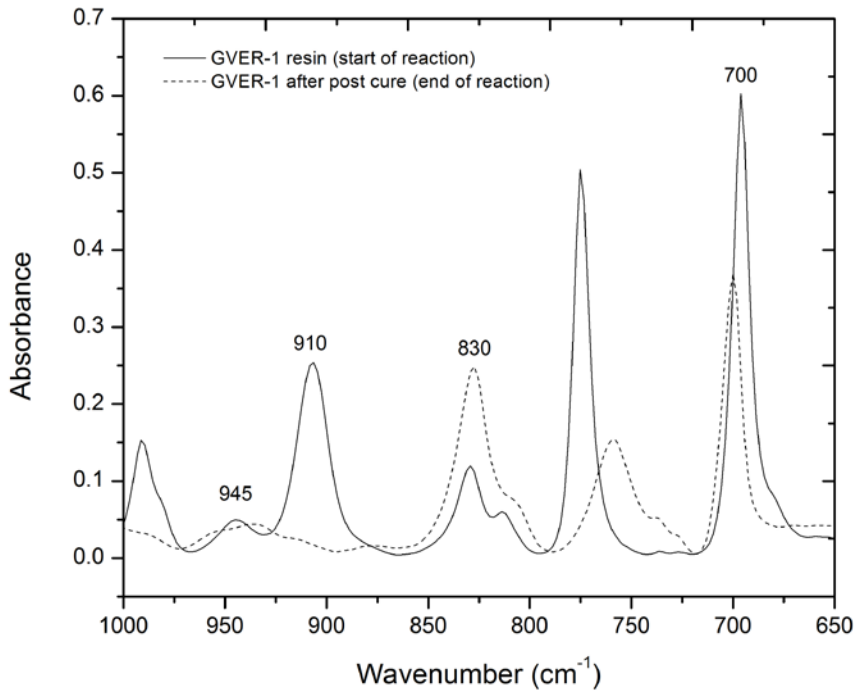


Figure 136. FTIR spectra of GVER-1 resin. The solid and dashed lines represent the uncured resin and the post-cured polymer, respectively.

The peaks at 910 and 945 cm^{-1} correspond to the bending of the carbon-hydrogen bond in the vinyl group, while the peaks at 830 and 700 cm^{-1} correspond to the bending of the aromatic carbon-hydrogen in the vinyl ester and styrene groups. Equations 1 and 2 have been adopted from previous studies to calculate the fractional conversion of the vinyl ester and styrene double bonds respectively,

$$\alpha_{VE} = 1 - \left(\frac{ABS(1)_{945cm^{-1}}}{ABS(0)_{945cm^{-1}}}\right)\left(\frac{ABS(0)_{830cm^{-1}}}{ABS(1)_{830cm^{-1}}}\right) \quad (1)$$

$$\alpha_{styrene} = 1 - \left(\frac{ABS(1)_{910cm^{-1}}}{ABS(0)_{910cm^{-1}}}\right)\left(\frac{ABS(0)_{700cm^{-1}}}{ABS(1)_{700cm^{-1}}}\right) \quad (2)$$

where ABS (0) and ABS (1) are the peak heights at the specified wavenumber for the resin and the post-cured specimens, respectively. Table 2 summarizes the fractional conversion of the styrene and vinyl ester for all seven resin compositions.

The total double bond conversion for all resin compositions was obtained by multiplying the fractional conversion of the vinyl ester and styrene double bonds by their respective mole fractions.

Table 31. Fractional conversion of methacrylate and styrene double bonds after resin post-cure.

Resin	Methacrylate conversion	Styrene conversion	Total double bond
CVER	0.41	0.88	0.76
FVER-1	0.43	0.88	0.76
FVER-2	0.44	0.84	0.72
FVER-3	0.39	0.75	0.62
FVER-4	0.51	0.82	0.70
FVER-5	0.48	0.79	0.64
FVER-6	0.50	0.90	0.60

The fractional conversion of the CVER is slightly lower in comparison to values reported in previous studies that have determined the conversion rates of the Derakane 411 series resin. As expected, the conversion of the methacrylate bonds is significantly lower than the fractional conversion of the styrene bonds for all resins. The methacrylate conversion rate increased significantly to 0.48-0.51 for FVER-4, FVER-5, and FVER-6 as compared to 0.41 for CVER. As shown in Table 31, the CVER has a significantly higher molecular weight as well as fewer moles of methacrylate per gram of resin than the FVER-4. For vinyl ester resins containing the same weight fraction of styrene (CVER & FVER-4), a decrease in molecular weight has two effects: 1) a decrease of molecular weight between crosslinks, and 2) an increase in the number of available vinyl ester terminal double bonds, which serve as crosslinkers for the polymerization reaction, per unit mass of resin. Therefore, it is expected that the lower VE conversion fraction should correlate to lower crosslink density and result in a lower storage modulus in the CVER. For the resins with the same molecular weight but decreasing styrene concentration (FVER-4 to FVER-6), the methacrylate conversion is the highest for FVER-4. This agrees with a previous study that has shown that increasing styrene concentration increases ultimate vinyl ester conversion. This occurs because the presence of a higher styrene concentration leads to greater molecular mobility and allows the vinyl groups to more easily diffuse to reach reactive sites after gelation occurs. The results also show that as the styrene fraction decreases for the same molecular weight resin, the styrene conversion also decreases. There are conflicting literature reports regarding whether resins with lower styrene content have either a higher or a lower styrene conversion. One explanation for decreasing styrene conversion is that the FVER-6 has the highest viscosity. As the reaction progresses and the vinyl ester-dominated microgel network forms, the styrene double bonds have less accessibility to the styryl radicals as compared to the reaction kinetics of FVER-4, thereby leading to a lower styrene conversion.

3.4.2.2. Cure kinetics of Br-GVER

The Br-VE prepolymer is viscous liquid and mixed with reactive diluent to obtain necessary flow properties for infusion purposes. In this study, the prepolymer was mixed with 40 wt.% styrene to obtain the baseline brominated bio-derived resin (FVER-10). This resin was then blended with the commercial resin, Derakane 510-40A, in ratios of 20, 50 and 80 wt. % to investigate the performance of blends of bio-sourced and traditional petroleum-based materials. Derakane 510-40A was selected as it is presently used for naval vessels and the target goal of this work was to develop and characterize a lower viscosity resin that could be used as a complete or partial substitute of Derakane 510-40A. In addition to these four formulations, two other formulations of GVER with a lower styrene content of 20 and 30 wt. %were also prepared. Table 30 shows the seven formulations that were examined in this study.

3.3 Cure Kinetics

The development of a new resin requires the characterization of the reaction mechanism to better understand cure kinetics. Previous studies have shown that the curing mechanism of the thermosetting resins, including epoxy, polyester, and vinyl ester resins, can be described using autocatalytic kinetics [75-81] from data fitted to isothermal DSC experiments. At the start of the reaction, a small concentration of the product is present and as the reaction progress, more product is formed and the reaction rate rises to a maximum. As all the reactant is consumed, the rate decreases to the end of the reaction. In a typical heat flow vs. time plot in an isothermal DSC test, the formation of a bell-shaped curved with a flat baseline before and after the plot is indicative of the reaction following autocatalytic behavior. The most widely used model to identify cure kinetics in an autocatalytic system is the Kamal-Sourour equation [82]. In this study, we use a modified version of this equation to model the behavior of the bio-derived resin as shown in Equation 1.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m) \cdot (\alpha_{max} - \alpha)^n \qquad (1)$$

where $d\alpha/dt$ is the cure rate, k_1 and k_2 are rate constants, $\alpha_{max}$is the maximum achievable degree of cure at the chosen isothermal temperature and m and n are exponential parameters used to describe the order of the reaction. The value for α_{max} was obtained from Equation 2,

$$\alpha_{max} = \frac{\Delta H_{iso}}{\Delta H_{iso} + \Delta H_{res}} \qquad (2)$$

where ΔH_{iso} is the heat of reaction obtained from an isothermal experiment and ΔH_{res} is the heat of reaction obtained from a subsequent ramp from 0 °C to 250 °C at 10 °C min^{-1} of the isothermally cured sample. The value for cure rate, $d\alpha/dt$, to be plugged into equation 1, was obtained from Equation 3,

$$\frac{d\alpha}{dt} = \frac{1}{(H_{iso} + H_{res})} \left(\frac{dQ}{dt}\right)_t \qquad (3)$$

where dQ/dt is the rate of heat generation at a given time on a plot from an isothermal experiment.

In this study, the cure kinetics of the brominated bio-derived vinyl ester resin (FVER-10) were examined using isothermal DSC at a range of temperatures (50 °C, 60 °C, and 70 °C). Figure 137 shows representative plots of heat flow as a function of time for the FVER-10 cured isothermally at 50 °C, 60 °C, and 70 °C.

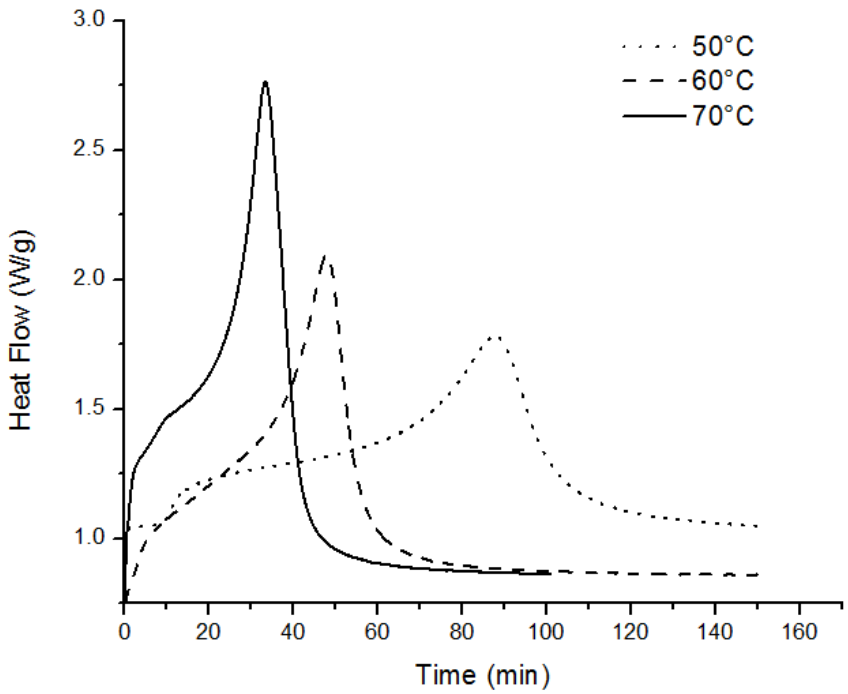


Figure 137. Isothermal plots for GVER-1 at 50°C, 60°C, and 70°C

The degree of conversion for the GVER-1 at the specified temperatures was calculated using Equation 2. Figure 138 shows the degree of conversion as a function of time while Table 32 summarizes the heats of reaction obtained from the isothermal experiments.

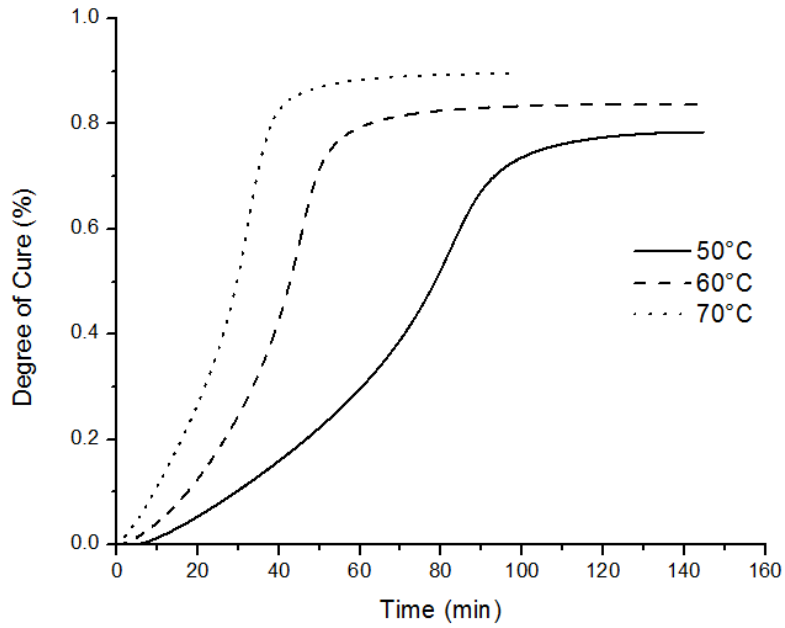


Figure 138. Experimental "degree of cure" profiles for GVER-1 at 3 different temperatures

The ultimate heat of enthalpy obtained from a scanning DSC of FVER-10 from 0 °C to 250°C at 10 °C min^{-1} was found to be 279 Jg^{-1}. As shown in Table 32, the sums of the isothermal and residual heats of reaction for each isothermal temperature are similar yet slightly lower than that obtained from the scanning DSC.

Table 32. Heats of reaction for FVER-10 measured by isothermal DSC

Temperature (°C)	ΔH_{iso} (J/g)	ΔH_{res} (J/g)	ΔH_{total} (J/g)	α_{max}
50°C	206.7	56.9	271.7	0.76
60°C	225.0	39.2	264.2	0.85
70°C	245.6	28.7	274.3	0.90

This phenomenon has been observed in previous studies [75, 76] and is attributed to increased diffusional limitations once the resin vitrifies at the tested isothermal temperature which restricts the accessibility of free radicals to vinyl ester double bonds as well as other free radicals below T_g. The residual heats of reactions were also found to decrease as the temperature because the degree of cure usually increases with increasing temperature [83].

The kinetic parameters, k_1, k_2, m, and n for the cure mechanism described previously by Equation 1 were obtained using a non-linear regression technique fitted to plots of the cure rate as a function of the degree of conversion as shown in Figure 139. Previous studies have shown these values to be calculated using non-linear regression by either; 1) setting the sum of m and n to be equal to 2 (i.e. m+n=2) or 2) calculating m and n as independent parameters. In this research, m

and n were calculated as independent parameters because they provided the best fit to the isothermal data obtained from DSC.

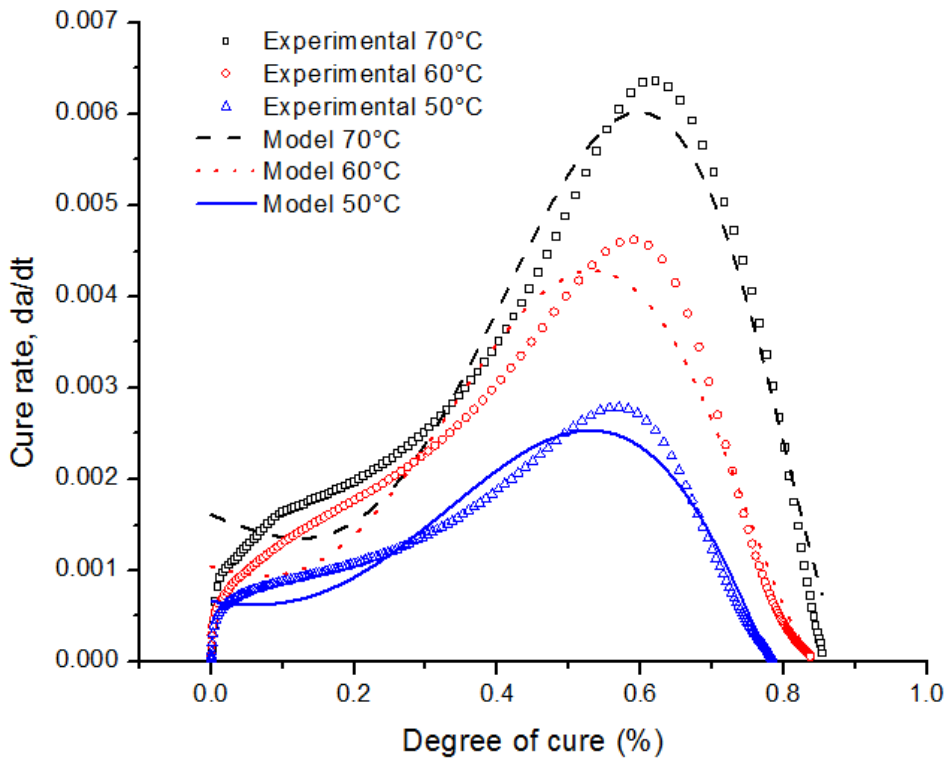


Figure 139. Comparison of isothermal data to autocatalytic model on a plot of cure rate as a function of the degree of cure.

The kinetic parameters obtained from the non-linear curve fitting of the isothermal data are shown in Table 33.

Table 33. Kinetic parameters for the autocatalytic model.

Temperature (°C)	k_1 (1/min)	k_2 (1/min)	m	n
50 °C	0.00087	0.062	2.65	1.15
60 °C	0.00137	0.187	2.99	1.69
70 °C	0.00193	0.265	3.53	1.64

The values of k_1 and k_2 for each isothermal curve were used to generate Arrhenius plots to determine the pre-exponential factors and activation energies to describe the reaction mechanism of the FVER-10 resin. Figure 140 shows the plots of the natural log of the rate constants as a function of the inverse of the product of the ideal gas constant and temperature.

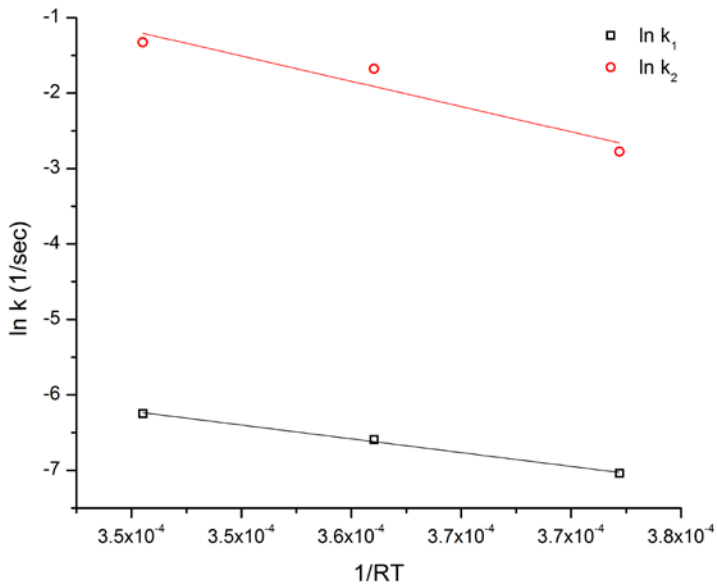


Figure 140. Arrhenius plot of rate constants for autocatalytic reaction

The linear fits of the rate constants in the Arrhenius plot shown in Figure 140 are summarized using Equations 5 and 6. The activation energies and pre-exponential factors are summarized in Table 34

$$\ln k_1 = 2.48\left(\frac{1}{RT}\right) - 36563 \qquad (5)$$

$$\ln k_2 = 18.2\left(\frac{1}{RT}\right) - 67119 \qquad (6)$$

Table 34. Arrhenius parameters describing the autocatalytic reaction

Rate Constant	E_a (J/mol)	A (1/min)
k_1	36563	7.16×10^2
k_2	67119	4.81×10^9

In addition to determining the cure kinetics using isothermal DSC, ATR-FTIR was conducted on 125 µm thick films made from all seven resin compositions. These films were cured at room temperature for 24 hours followed by a two-hour post-cure at 120 ºC per the manufacturer recommended cure cycle for the commercial Br-VER resin. The double bond conversion of the vinyl ester and styrene fractions was determined using the ratio of peak heights in the uncured resin and the cured film according to methods detailed in previous FTIR studies [70, 84, 85]. The overall double bond conversion was then calculated by multiplying the respective conversion

fractions by the molar ratio of vinyl ester to styrene double bonds identified from NMR data as shown in Table 35.

Table 35. Total double bond conversion for all seven resin compositions

Resin	Methacrylate conversion	Styrene conversion	Methacrylate: Styrene	Total double bond conversion
Br-CVER	0.33	0.96	1:4.99	0.85
FVER-7	0.41	0.95	1:4.28	0.85
FVER-8	0.42	0.96	1:3.41	0.84
FVER-9	0.54	0.97	1:2.93	0.86
FVER-10	0.68	0.96	1:2.65	0.88
FVER-11	0.68	0.96	1:1.70	0.86
FVER-12	0.69	0.99	1:0.99	0.84

The total VER double bond conversion increases as the viscosity and molecular weight decrease from Br-CVER to FVER-10. For vinyl ester resins containing the same weight fraction of styrene (Br-CVER & FVER-10), a decrease in molecular weight has two effects: 1) a decrease of molecular weight between crosslink points, and 2) an increase in the number of available vinyl ester terminal double bonds, which serve as crosslinkers for the polymerization reaction, per unit mass of resin [86]. Therefore, it is expected that the lower VE conversion fraction should correlate to lower crosslink density and in turn a lower storage modulus in the Br-CVER [87]. For the resins with the same molecular weight but decreasing styrene concentration (FVER-10 to FVER-12), the methacrylate conversion is almost equal for all three resin compositions. While it is expected that increasing the styrene concentration should increase ultimate vinyl ester conversion [84], there is no discernible trend in methacrylate conversion across FVER-10 to FVER-12 seen in Table 35. The styrene conversion across all seven resin compositions is the same and independent of molecular weight. This can be attributed to the fact that at elevated temperatures, styryl radicals are able to homopolymerize whereas the vinyl ester radicals become trapped in a microgel network after the initial low-temperature cure period.

ATR-FTIR was also conducted on an FVER-10 film that was cured isothermally for 2 hours at 50 ºC to verify the degree of conversion data obtained from resin cured isothermally at 50 ºC using DSC. Figure 141 shows the difference in peak heights between the IR spectra of the neat FVER-10 resin and the IR spectra of a film cured at for 2 hours at 50ºC.

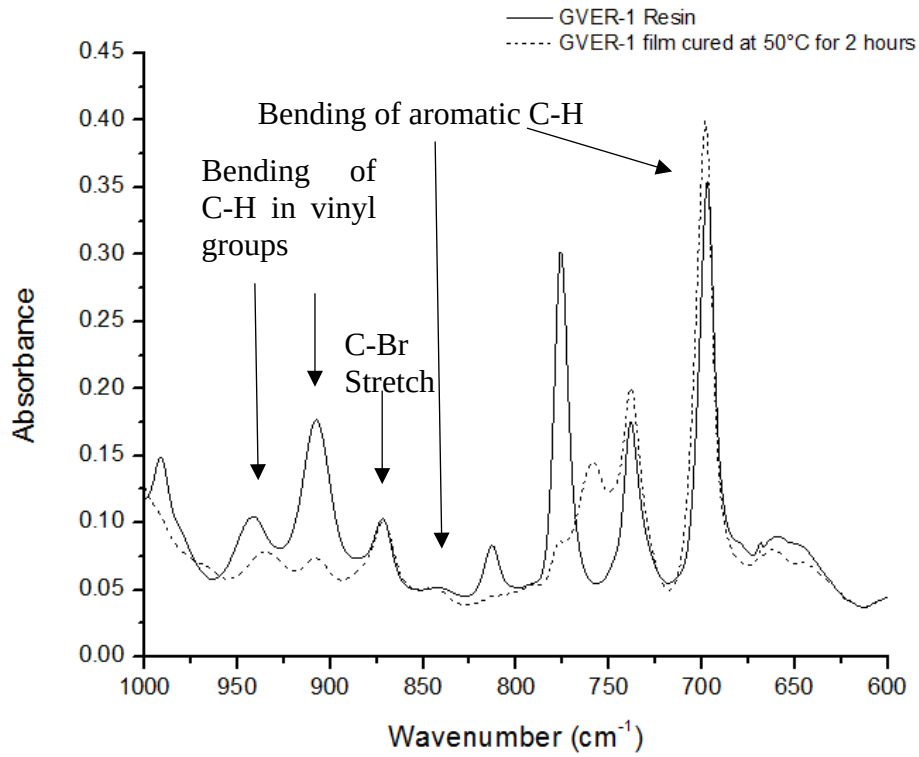


Figure 141. FTIR Plots for GVER-1 before and after 2-hr cure cycle at 50 °C

The double bond conversion fractions of styrene (α_{sty}) and vinyl ester double bonds (α_{GVER}) were determined from the peaks in Figure 141. As shown in Table 5, the ratio of the functionality of styrene to vinyl ester in the FVER-10 resin was determined to be 2.65:1. Using this ratio, the overall double bond conversion was determined and compared to the conversion data obtained from the isothermal DSC conducted at 50 ºC as shown in Table 36.

Table 36. Total degree of conversion for FVER-10 using DSC and FTIR

Method	Geometry	α_{GVER}	α_{sty}	α_{total}
Isothermal DSC (50 °C)	Activated Resin	-	-	0.76
ATR-FTIR (50 °C)	125 µm film	0.60	0.83	0.74
ATR-FTIR (24-hr 25ºC + 2-hr 120 °C post cure)	125 µm film	0.68	0.96	0.88

The data for the total degree of conversion at 50 ºC using DSC and ATR-FTIR are within 2%. DSC data only provides an overall degree of conversion and not the individual fractional conversion of the styrene and vinyl ester components and this is reflected in Table 36. When comparing the FTIR data for the 50 ºC cure to that of the film cured for 24 hours at 25 ºC followed by a two-hour post-cure at 120 ºC, the double bond conversion for the vinyl ester is almost equal while the double bond conversion for the styrene is significantly lower. The lower styrene double bond conversion in the sample cured at 50ºC is attributed to the fact that at lower temperatures, the vinyl ester radicals favor polymerization with other vinyl ester radicals rather than with styryl radicals prior to microgel formation resulting in the loss of mobility and access of styryl radicals to terminal double bonds once a semi-rigid network is formed [70]. However, at elevated temperatures, the styryl radicals are still able to homopolymerize and as a result, we see a higher conversion of styrene for the film that was postcured at 120 ºC.

In summary, the cure kinetics for the bio-derived brominated vinyl ester resin are determined to follow an autocatalytic behavior. Kinetic parameters obtained using a non-linear regression fitting as well as the maximum degree of conversion for different isothermal cure profiles have been identified and provide insight into the cure behavior of the FVER-10 resin. Cure of the FVER-10 resin for 2 hours at 50 °C leads to a similar vinyl ester double bond conversion as that of the same resin cured for 24 hours at 25 °C followed by a post cure at 120 °C. Based on these results, a curing cycle of 50 °C for 6-8 hours followed by a post cure of 120 °C for 2 hours is recommended if this resin is to be utilized for industrial applications. The post cure at 120 °C after initial curing at 50 °C ensures a higher degree of conversion of the styrene double bonds in FVER-10 in comparison to that of the 50 °C cure cycle seen in Table 36.

3.5. Task 5 - Fabricate composites with VARTM

At UML's mechanical engineering department, with the guidance of Prof. Hansen, we setup the VARTM system. we have successfully fabricated neat resin panels (Figure 144) to investigate the flame retardant performance of the commercial and GVER resins. The method to fabricate neat resin coupon was also established at Prof. Hansen's laboratory.

3.5.1. Neat Resin Coupons Preparation

The following procedure was followed to fabricate neat resin coupons:

1) Creating silicone gaskets with the following dimensions; a) 3"x3"x0.25" and b) 4"x4"x0.25".
2) Sandwiching the silicone gasket between two glass plates.
3) Inserting two syringe needles in opposite corners of the glass plates.
4) Mix the resin and degas to ensure removal of all bubbles.
5) Clamp the glass plates and the gasket to ensure no air pockets are present during injection of resin.
6) Using a 60 mL syringe, inject resin into the mold.
7) As resin is injected into the mold, hold the mold vertically so any air bubbles present rise to the surface and pop on their own, guaranteeing void free coupons.
8) Once the mold is filled completely, inject excess resin to ensure no part of the mold is left unfilled.
9) While the gasket is still clamped between the glass plates, use a syringe needle to pop any bubbles that are present on the edges of the neat resin coupon. This can be achieved by rotating the entire mold to the desired position and then pushing the syringe needle through the desired edge of the silicone gasket.
10) Allow the resin to sit and cure in the mold for 24 hours.
11) Once this is complete, remove clamps and place mold with resin coupon still inside, onto an aluminum plate and allow to post cure at 120 °C for 2 hours.

Figure 142 shows the set-up of the neat resin coupon manufacturing process. Figure 143 shows a progression of resin flow in the mold. Different thickness coupons were fabricated for various testing using same protocol discussed in Figure 142. Injection molding of Derakane Vinyl Ester resin into cavity mold to create void-free neat resin coupons.

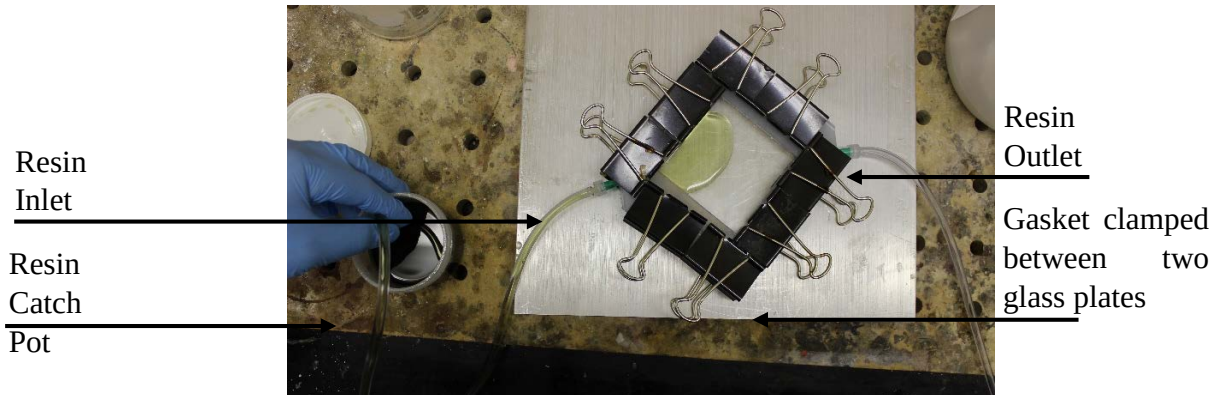


Figure 142. Injection molding of Derakane Vinyl Ester resin into cavity mold to create void-free neat resin coupons.

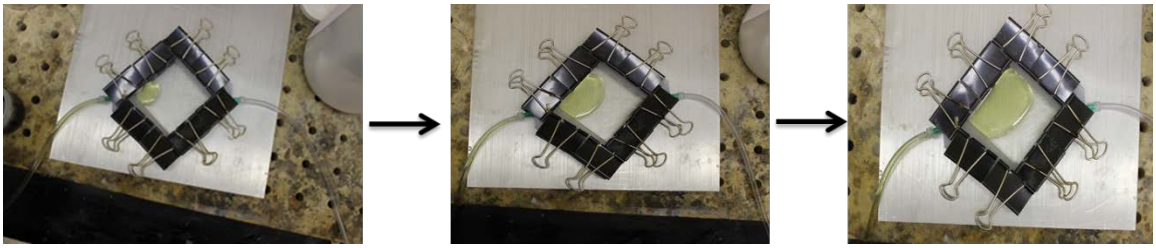


Figure 143. Specimen develops no voids or surface defects as it fills the entire mold.

Figure 144. Neat brominated vinyl ester resin coupon which was sent for flammability testing.

3.5.2. Neat resin's mechanical Properties

The mechanical performance of the resin directly contributes to key mechanical properties of a polymer materials composite (PMC). The neat resin's mechanical property was mainly

examined by Dynamic Mechanical Analysis (DMA) was conducted using a TA Instruments Dynamic Mechanical Analyzer Q800. The specimens were approximately 12 mm wide, 3 mm thick, and were clamped using a dual cantilever fixture with a support span of 35 mm. The sinusoidal transverse displacement was applied with a 6 N amplitude load at 1 Hz. The experiments were ramped at 5 °C min^{-1} from 0 to 150 °C.

3.5.2.1. Nonbrominated GVER mechanical properties.

The neat matrix mechanical properties were assessed DMA. All compositions were tested at room temperature (Figure 145. a), as well as up to 150 °C (Figure 145. b). At room temperature, the elastic storage modulus increases by 20 % for the FVER-4 relative to the CVER. There is no statistically significant difference observed in FVER-4 modulus as a function of styrene fraction, consistent with reports of a 20 wt. % decrease in styrene content.

The elastic storage modulus behavior as a function of temperature is comparable between the CVER and FVER-4. The elastic plateau values decrease at the rate, reaching 90 % of their room temperature value at 53-55 °C. The glass transition temperature (T_g), as defined by the temperature of maximum tan δ, likewise, shows minimal change with composition. The T_g increases linearly with GVER content, from 128 °C for CVER to 138 °C for FVER-4. No discernible trend is observed as a function of styrene monomer content in the FVER-4, -5, and -6 formulations, with a T_g ranging from 134 °C to 138 °C. Literature reports have found mixed effects of styrene content on the glass transition temperature, with either a maximum observed at 30-40 wt. % styrene, or a decrease as styrene content increases. However, the 4 °C shift in T_g for a 20 wt. % variation in styrene is comparable to these reports.

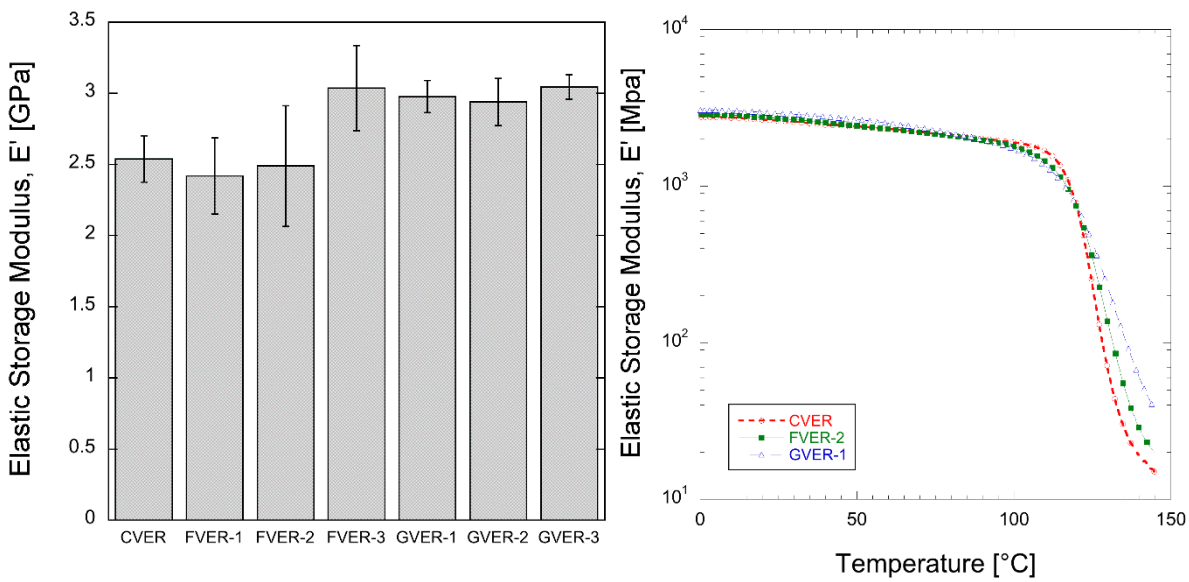


Figure 145. Elastic Storage Modulus (E') (a) at room temperature for VER compositions. (b) for CVER, FVER-2, and FVER-4 as a function of temperature.

3.5.2.2. Br-GVER Matrix mechanical properties

The neat matrix mechanical properties were assessed by DMA. Figure 146.a shows the storage modulus at room temperature for all resin compositions. The data shows a monotonically increasing trend of elastic storage modulus for compositions from Br-CVER TO FVER-10.

The VER cure reaction is a copolymerization of vinyl and divinyl monomers, in which the vinyl ester serves as the crosslinking reagent. The bio-derived GVER has a lower molecular weight than the Br-CVER. For VER containing the same weight percentage of styrene (Br-CVER to FVER-10), this decrease in molecular weight has two effects; 1) a decrease of molecular weight between crosslinks and 2) an increase of available terminal double bonds which serve as crosslinkers for the polymerization reaction[88]. As a result, the crosslink density and the elastic storage modulus increase steadily from Br-CVER to FVER-10 and this is clearly seen in Figure 146.a. For the same VE composition (FVER-10 to FVER-12), the decrease in styrene content leads to an increase in the percentage of vinyl ester crosslinker and this results in higher crosslink densities and a higher elastic storage modulus [88].

Figure 146.b shows the storage modulus as a function of temperature for three compositions: Br-CVER, FVER-8, and FVER-10. The drop in storage modulus is shifted to higher temperatures as the FVER-10 content increases. The elastic storage modulus behavior as a function of temperature is comparable between the CVER and FVER-10. The elastic plateau values decrease at the same rate, reaching 90% of their room temperature value at 53-55 °C. However, the T_g, as defined by the temperature of maximum tan δ, increases linearly with increasing GVER content and is consistent with previous reports in the literature [71, 88].

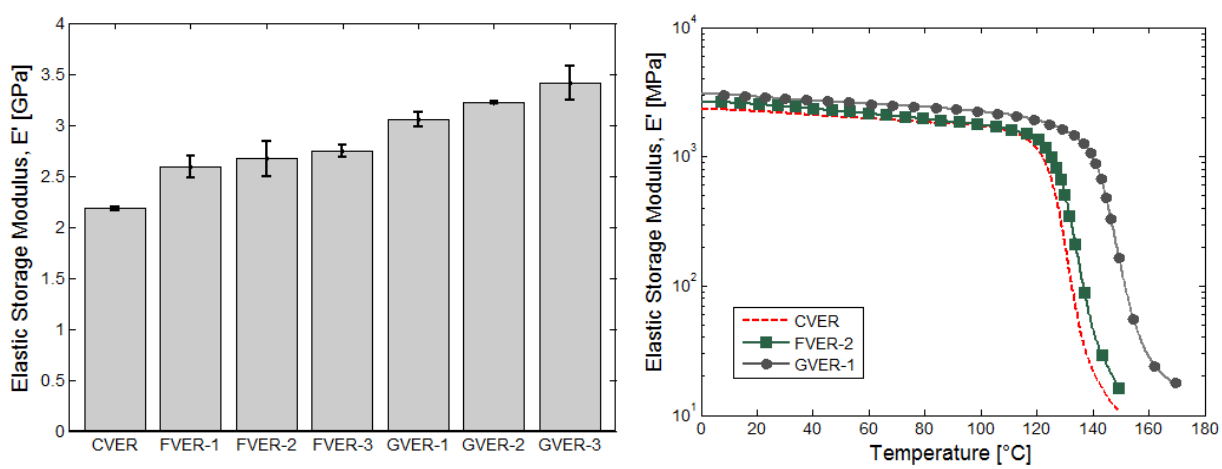


Figure 146. (a) Elastic storage modulus (E′) at 25°C for Br-VER compositions. (b) Elastic storage modulus (E′) for Br-CVER, FVER-8, and FVER-10 as a function of temperature.

Figure 147 shows the T_g increasing linearly with GVER content, from 135 °C for Br-CVER to 150 °C for FVER-10. The T_g also increases linearly as styrene content decreases across the same VE composition with the T_g increasing from 150 °C for FVER-10 to 160 °C for FVER-12. The

increase in storage modulus is consistent with the increase in T_g and this is expected because an increase in crosslink density always results in an increase in T_g of the polymer network [88].

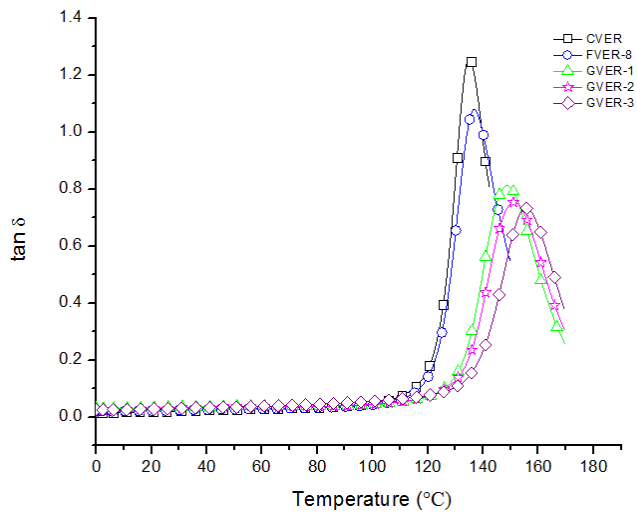


Figure 147. Plot of tan δ as a function of temperature used to determine the Tg for all seven resin compositions

3.5.3. VARTM processing at UML and NAVAIR.

Vacuum Assisted Resin Transfer Molding (VARTM) is a commonly used technique for manufacturing high performance, void-free composites on a broad range of mold geometries in the aerospace, marine and automotive industries. The mechanical engineering department at UMass Lowell has an open mold VARTM set-up to fabricate composite coupons to be used for mechanical testing. Figure 148 below shows the VARTM set-up used to create a sandwich structure comprising a polyurethane foam core between two cross-ply fiberglass cloths with fibers oriented in the 0° and 90° directions. The matrix was an epoxy resin and amine hardener system (2000 epoxy resin and 2060 epoxy hardener, Fibreglast System) mixed in a ratio of 100:27 parts by weight and degassed prior to infiltration of the composite preform.

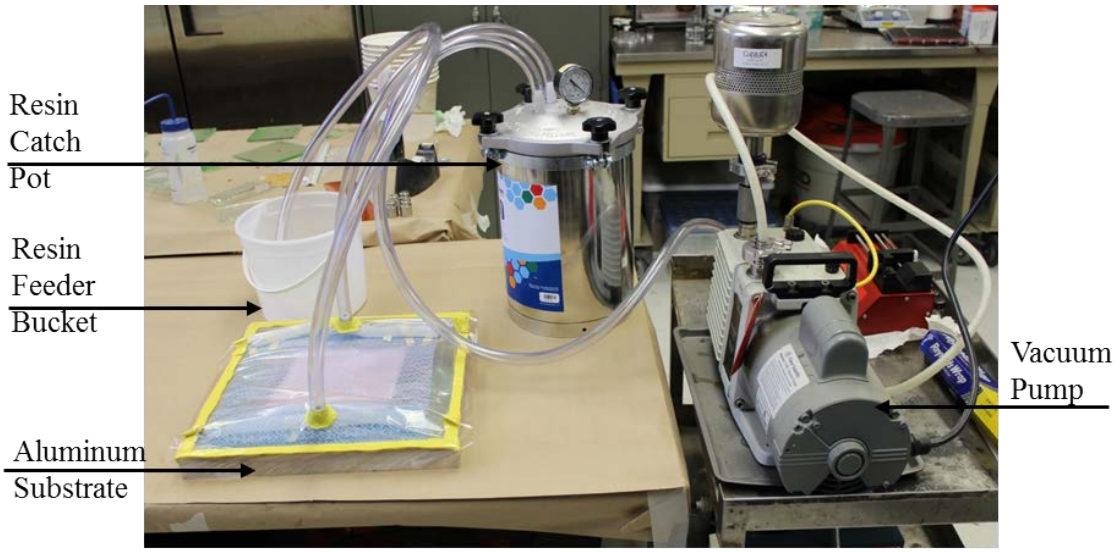


Figure 148. VARTM set-up showing different components that enable successful resin infusion of the composite sandwich structure.

Procedure

1. The glass substrate was prepared using Partall Paste Wax #2 from Rexco.
2. Carbon fiber (CF) sheets were cut to size using a rotary cutter. 32 sheets were needed to achieve the 0.25” desired thickness. CF sheets were cut to 13”x10” to create plates, from which multiple specimens were cut from one VARTM infiltration run.
3. Position CF sheets on a glass substrate.
4. Rubber dams were placed edges of the CF sheets to promote uniform sample thickness via reduced edge tapering as shown in Figure 149.

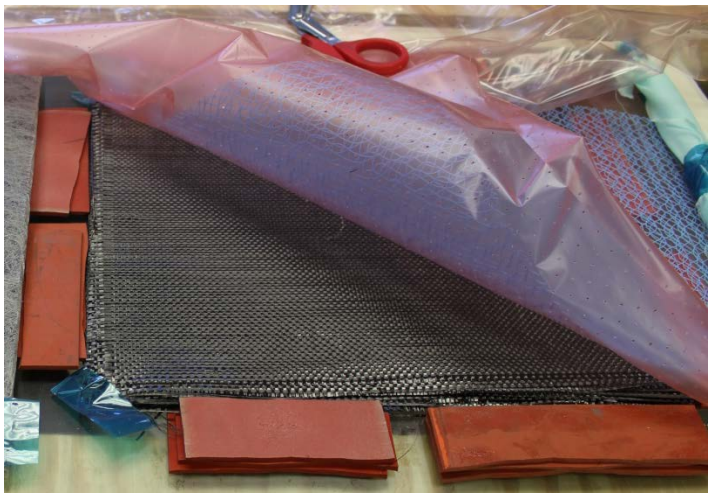


Figure 149. Stacking of multiple layers of carbon fabric ply on a glass plate.

5. Cut a piece of peel-ply to be oversized to ensure the entire sample is covered. The peel-ply used was Fibre Glast 1580-A which is a low-temperature perforated peel ply that is approximately 0.001” thick.
6. Cut resin flow media to a size such that it provides a path from the inlet, but so that it ends at a position 1” from the end of the plate length. The flow media is laid on top of the perforated peel ply as shown in Figure 150

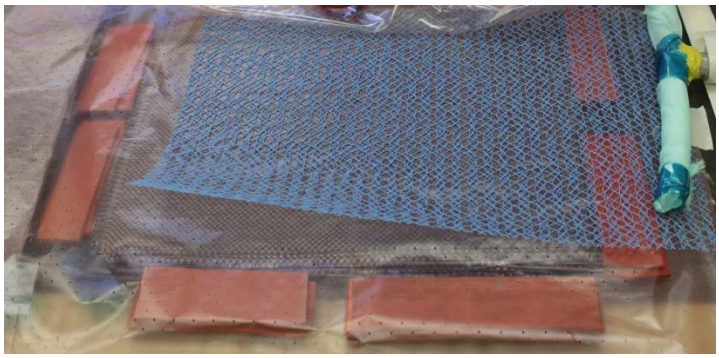


Figure 150. Covering of the stacked carbon fabric ply with peel-ply and resin flow media.

7. For the inlet: wrap spiral tubing with nylon peel-ply to reduce infusion flow rate and to prevent damage to the vacuum bagging material. Spiral tubing should be cut to be approximately as wide as the sample to be infused as shown in Figure 151.

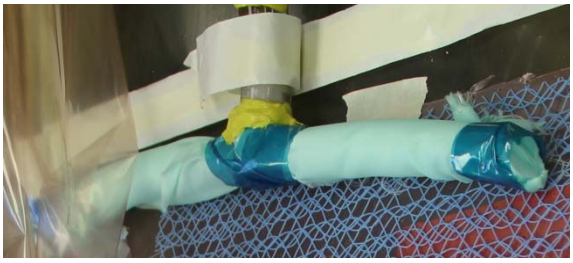


Figure 151. Wrapped spiral tubing with nylon peel-ply to reduce infusion flow rate and to prevent damage to the vacuum bagging material.

8. For the outlet: A small piece of spiral tubing was used between layers of porous flow media. Vacuum hoses were connected to the inlet and outlet spiral tubing with a ball valve in-line with the hose as shown in Figure 152.

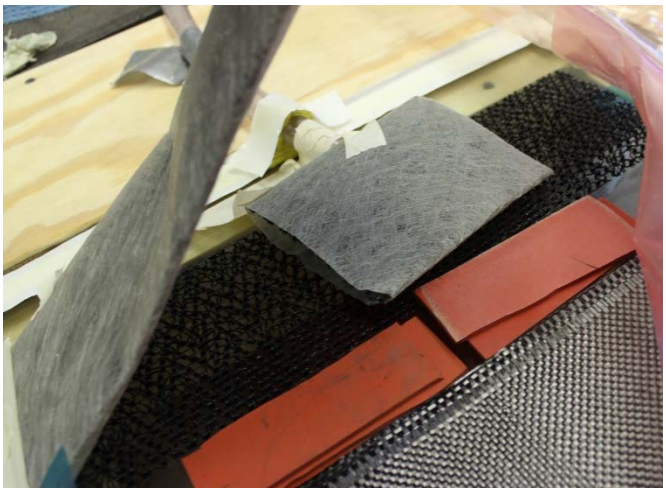


Figure 152. A small piece of spiral tubing between layers of porous flow media.

9. The stack-up was then bagged using vacuum bagging tape and Stretchlon© 800 bagging film, leaving pleats in the bagging material to accommodate for curvatures caused by pulling a vacuum as shown in Figure 153
10. The outlet hose was connected to a resin catch pot so no resin could enter the vacuum pump.
11. 28 in Hg of vacuum was applied and the bag was inspected for leaks. To test the seal of the vacuum, the valves were shut and the vacuum was turned off. The bagged material was allowed to sit for 10-15 minutes and re-inspected for leaks.

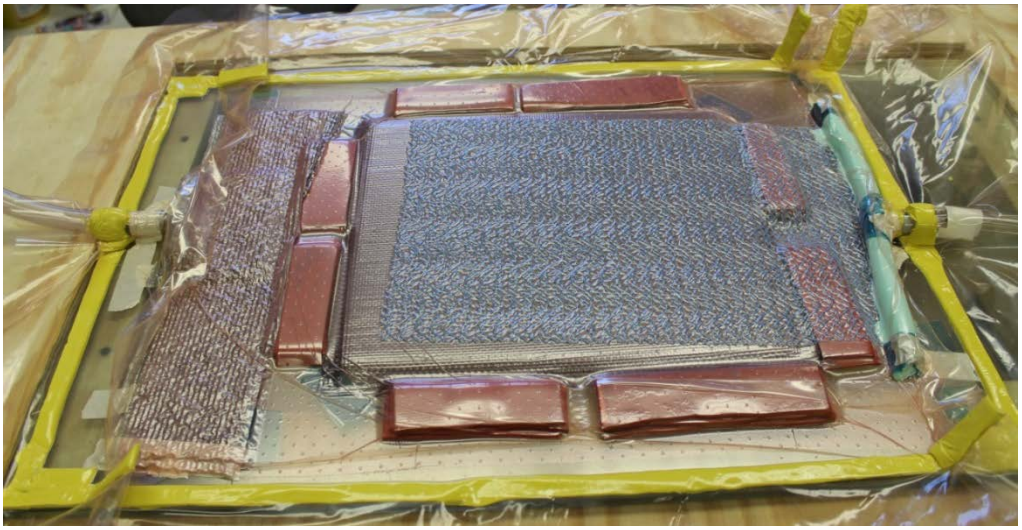


Figure 153. 11.28 in Hg of vacuum was applied and the bag was inspected for leaks.

12. The outlet hose was unclamped to ensure a full vacuum is pulled.
13. The inlet hose was placed into the resin to ensure no additional air may enter the lay-up.

14. The inlet hose valve was then opened, allowing the resin to flow across the plate as shown in Figure 154.

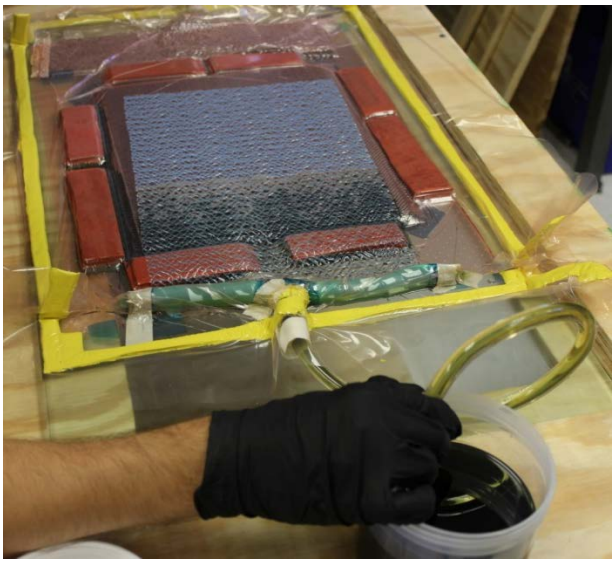


Figure 154. Resin flows across the plate.

15. Upon wetting out, each valve was closed and the sample was cured at room temperature for 24 hours inside of the vacuum bag.

The plate shown in the in this document was then cut into 3”x3”x0.25” and 4”x4”x0.25” samples which were then submitted for flame retardant property testing as shown in Figure 156. Some of the issues observed during this infusion included race-tracking around the entire sample in the slight gap that was present between the carbon fiber ply stack up and the rubber dams. Our team will attempt to make a larger sample without the rubber dams to reduce the likelihood of race-tracking. We will then cut off the sloping edges and discard them. The switch from 0.5” to 0.25” tubing allowed us to carry out the infusion at a more controlled rate because of the smaller amount of resin flowing in at the entry point.

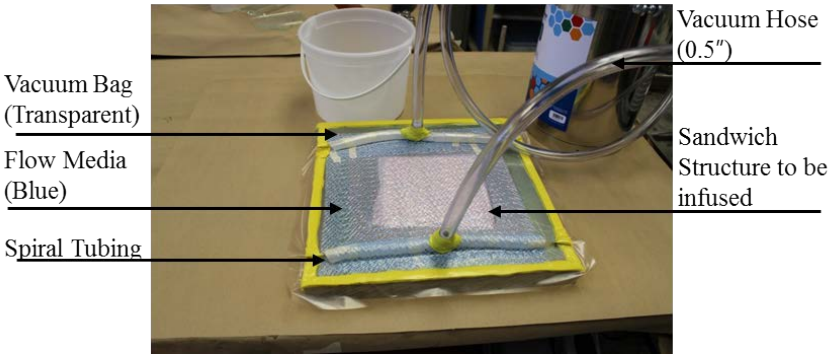


Figure 155. Shows the composite sandwich structure formed using the VARTM.

Figure 155 is the setup to fabricate coupon shows a second infusion experiment that was conducted by the research team at UMass Lowell. In this VARTM set up, a 12 ply stack up of unidirectional glass fibers was infused with epoxy resin. Detailed functions of each part described in Figure 155 are explained in Table 37.

Table 37. Description of each component in VARTM system

Components/Material	Purpose
Vacuum Pump	Creates vacuum pressure that draws the air out of the vacuum bag and maintains this vacuum pressure throughout the cure cycle of the composite.
Resin Catch Pot	Catch pot sits between the composite and the vacuum pump and prevents any excess resin from the composite being drawn into the vacuum tube and into the pump. The catch pot is lined with PVA mold release to increase ease of removal of resin within the catch pot.
Vacuum Gauge	Measures and displays the level of vacuum in the system. Helps to identify leaks within the vacuum bag. The infusion should optimally be conducted when the vacuum pump reads 30 in Hg.
Bleeder Valve	Bleeder valve allows easy adjustment of vacuum within the system. While the vacuum pressure should be maintained at 30 in Hg during the initial stages of infusion, the bleeder valve is used to adjust the vacuum to reduce the likelihood of resin rich pockets within the setup.
Tube Clamp	Used to close off the flow of resin from the resin bucket to restrict resin flow into the composite.
T-connector	Used to join the vacuum hose to the spiral tubing to allow infusion of resin into the composite part.
Vacuum Hose	Connects the vacuum pump, resin catch pot and resin feeder bucket to the composite in the mold.
Peel Ply (Porous)	Thin plastic film is the first removable layer between the composite and the vacuum bag. Creates a surface that can absorb excess resin.

Resin Flow Media	Flow media is a plastic mesh pattern designed to promote resin flow during the infusion process. The rate of infusion can be varied based on the pattern of flow media.
Resin Infusion Spiral	Plastic spiral is used to provide a free-flowing channel through which resin is distributed near the point where resin first enters into the composite. Resin flows freely through the center of the spiral tube but also out of the spirals in the side, allowing the resin to be supplied all the way along the edge of a composite.
Vacuum Bagging Tape	This tape is used to create air-tight seals between the vacuum bag and the mold surface.
Breather	This material is optional. Used to create an absorbent barrier between the composite and the spiral tubing.
Infusion Resin	Composite, this can be either epoxy, resin to the initiator and to the accelerator is critical in how it affects pot life, curing time and quality of the final composite part.

We have prepared C-fabric reinforced composites using VARTM and performed several mechanical testing. We have prepared C-fabric reinforced specimen for tensile, flexural, short beam shear strength, cone calorimetry, and smoke density testing using commercial or formulated resins. For curing of the resin, we used 0.20 wt. % cobalt naphthenate (CoNap) as a promoter, 1.00 wt. % cumene hydroperoxide (CHP) as an initiator, and 0.30 wt. % 2,4-pentanedione (acetylacetone) as retarder. Different numbers of plain weave carbon fabric were used for preparing specimen with different thickness. The composites were cured at room temperature for 24 h and at an elevated temperature for 2 h. The C-fabric reinforced composites with different thickness are shown in Figure 156.

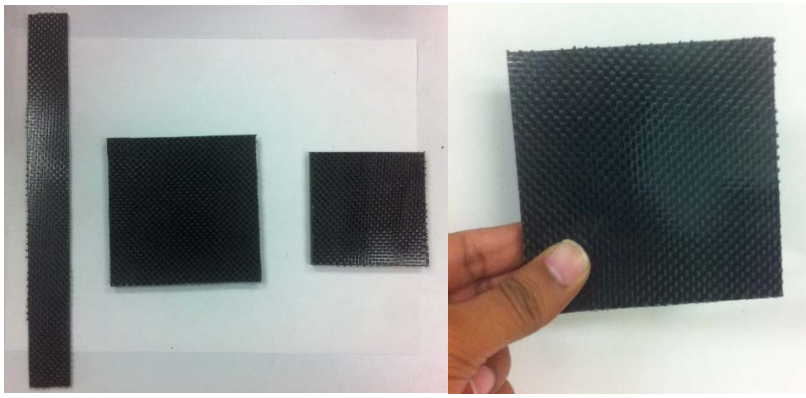


Figure 156. Different specimen prepared using multiple VARTM for various testing.

The material comprising the VARTM setup and surface treatment agents are listed in Figure 157.

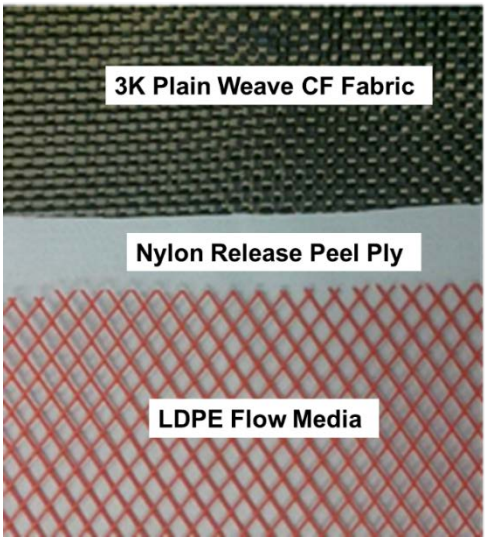


Figure 157. Different Material used in VARTM Process.

Surface treatment agents for VARTM:

- 3K Plain Weave CF Fabric (Textile Products Inc.)
- Nylon release peel ply (Fibre Glast)
- LDPE Flow Media (Fibre Glast)
- Stretchlon 800 vacuum bagging film (Fibre Glast)
- Breather material
- PVC Double barb ball valves (Grainger)
- Sealant tape (Fibre Glast)
- Ply release agent (Rain-X water repellent)
- Surface cleaning agent (Rain-X X-treme Clean)
- Spiral-cut tubing
- Translucent plastic tubing
- Silicone connectors

The following is the sequence of vacuum bagging and infusing the stack-up:

The 42” wide CF tow is cut into multiple sections to create ply stack-ups of desired dimensioned laminates which can either be uniform thickness for one type of test coupon or a ply drop-off laminate as shown in Figure 158 and Table 38 to obtain multiple types of coupons.

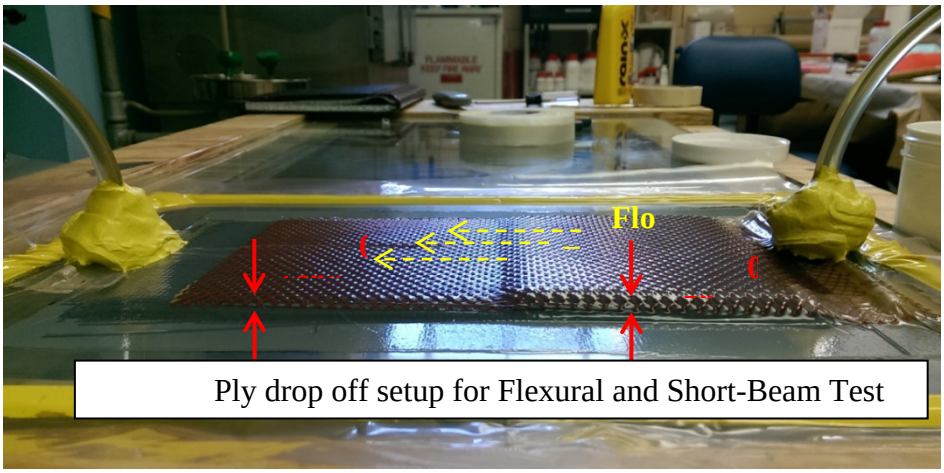


Figure 158. Preparation of C-Fabric Reinforced Coupons using VARTM.

Table 38. Number of Plies and the Thickness Achieved During VARTM.

11 ply stack up → 0.1” desired thickness
18 ply stack up → 0.16” desired thickness
34 ply stack up → 0.5” desired thickness

A top view schematic used to obtain individual plies for the ply drop-off laminate shown in the previous figure is shown in Figure 159.

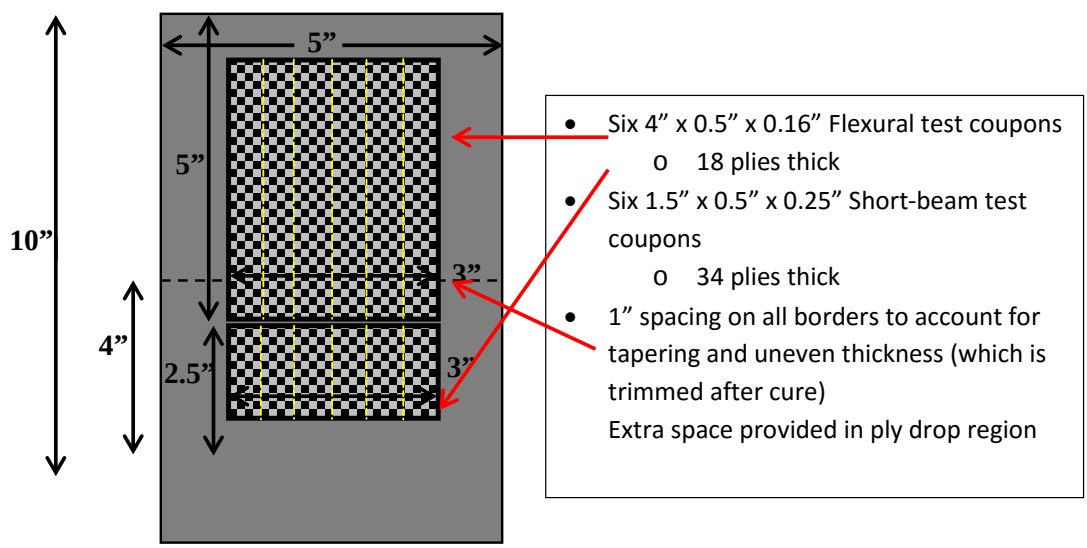


Figure 159. Schematic Diagram of VARTM Plate Explaining the Fabrication of Different Samples.

The glass surface used for the VARTM setup is first cleaned using a glass cleaner as shown in Figure 160 in order to remove any dirt and left over mold release (NOTE: mold release will only come off with this particular glass cleaner). This is done in order to ensure a robust vacuum seal and prevent cosmetic defects.

Figure 160. Image of Mold Release Material and Glass Cleaner.

Mold release (hydrophobic material) is applied to the tentative region under the CF ply stack-up in order to ensure easy release post cure. The CF is entirely covered with a nylon peel ply material. The flow media is placed over the peel ply material which has the same width as the stack-up. It has been determined that the amount of flow media material required to ensure even and complete infusion varies depending on the size of the stack-up.

- For smaller laminates such as 4” x 4” x 0.25”, the length of the flow media is only required to be approximately 3/5th the length of the stack-up.
- For larger laminates such as 18” x 10” x 0.25”, the flow media is almost as the length of the stack-up as shown in Figure 161. Breather Material, Spiral-Cut Tubing and Silicon Infusion Connector in Vacuum Bagging.

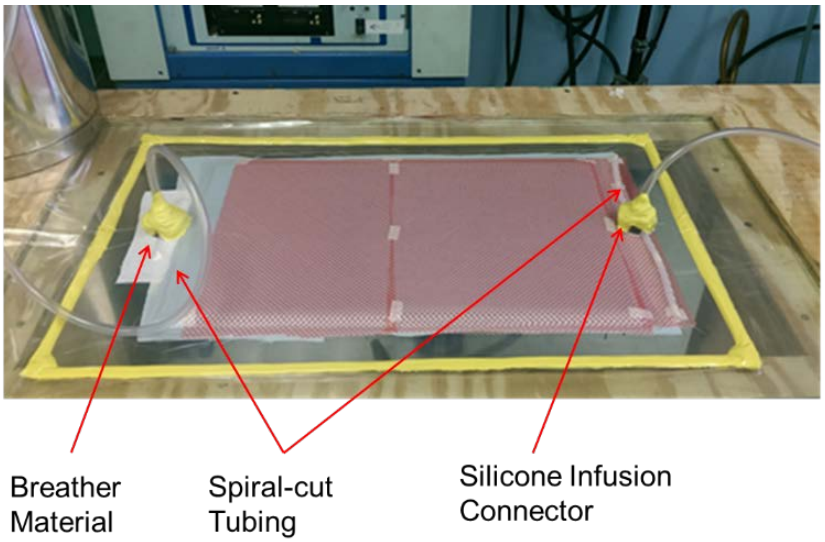


Figure 161. Breather Material, Spiral-Cut Tubing and Silicon Infusion Connector in Vacuum Bagging.

Breather material is introduced at the exit location of the setup in order to ensure drainability of excess resin. Spiral-cut tubing is used in combination with silicone infusion connector with the length at entry running along the entire width of the stack-up and a smaller version at the exit. The setup is sealed in vacuum baggin as shown in Figure 161, material and the tubing entry and exit points into the silicone connectors are further sealed using sealant tape. The tube terminals at the valves are in a similar manner as shown in Figure 162.

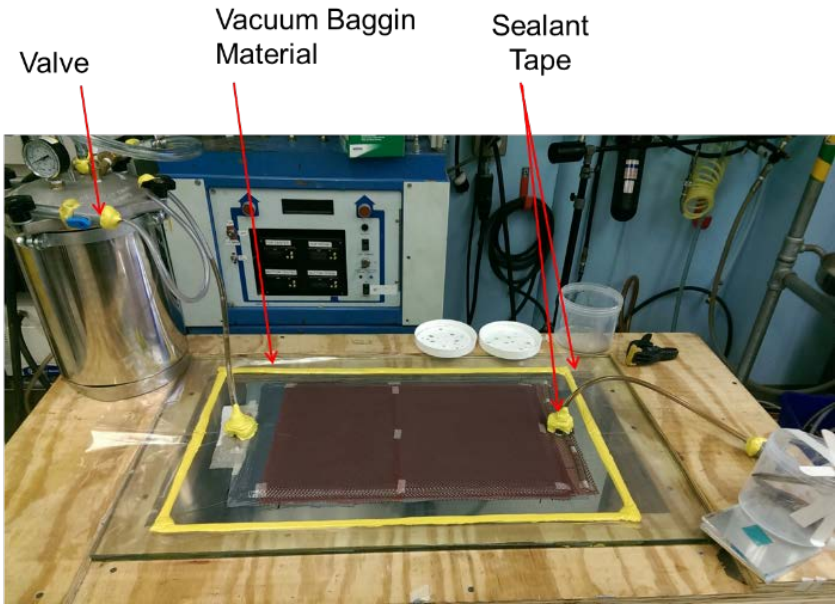


Figure 162. Picture of Valve, Vacuum Baggin Material, and Sealant Tape.

Vacuum is pulled at a final pressure of approximately -27 in. of Hg (-90 kPa) and the valves are shut off. The vacuumed bag is left overnight to ensure there are no leaks prior to infusion. The finished (post-cure, sawed to dimension) ASTM test coupons are shown in Figure 163.

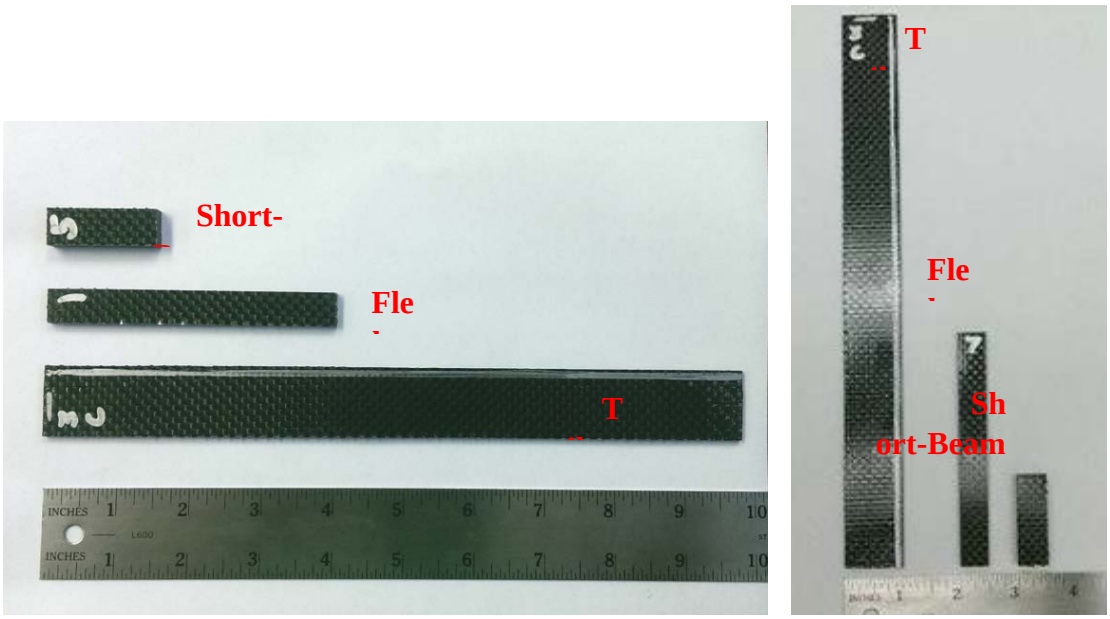


Figure 163. Different specimen prepared using multiple VARTM for various testing.

3.6. Task 6 - Conduct Structural Testing for Equivalence

Neat resin coupons and CF reinforced composite coupons were fabricated as described in Task 5. CF reinforced coupons were subjected to wide range of mechanical testing and fire retardant testing to examine their performance equivalence with commercial Derakane resins. We have conducted tensile and flexural tests on the coupons in accordance with ASTM D3039 and D7264 respectively. The tensile test on the neat resin coupons had been conducted in accordance with ASTM D638. The flammability properties of the composites have also been intensely investigated.

There are three general mechanisms that all types of flame retardant (FR) chemistries fall into; i) gas phase FRs, ii) endothermal FRs and iii) char-forming FRs [89]. The first category includes halogen and phosphorous based FRs which act by reducing the heat released in the gas phase from combustion by reacting with available free radicals [90-92]. The most common halogenated FRs use chlorine or bromine rather than fluorine or iodine because the (bromine/chlorine)-carbon bond is considered to be relatively weaker and is, therefore, most susceptible to thermal decomposition [93]. Some of the most commonly utilized compounds based on brominated FRs include TBBPA, hexabromocyclododecane and polybrominated diphenyl ethers [94, 95]. Besides halogenated compounds, gas phase flame retardants also include materials that have phosphorus incorporated into their chemical structure. It has been well documented in

the literature that phosphorous containing compounds can have promising fire retardant behavior in epoxy resins [96-98].However, they are not as useful as halogenated flame retardants because they generate more smoke and carbon monoxide in fire conditions and are sometimes not very effective when acting alone in styrenic polymers [89]. The second family of FRs (i.e. endothermic FRs) work by releasing non-flammable gasses like water vapor and carbon dioxide which cool the polymeric materials through endothermic decomposition of the flame retardant additive. This drop in temperature helps slow the rate of pyrolysis and thereby the thermal decomposition of the material. The most common FR additives for this mechanism include mineral fillers like metal hydroxides and metal carbonates. Recent advancements in the study of mineral fillers have seen the incorporation of various other mineral fillers alongside these metal additives such as organo-modified montmorillonite nanoparticles [99, 100], carbon nanotubes [101] and delaminated talc [102] to name a few [103]. While mineral filler technology has proven highly effective at lowering smoke and other toxic emissions when the material is exposed to fire, the high loading fraction required for it to be effective can lead to some of the polymer's mechanical properties being compromised. In addition, once all the mineral filler has been consumed the material loses its flame retardant properties and is ineffective in situations where there is exposure to a constant and prolonged source of extreme heat [104].

The third and final group of FRs comprises intumescent flame retardants (IFRs) and polymer nanocomposites. IFRs create a layer of protective carbon foam when exposed to fire and swell when heated thereby protecting the substrate beneath. Some examples of research conducted on IFRs include the development of intumescent coatings on cotton and ramie fabrics using a layer by layer assembly [105-107] as well as the incorporation of IFR materials into the matrix of polypropylene-wood flour composites [108]. Polymer nanocomposites are the newest class of material utilized for flame retardancy amongst all the previously described materials. They reduce the rate of polymer mass loss in a fire by creating a protection barrier rich in nanoparticles. This layer leads to the reduction of peak heat release rate which in turn makes the polymer burn less intensely over time. While both these material classes show plenty of promise for FR applications, IFRs can suffer from water absorption issues, a potential problem if used in hulls of naval vessels, while the uncertainty and newness of nanocomposite technology mean much research has yet to be conducted prior to it seeing widespread industrial application [89].

Methods to improve flammability properties of polymers and their composites are being studied extensively with the goal of developing materials that are cost effective, environmentally friendly and have the potential to be utilized in a wide variety of industrial applications. While all FR technologies have their cons, there are a few that stand out as being the most viable options because their benefits simply outweigh those of their competitors. Halogen FRs, despite being under scrutiny for their potential environmental toxicity, are still the most widely utilized compounds for fire suppression in various applications because; 1) they are the most cost-effective technology, 2) a small halogenated molecule can deliver a high amount of halogen to combat a fire and 3) they can be easily combined with other chemistries to create an even more effective FR.

These are the primary reasons why this research focuses on investigating the properties of a novel brominated vinyl ester resin.

3.6.1. Flammability Testing

Our collaborator NAVSEA has performed various flame retardant testing on composites received from either UML or the second collaborator NAVAIR. The composites were evaluated using following test methods:

- ASTM E-1354: Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter
- ASTM E-662: Specific Optical Density of Smoke Generated by Solid Materials in flaming and nonflamming mode.

3.6.1.1. ASTM E-1354 Cone Calorimeter

ASTM E-1354 determines heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter. It is also called cone calorimeter test, which requires three specimens of 4” x 4” x 0.25” thickness and heat flux of 50 kW/m^2

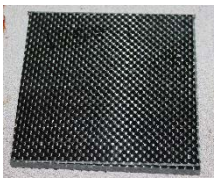
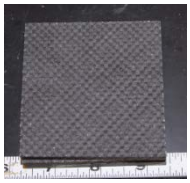
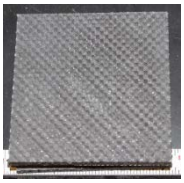
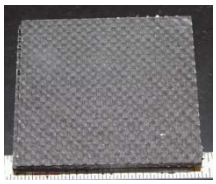
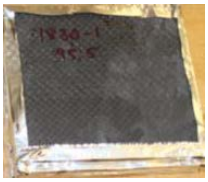
Figure 164. Setup of ASTM E-1354.

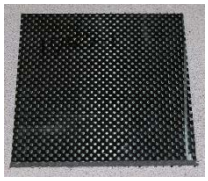
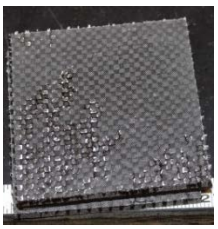
Description: A conical shaped heater irradiates uniform heat to a 4” x 4” x 0.25” square test specimen. The specimen is positioned on a load cell that continuously measures its mass throughout the test. Oxygen concentration and air flow are also constantly measured. The heated specimen is ignited by a high voltage spark source. Throughout the test, the combustion gasses are drawn away through a calibrated hood and sampled at a known rate. Smoke obscuration is measured in the flow system by means of a laser photometer system. Data for each parameter is

collected during the test and computer processed to provide heat release rates based on oxygen consumption calorimetry. Oxygen consumption principle states that, generally, the net heat of combustion is directly related to the amount of oxygen required for combustion. The relationship is that approximately 13.1 MJ of heat are released per 1 kg of oxygen consumed. The output from this test method includes Peak Heat Release Rate, Average Heat Release Rate, Total Heat Released, Specific Extinction Area, Mass Loss Rate, and Time to Sustained Ignition. This output may also be used in fire models to determine flashover potential of combustible lining materials in confined spaces. ASTM E-1354 has been shown in Figure 164.

We have prepared three CF reinforced coupons for each formulation using VARTM as mentioned in Table 39, and NAVSEA has performed various flame retardant testing on these coupons.

Table 39. Sample Types and Their Appearance.

Material ID	Material Description 1742	Photo 1750
CVER	‘C’ Fabric Reinforced Vinyl Ester Resin	
FVER-1	20% Green VER and 80% Derakane Momentum 411-350	
FVER-2	50% GVER and 50% Derakane Momentum 411-350	
FVER-3	80% GVER and 20% Derakane Momentum 411-350	
FVER-4	100% GVER with 40 wt. % Styrene	
FVER-5	100% GVER with 30% Styrene	
FVER-6	100% GVER with 20% Styrene	

Br-CVER	‘C’ Fabric Reinforced / Brominated Vinyl Ester Resin	
FVER-7	20% Brominated GVER and 80% Derakane 510A-40	
FVER-8	50% Brominated GVER and 50% Derakane 510A-40	
FVER-9	80% Brominated GVER and 20% Derakane 510A-40	
FVER-10	100% Br-GVER with 40 wt. % Styrene	
FVER-11	100% Br-GVER with 30 wt. % Styrene	
FVER-12	100% Br-GVER with 20 wt. % Styrene	

4.6.1.1.1. Cone calorimetry test of nonbrominated VER composites.

A heat of combustion is a total amount of energy released when the material is burned. Each material possesses a given amount of potential energy. The heat release rate is a measurement of heat energy released over a specific unit of time. This energy is measured in megajoule per kilogram. Heat release rate for the study of fires was only accessible in theory prior to 1980; the tools available to quantify the heat release rate of a material were merely bench-scale devices which did not have the capability of gathering data on a more useful large scale. In 1982, Dr. Vytenis Babrauskas developed the Cone Calorimeter with enabled precise measurement of heat release rate on a macro scale. ASTM E-1354 determines heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter. Table 40 explains the heat release rate of the CF-reinforced panels of non-brominated vinyl ester resin coupons as shown in Figure 165.

Table 40. ASTM E1354 Heat Release Rate of CF-reinforced nonbrominated VER formulations.

Sample ID	Time to Ign. (sec)	Flame Duration (sec)	% Mass Loss	Average Effective Heat of Combustion (MJ/kg)	Avg. HRR at 60 sec (kW/m^2)	Avg. HRR at 180 sec (kW/m^2)	Avg. HRR at 300 sec (kW/m^2)	Peak HRR (kW/m^2)	Time of Peak HRR (sec)	Total HRR/A (MJ/m^2)	SEA (m^2/kg)
Carbon Fabric Reinforced Non-Brominated Resin Panel											
VER-1	114	449	25	30	134	166	206	289	370	79	1320
VER-2	93	342	26	27	142	195	235	343	322	75	1245
VER-3	103	434	24	34	157	189	232	319	332	87	1417
Average	**103**	**408**	**25**	**30**	**144**	**183**	**224**	**317**	**341**	**80**	**1327**
20% Green VER and 80% Derakane Momentum 411-350											
FVER-1-1	94	427	27	27	158	182	198	269	381	79	1169
FVER-1-2	100	576	30	28	165	188	205	261	355	87	1210
Average	**97**	**502**	**29**	**28**	**162**	**185**	**202**	**265**	**368**	**83**	**1190**
50% Green VER and 50% Derakane Momentum 411-350											
FVER-2-1	105	474	34	26	137	182	218	320	385	100	1446
FVER-2-2	66	503	31	28	100	162	197	327	381	100	1421
FVER-2-3	89	487	32	28	117	185	225	352	368	103	1495
Average	**87**	**488**	**32**	**27**	**118**	**176**	**213**	**333**	**378**	**101**	**1454**
80% Green VER and 20% Derakane Momentum 411-350											
FVER-3-1	84	536	33	25	162	173	200	265	124	95	1295
FVER-3-2	103	436	28	28	131	158	212	322	356	88	1427
FVER-3-3	100	496	31	26	162	163	209	299	341	92	1236
Average	**96**	**489**	**31**	**27**	**152**	**165**	**207**	**295**	**274**	**91**	**1319**
100% GVER with 40 wt. % of styrene											
FVER-4-1	85	463	30	26	138	190	218	277	335	87	1312
FVER-4-2	89	481	29	28	158	168	206	287	326	91	1479
FVER-4-3	87	462	29	27	142	191	216	287	300	88	1336
Average	**87**	**469**	**29**	**27**	**146**	**183**	**213**	**284**	**320**	**88**	**1376**
100% GVER with 30 wt. % of styrene											
FVER-5-1	98	573	28	27	142	173	200	260	348	82	1309
FVER-5-2	102	458	25	29	124	189	213	284	278	78	1286
FVER-5-3	103	411	29	25	128	191	223	326	309	81	1311
Average	**101**	**481**	**27**	**27**	**131**	**184**	**212**	**290**	**312**	**80**	**1302**
100% GVER with 20 wt. % of styrene											

FVER-6-1	99	18	4	4	N/A	N/A	N/A	124	106	2	568
FVER-6-2	89	353	28	13	110	118	126	146	323	42	1796
FVER-6-3	93	325	29	12	106	120	129	172	313	40	1823
Average	**91**	**339**	**29**	**13**	**108**	**119**	**128**	**159**	**318**	**41**	**1809**
20% Brominated GVER and 80% Derakane 510A-40											
FVER-6-1	126	346	26	13	90	120	124	167	319	39	1849
FVER-6-2	121	326	28	12	91	120	120	168	287	37	1750
FVER-6-3	121	326	26	12	113	115	117	145	332	37	1611
Average	**123**	**333**	**27**	**12**	**98**	**118**	**120**	**160**	**313**	**37**	**1737**

Heat release rate is the single most important variable in the development of fire. Dr. Babrauskas has developed the three principles for this.

1. Heat release rate (HRR) is the driving force for fire, which is an exponential phenomenon as higher the generate heat will make more heat. HHR is very critical compared with other variables that contribute to the lethality of fires as toxic gasses do not create more toxic gasses; smoke does not create more smoke; etc.

2. Most other variables such as smoke, toxic gasses, and fire spread are correlated to HRR. As the HRR increases so do the products of combustion such as. This is clearly depicted with the fire development curve we are all familiar with.

3. High HRR directly indicates a high threat to life. For example, a sheet of paper is easily ignitable and has a high flame spread rate. This alone does not make a burning sheet of paper dangerous. However, a high heat release rate translates to rapid temperature changes, faster flashover times and an increase in the production of the products of combustion.

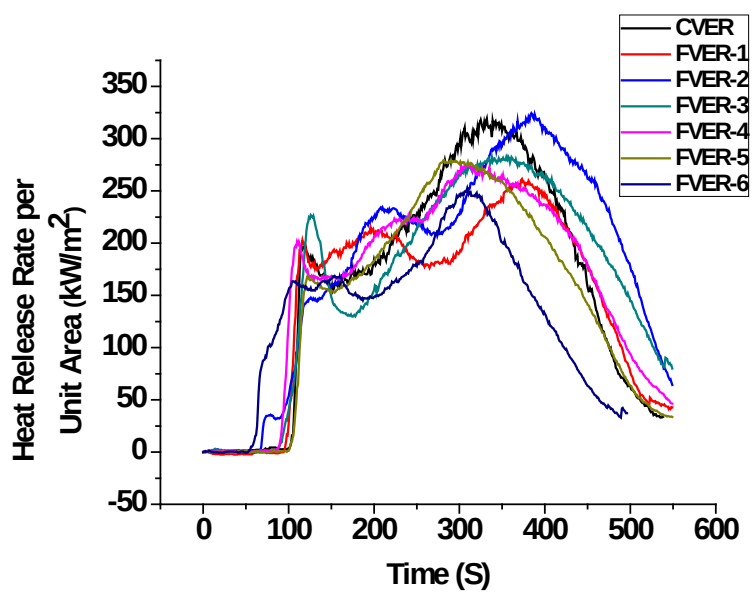
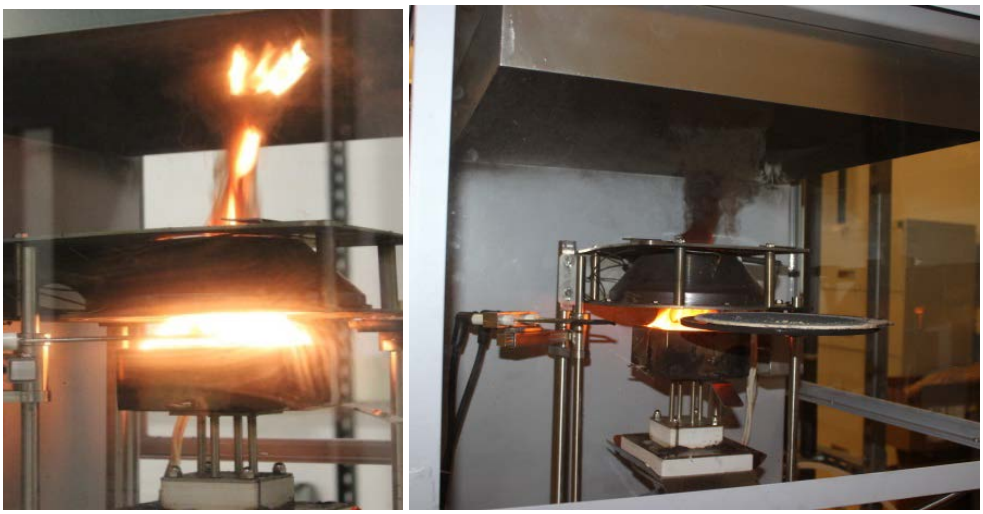


Figure 165. The plot of Heat Release Rate per Unit Area Vs Time of C-Fabric Reinforced Composites of Non-brominated GVER.

Brominated resin has low ignition time but very low HRR compared with non-brominated resin. The same thing was observed for carbon fabric reinforced coupons.

(a)



(b)

Figure 166. Various stages during cone calorimetry testing (a) maximum flame and smoke generation, (b) coupons after flammability testing.

When the coupons were examined by cone calorimetry test, once they start burning it reaches maximum, and after all, the resin is burnt off, it starts s to generate smoke, which is shown in Figure 166.a. The pictures of the specimen after the test are shown in Figure 166.b, which has only remaining carbon fabric.

3.6.1.2. Cone calorimetry test of brominated VER composites.

Composited fabricated by infusion of each formulation of brominated VER material were investigated for their flammability performance similar like the nonbrominated formulations discussed in the previous section. Composite fabricated from all seven formulations Br-CVER to FVER-12 were investigated by cone calorimetry test as shown in Table 41.

Table 41. ASTM E1354 Heat Release Rate Results of C-Fabric Reinforced Composites of Br-GVER.

Sample ID	Time to Ign. (sec)	Flame Duration (sec)	% Mass Loss	Average Effective Heat of Combustion (MJ/kg)	Avg. HRR at 60 sec (kW/m^2)	Avg. HRR at 180 sec (kW/m^2)	Avg. HRR at 300 sec (kW/m^2)	Peak HRR (kW/m^2)	Time of Peak HRR (sec)	Total HRR/A (MJ/m^2)	SEA (m^2/kg)
Carbon Fabric Reinforced Brominated Resin Panel											
Br-CVER-1	99	18	4	4	N/A	N/A	N/A	124	106	2	568
Br-CVER-2	89	353	28	13	110	118	126	146	323	42	1796
Br-CVER-3	93	325	29	12	106	120	129	172	313	40	1823
Average	**91**	**339**	**29**	**13**	**108**	**119**	**128**	**159**	**318**	**41**	**1809**
20% Br-GVER and 80% Derakane 510A-40											
FVER-7-1	126	346	26	13	90	120	124	167	319	39	1849
FVER-7-2	121	326	28	12	91	120	120	168	287	37	1750
FVER-7-3	121	326	26	12	113	115	117	145	332	37	1611
Average	**123**	**333**	**27**	**12**	**98**	**118**	**120**	**160**	**313**	**37**	**1737**
50% Br-GVER and 50% Derakane 510A-40											
FVER-8-1	78	368	28	12	90	102	113	145	340	40	1569
FVER-8-2	78	397	28	13	81	104	113	134	282	39	1894
FVER-8-3	78	380	29	12	72	101	116	147	327	40	1698
Average	**78**	**382**	**28**	**12**	**81**	**102**	**114**	**142**	**316**	**40**	**1720**
80% Br-GVER and 20% Derakane 510A-40											
FVER-9-1	62	377	29	13	80	104	120	166	311	42	1601
FVER-9-2	60	407	30	12	83	99	113	148	331	42	1500
FVER-9-3	59	308	27	12	85	91	99	127	313	37	1579
Average	**60**	**364**	**29**	**12**	**83**	**98**	**111**	**147**	**318**	**40**	**1560**
100% GVER with 40 wt. % of styrene											
FVER-10-1	50	493	30	13	42	82	98	138	328	48	1700
FVER-10-2	73	422	32	12	80	103	115	143	332	44	1562
FVER-10-3	55	452	33	12	73	102	115	150	298	47	1437
Average	**59**	**456**	**32**	**12**	**65**	**96**	**109**	**144**	**319**	**46**	**1566**
100% GVER with 30 wt. % of styrene											
FVER-11-1	90	388	30	11	89	104	113	142	301	39	1248
FVER-11-2	94	407	31	11	79	108	119	153	303	41	1253
FVER-11-3	82	417	27	13	76	99	116	154	283	42	1382
Average	**89**	**404**	**29**	**12**	**81**	**104**	**116**	**150**	**296**	**41**	**1294**
100% GVER with 20 wt. % of styrene											
FVER-12-1	66	262	25	11	92	114	DNR	160	263	31	1073
FVER-12-2	78	241	25	10	89	117	DNR	153	251	28	1115
FVER-12-3	79	251	26	10	98	113	DNR	171	278	30	1094
Average	**74**	**251**	**25**	**11**	**93**	**115**	**DNR**	**161**	**264**	**30**	**1094**

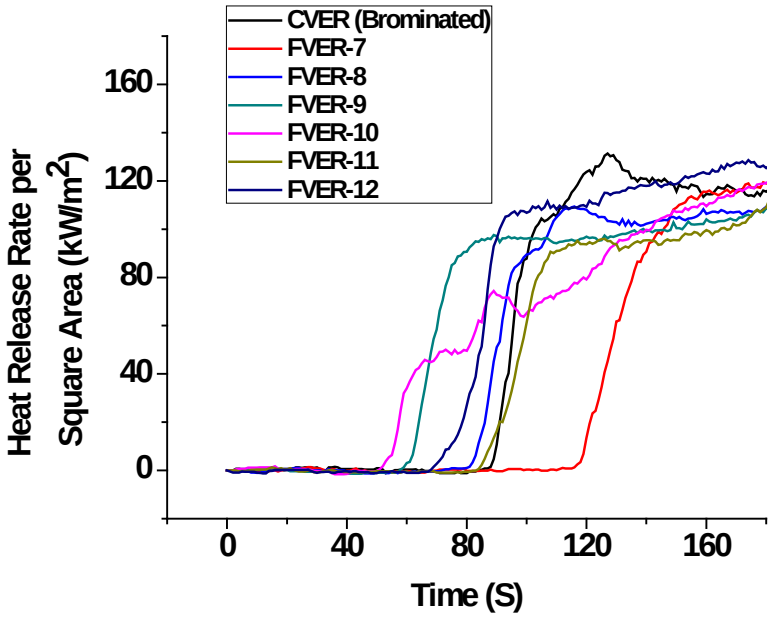


Figure 167. The plot of Heat Release Rate per Unit Area Vs Time of C-Fabric Reinforced Composites of Brominated GVER.

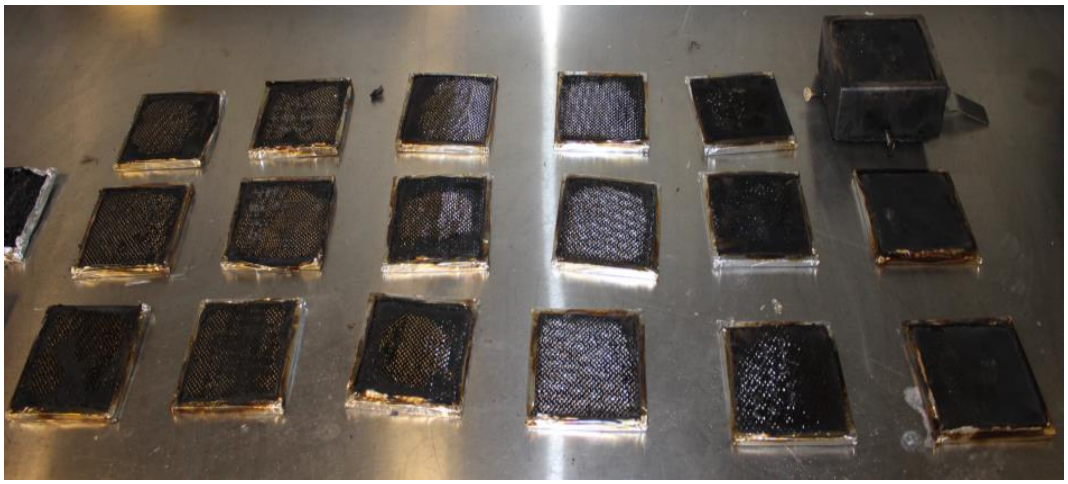


Figure 168. Brominated VER samples after cone calorimetry testing.

As shown in Figure 167, Br-GVER (FVER-10) with 40 wt. % styrene had much lower HRR compared with all other formulation. In addition, Br-GVER, when mixed in part with commercial resin have very long ignition time. This data suggest that Br-GVER has better flammability performance compared with Br-CVER. The composites samples with Br-CVER formulation after the testing are shown in Figure 168.

3.6.1.3. ASTM E-662 Smoke generation and fire gas toxicity.

ASTM E-662 determines the specific optical density of smoke generated by solid materials. It is also called NBS Smoke Chamber Test, which needs six specimens of 3” x 3” x 0.25” thickness.

Description: A 3” x 3” x 0.25” sample is heated using an electrical radiant source which produces an irradiance level of 2.5 W/ cm^2 over the central area of a vertically mounted specimen. The test specimens are exposed to flaming and nonflaming conditions within a closed chamber. A photometric system with a vertical light path is used to measure the varying light transmission as smoke accumulates. The light transmittance measurements are used to calculate the specific optical density of the smoke generated during the test. ASTM E-662 is shown in Figure 169.

Figure 169. Picture of ASTM E-662.

he ASTM E 662 smoke density test method described above is used to measure fire gas toxicity as well. During the test period, the gasses from the smoke chamber are analyzed by Draeger (colorimetric) tubes or Fourier Transform Infra-Red Spectrometer (FTIR). The gasses most commonly analyzed are carbon monoxide, carbon dioxide, hydrogen chloride, and hydrogen cyanide. Other gasses may also be analyzed depending upon the specific composition of the test material.

This test measures light beam attenuation (photometry) due to smoke products using electrical radiant heat. Dräger tubes will be used to determine concentrations of gasses present in the combustion byproducts. The gasses required to be measured are carbon monoxide (CO), carbon dioxide, hydrogen chloride (HCl), hydrogen cyanide (HCN), formaldehyde (HCHO) and nitrogen dioxide (NO_2). The mass of filler material applied to each sample will be documented. All samples will be evaluated in non-flaming and flaming mode.

(a) Smoke density test of nonbrominated VER composites.

Table 42 represents the smoke density test results in flaming and non-flaming conditions. The graphical and pictorial presentation of the smoke density results is shown in Figure 170 and Figure 174.

Table 42. ASTM E662 Results in Flaming and Non-flaming Mode.

Sample ID	Mode of Combustion	D_m	CO (ppm)	CO_2 (%)	HCN (ppm)	HCl (ppm)
Non-Brominated Neat Resin Panels						
1750_1	Non-Flaming	192	187	100	N/D	N/D
1750_2		183	178	100	N/D	N/D
1750_3		205	196	150	N/D	N/D
Average		**193**	**187**	**117**	**N/D**	**N/D**
1750-4	Flaming	>924*	772	1000	1.5	N/D
1750-5		>924*	796	1000	1	N/D
1750-6		>924*	797	1000	1	N/D
Average		**>924***	**788**	**1000**	**1**	**N/D**
C-Fabric reinforced Vinyl Ester Resin						
VER-1	Non-Flaming	25	10	N/D	1	N/D
VER-2		24	10	N/D	0.5	N/D
VER-3		26	10	N/D	1	N/D
Average		**25**	**10**	**N/D**	**1**	**N/D**
VER-4	Flaming	337	100	1	4	N/D
VER-5		447	500	1.5	4	N/D
VER-6		205	500	1	4	N/D
Average		**330**	**367**	**1**	**4**	**N/D**
20 wt. % GVER and 80 wt. % Derakane Momentum 411 350						
FVER-1-4	Flaming	221	500	2	0.5	N/D
Average		**221**	**500**	**2**	**0.5**	**N/D**
50 wt. % GVER and 50 wt. % Derakane Momentum 411 350						
FVER-2-1	Non-Flaming	30	25	N/D	N/D	N/D
FVER-2-2		30	30	N/D	N/D	N/D
FVER-2-2		29	10	N/D	N/D	N/D
Average		**30**	**22**	**N/D**	**N/D**	**N/D**
FVER-2-4	Flaming	152	152	500	3	0.5
FVER-2-5		171	171	500	2	0.5
FVER-2-6		137	137	500	0.5	0.5
Average		**153**	**153**	**500**	**1.8**	**0.5**
80 wt. % GVER and 20 wt. % Derakane Momentum 411 350						
FVER-3-1	Non-Flaming	27	10	N/D	N/D	N/D
FVER-3-2		32	10	N/D	N/D	N/D
FVER-3-2		32	10	N/D	N/D	N/D
Average		**30**	**10**	**N/D**	**N/D**	**N/D**
FVER-3-4	Flaming	127	500	1	0.5	N/D
FVER-3-5		145	500	2	0.5	N/D
FVER-3-6		155	500	1.5	0.5	N/D
Average		**142**	**500**	**1.5**	**0.5**	**N/D**
GVER with 40 wt. % of Styrene						

FVER-4-1	Non-Flaming	34	10	N/D	N/D	N/D
FVER-4-2		36	25	N/D	N/D	N/D
FVER-4-2		34	25	N/D	N/D	N/D
Average		**35**	**20**	**N/D**	**N/D**	**N/D**
FVER-4-4	Flaming	132	500	0.5	1	N/D
FVER-4-5		163	500	2	0.5	N/D
FVER-4-6		156	500	0.5	0.5	N/D
Average		**150**	**500**	**1.0**	**0.7**	**N/D**
GVER with 30 wt. % of Styrene						
FVER-5-1	Non-Flaming	29	10	N/D	N/D	N/D
FVER-5-2		29	20	N/D	N/D	N/D
FVER-5-3		31	30	N/D	N/D	N/D
Average		**30**	**20**	**N/D**	**N/D**	**N/D**
FVER-5-4	Flaming	167	500	0.5	0.5	N/D
FVER-5-5		135	500	0.5	0.5	N/D
FVER-5-6		92	500	0.5	1	N/D
Average		**131**	**500**	**0.5**	**0.7**	**N/D**
GVER with 20 wt. % of Styrene						
FVER-6-1	Non-Flaming	32	Trace	N/D	N/D	N/D
FVER-6-2		84	10	N/D	N/D	N/D
FVER-6-3		92	10	N/D	N/D	N/D
Average		**69**	**10**	**N/D**	**N/D**	**N/D**
FVER-6-4	Flaming	597	500	0.5	1	0.5
FVER-6-5		623	500	0.5	0.5	0.5
FVER-6-6		650	500	0.5	0.5	0.5
Average		**623**	**500**	**0.5**	**0.7**	**0.5**
Carbon Fabric Reinforced Non-Brominated Resin Panels (NAVAIR)						
1760-1	Non-Flaming	16	16	10	N/D	0.5
1760-2		27	27	10	N/D	1
1760-3		14	14	10	N/D	1
Avg.		**19**	**19**	**10**	**N/D**	**1**
1760-4	Flaming	205	201	500	1	2
1760-5		343	335	500	1.5	2
1760-6		366	353	500	1	3
Avg.		**305**	**296**	**500**	**1.2**	**2**

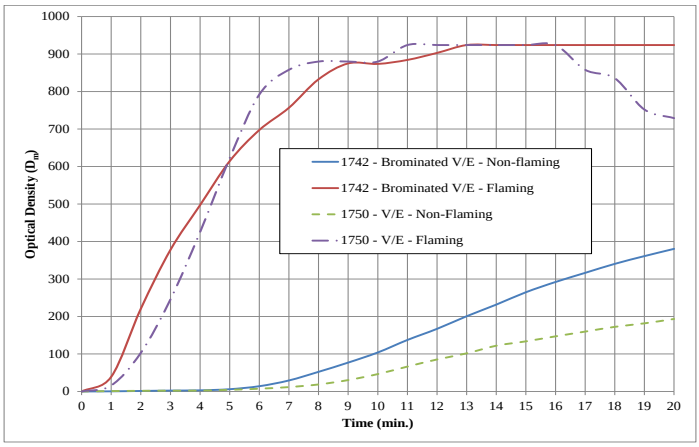


Figure 170. ASTM E662 – Average Optical Density Plot of (a) neat resin panels (UML).

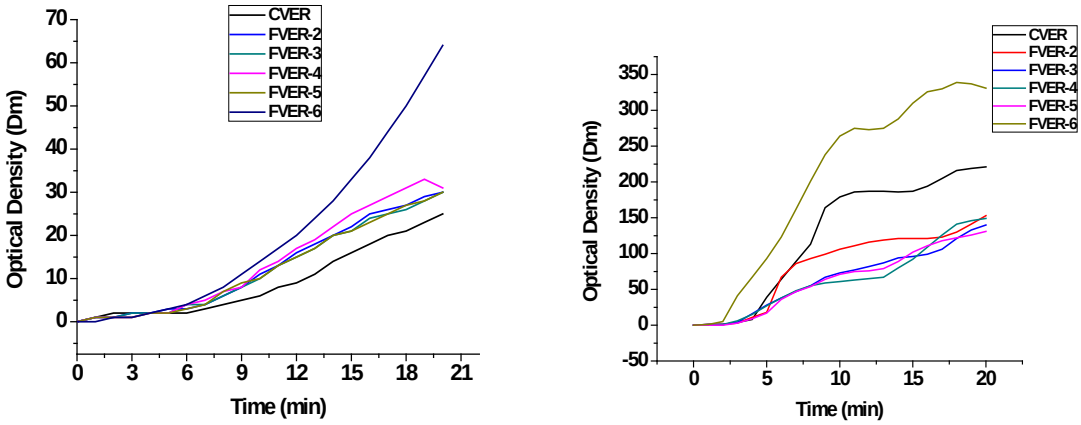


Figure 171. ASTM E662 – Average Optical Density Plot in (a) Non-Flaming Mode and (b) Flaming Mode of C-Fabric Reinforced Composites of Nonbrominated GVER.

All brominated neat coupon optical density plots are shown in Figure 170, whereas, the optical density plots of the carbon fiber reinforced composites of the nonbrominated resin formulation are shown in Figure 171.

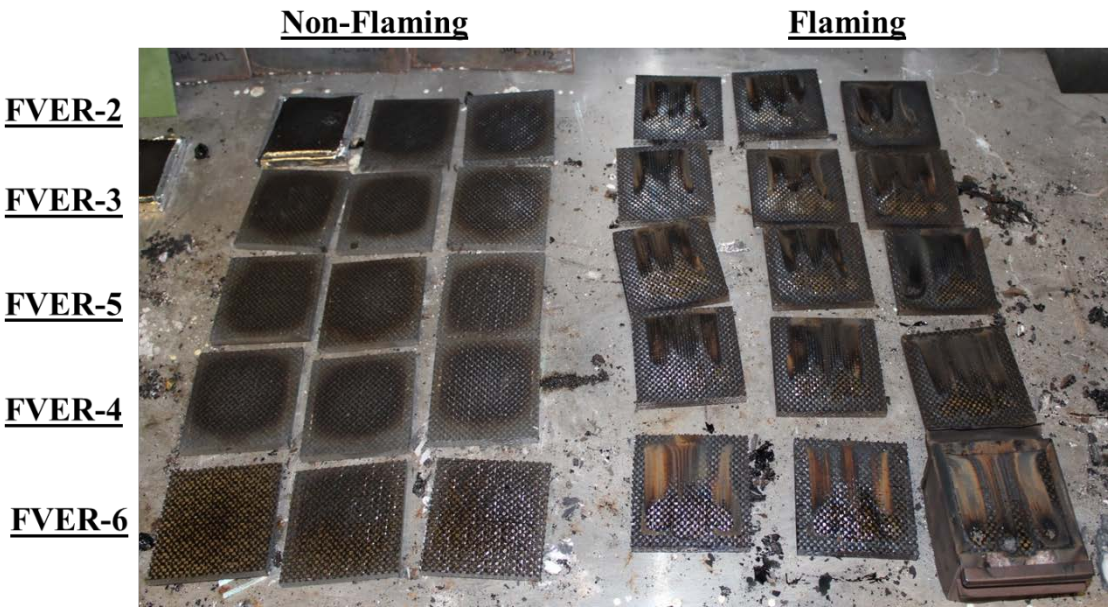


Figure 172. ASTM E662 Smoke Density Test Sample After Testing.

The specimen after the smoke density test in flaming and nonflamming mode are shown in Figure 172.

(b) Smoke density test of brominated VER composites.

Table 43 represents the smoke density test results in flaming and non-flaming conditions. The graphical and pictorial presentation of the smoke density results is shown in Figure 173. The FVER-7 exhibited the best optical density compared with all other formulations in nonflamming mode.

Table 43. Smoke Density and Toxicity Data in Flaming and Non-Flaming Mode

Sample ID	Mode of Combustion	D_m	CO (ppm)	CO_2 (%)	HCN (ppm)	HCl (ppm)
Brominated resin neat coupon						
1742_1	Non-Flaming	409	N/R	300	Trace	Trace
1742_2		359	N/R	100	Trace	Trace
1742_3		373	N/R	300	N/D	Trace
Average		**380**	**N/R**	**233**	**Trace**	**Trace**
1742-4	Flaming	>924*	N/R	1000	2	0.5
1742-5		>924*	899	2500	1	0.5
1742-6		>924*	891	2000	0.5	Trace
Average		**>924***	**895**	**1833**	**1.17**	**0.5**
C-Fabric Reinforced Derakane 510-40A						
Br-VER-1	Non-Flaming	102	10	N/D	1	0.2
Br-VER-2		122	10	N/D	1	0.2
Br-VER-3		178	10	N/D	1	0.2
Average		**134**	**10**	**N/D**	**1**	**0.2**
Br-VER-4	Flaming	655	100	0.5	2	Trace
Br-VER-5		620	250	0.5	2	Trace
Br-VER-6		401	100	Trace	2	Trace
Average		**559**	**150**	**0.5**	**2**	**Trace**
20 wt. % Br-GVER and 80 wt. % Derakane 510-40A						
FVER-7-1	Non-Flaming	32	Trace	N/D	N/D	N/D
FVER-7-2		84	10	N/D	N/D	N/D
FVER-7-3		92	10	N/D	N/D	N/D
Average		**69**	**10**	**N/D**	**N/D**	**N/D**
FVER-7-4	Flaming	597	500	0.5	1	0.5
FVER-7-5		623	500	0.5	0.5	0.5
FVER-7-6		650	500	0.5	0.5	0.5
Average		**623**	**500**	**0.5**	**0.7**	**0.5**
50 wt. % Br-GVER and 50 wt. % Derakane 510-40A						
FVER-8-1	Non-Flaming	82	10	N/D	Trace	Trace
FVER-8-2		132	50	N/D	Trace	Trace
FVER-8-3		132	50	N/D	Trace	Trace
Average		**115**	**37**	**N/D**	**Trace**	**Trace**
FVER-8-4	Flaming	646	1000	0.5	Trace	1
FVER-8-5		593	1000	0.5	Trace	1
FVER-8-6		650	1500	0.5	Trace	1
Average		**630**	**1167**	**0.5**	**Trace**	**1**
80 wt. % Br-GVER and 20 wt. % Derakane 510-40A						
FVER-9-1	Non-Flaming	165	75	N/D	Trace	Trace
FVER-9-2		164	50	N/D	Trace	Trace
FVER-9-3		132	50	N/D	Trace	Trace
Average		**154**	**58**	**N/D**	**Trace**	**Trace**
FVER-9-4	Flaming	557	1000	0.5	0.5	1

FVER-9-5		578	500	0.5	N/D	1
FVER-9-6		581	1000	0.5	N/D	1
Average		**572**	**833**	**0.5**	**0.5**	**1**
Br-GVER with 40 wt. % of Styrene						
FVER-10-1	Non-Flaming	164	50	N/D	Trace	1
FVER-10-2		183	50	N/D	Trace	2
FVER-10-3		157	50	N/D	Trace	1
Average		**168**	**50**	**N/D**	**Trace**	**1**
FVER-10-4	Flaming	561	1000	0.5	N/D	Trace
FVER-10-5		583	1500	0.5	N/D	Trace
FVER-10-6		603	1000	0.5	N/D	Trace
Average		**582**	**1167**	**0.5**	**#DIV/0!**	**N/D**
Br-GVER with 30 wt. % of Styrene						
FVER-11-1	Non-Flaming	155	10	N/D	N/D	4
FVER-11-2		163	100	N/D	N/D	10
FVER-11-3		178	100	N/D	N/D	10
Average		**165**	**70**	**N/D**	**N/D**	**8**
FVER-11-4	Flaming	641	100	0.5	Trace	Trace
FVER-11-5		645	500	0.5	Trace	1
FVER-11-6		607	500	0.5	Trace	2
Average		**631**	**367**	**0.5**	**Trace**	**2**
Br-GVER with 20 wt. % of Styrene						
FVER-12-1	Non-Flaming	148	100	N/D	Trace	6
FVER-12-2		89	50	N/D	Trace	Trace
FVER-12-3		172	50	N/D	Trace	1
Average		**136**	**67**	**N/D**	**Trace**	**4**
FVER-12-4	Flaming	597	750	0.5	0.5	4
FVER-12-5		592	500	0.5	0.5	4
FVER-12-6		552	500	0.5	0.5	4
Average		**580**	**583**	**0.5**	**0.5**	**4.0**
C-Fabric Reinforced Derakane 510-40A (NAVAIR)						
1763-1	Non-Flaming	132	125	50	N/D	1
1763-2		46	45	10	N/D	0.5
1763-3		84	80	10	N/D	0.5
Avg.		**87**	**83**	**23**	**N/D**	**1**
1763-4	Flaming	680	647	2000	1.5	Trace
1763-5		713	701	2000	1.5	Trace
1763-6		924	901	2000	1.5	Trace
Avg.		**772**	**750**	**2000**	**1.5**	**Trace**

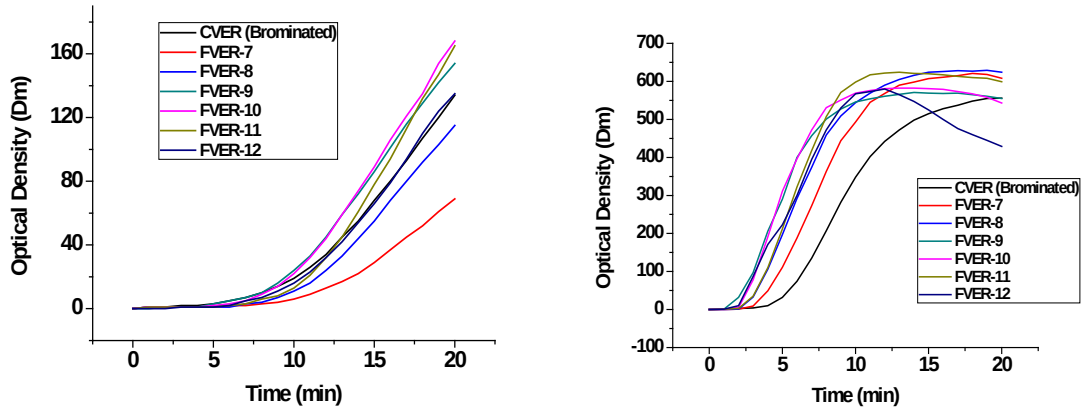


Figure 173. ASTM E662 – Average Optical Density Plot in (a) Non-Flaming Mode and (b) Flaming Mode of C-Fabric Reinforced Composites of Brominated GVER.

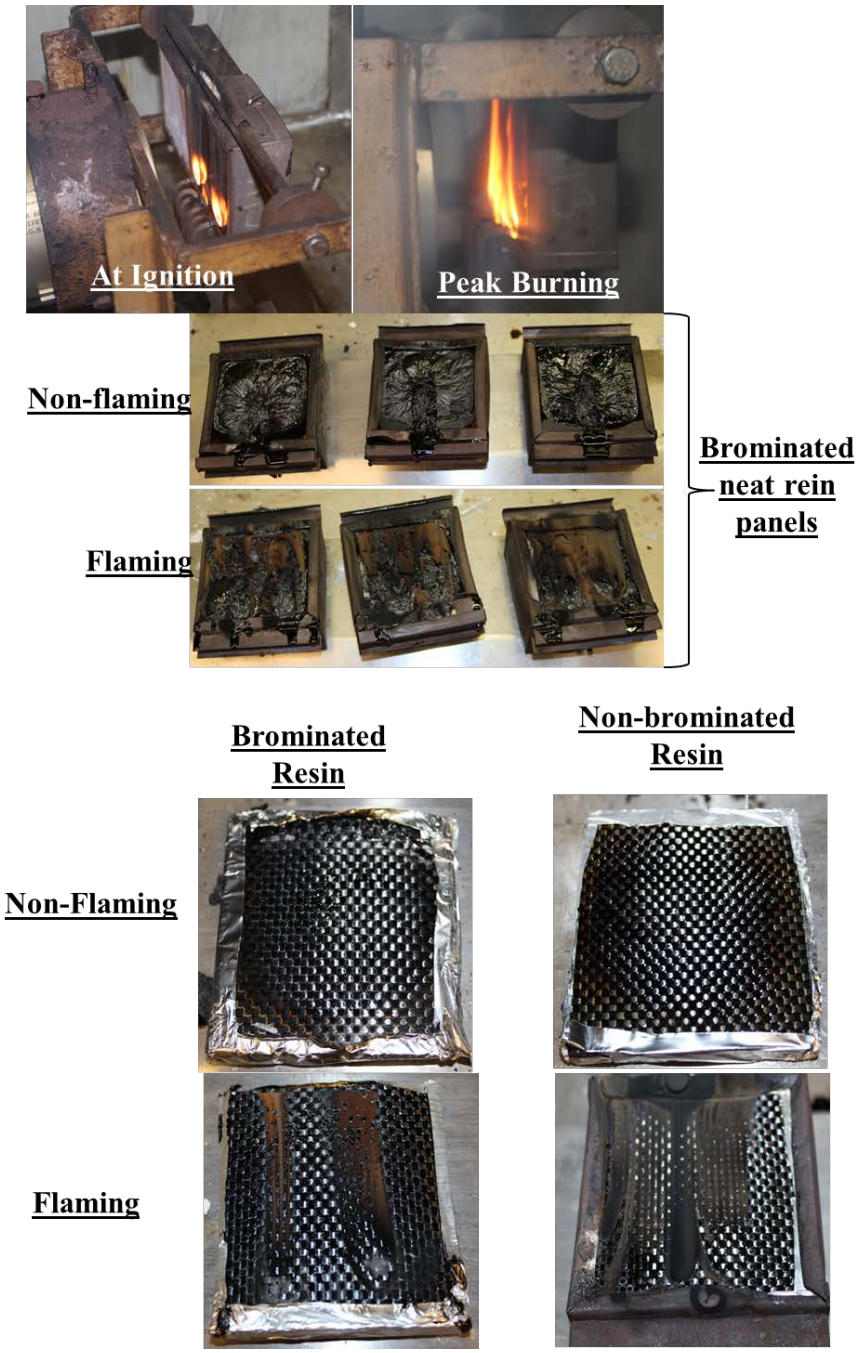


Figure 174. Brominated neat resin panels and carbon fabric reinforced brominated and non-brominated resin coupons after testing smoke density testing.

Figure 174 shows the sample subjected to test under flaming and nonflamming mode. The specimen after the smoke density test in flaming and nonflamming mode are shown.

3.6.2. Mechanical testing.

We have performed different kinds of mechanical testing on neat resin as well as carbon fabric reinforced panels of all formulated resins. We mainly performed (a) tensile testing on VER and Br-VER composite specimen and on neat VER and Br-VER specimen, (b) flexure testing (three point bend) on VER and Br-VER composite specimen and on neat VER and Br-VER specimen, and (c) short beam strength test on VER and Br-VER composite specimen.

The composites were assessed for their tensile, flexural and short beam shear properties. Tensile testing was performed to ASTM D3039, with specimens having a 2.54 mm thickness and 125 mm gauge length. The tensile specimens were tested using an Instron 1332 with a 90kN load cell and strain gauge voltage and resistance data were collected (Agilent 34970A and Agilent 34902A). Flexural and short beam shear properties were tested per ASTM D7264 and ASTM D2344, respectively, using an Instron 8511 servo-hydraulic testing machine with a 20 kN load cell. Flexural specimens had a 3.55 mm thickness and a span-to-thickness ratio of 20:1. Short beam strength specimens had a 6.35 mm thickness. A total of three specimens were tested per test condition.

3.6.2.1. Tensile Testing (ASTM D3039):

For tensile testing, the specimen were prepared using VARTM technique. Specimens were made up of 10” X 1” X 0.10” in dimension using 12 plies of Carbon Fiber. 6” Gauge length was applied. During tensile testing, machine compliance was an issue in strain measurement. So, samples were tested again with strain gauges attached. explained about the detailed size of each specimen of VER and Br-VER’s carbon fabric reinforced composites.

Figure 175. Setup for tensile testing of VER and Br-VER composite specimens.

Tensile testing is used to analyze a controlled tension until failure. Based on the results of tensile testing, various applications of materials are selected and the material's compatibility with other material determined. During tensile test, we can also get ultimate tensile strength, maximum elongation, and reduction in area. We can also determine Young's modulus, Poisson's ratio, yield strength, and strain-hardening characteristics.

The equipment for the tensile test is shown in Figure 175. The commonly used machine for tensile testing is the universal testing machine, which has two crossheads; one is adjusted for the length of the specimen and the other is driven to apply tension to the test specimen.

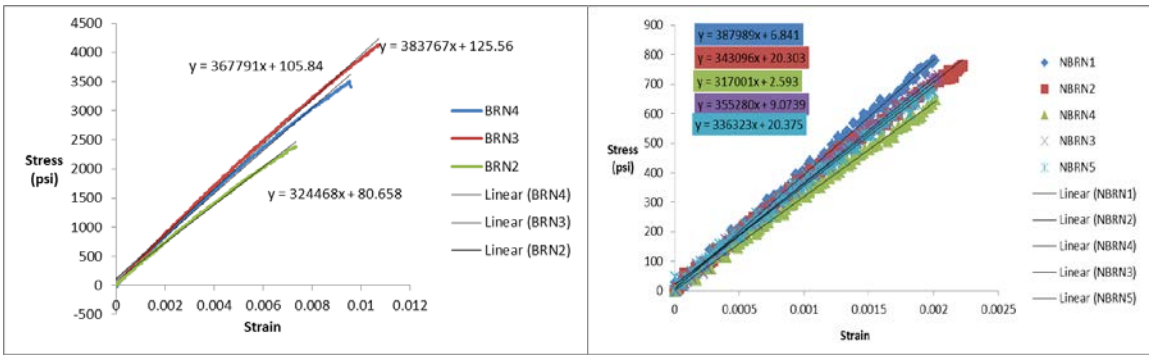


Figure 176. Stress vs. Strain of (a) Br-VER and (b) VER neat resin specimens.

The stress vs strain data of the neat VER and Br-VER panels are shown in Figure 176 and their elastic modulus and tensile strength are discussed in Table 44, which suggested that both materials exhibited similar properties.

Table 44. Elastic modulus and tensile strength of neat CVER and Br-CVER specimen.

Neat Br-CVER specimen				
Sample	Elastic Modulus		Tensile Strength	
	E		UTS	
	psi	MPa	psi	MPa
BRN 4	367791	2535	3500	24
BRN 3	383767	2645	4135	28
BRN 2	324468	2237	2388	16
AVERAGE	358000 ± 30000	2500 ± 200	3300 ± 800	23 ± 6
Neat CVER specimen				
NBR-N1	387989	2675	4694	32
NBR-N2*	343096	2365	1170	8
NBR-N3*	355280	2450	1799	12
NBR-N4	317001	2186	4574	31.5
NBR-N5*	336323	2319	1792	12

AVERAGE	348000 ± 24000	2400 ± 162	4630 ± 60	31.8 ± 0.3

*** Potential Outliers because of low failure**

The neat data does not match the data sheets provided by Ashland very well. This could be due to the geometry of the specimens and the method using which they were manufactured. The specimens were manufactured in an open mold due to time constraints. This meant the likelihood of shrinkage was greater and caused a meniscus to form on one surface of the neat specimens. This could have led to the specimens having built in stress concentrations. In addition, the specimen dimensions could have been measured to be falsely thicker than what they actually were because of the presence of the meniscus.

Strain gages were attached to each of the composite specimens prior to testing. These strain gages were then wired to the 39470A Data Logger to generate voltage and resistance data during the test. This data was then reduced to obtain stress and strain values. This was not done for the neat specimens because the loads were assumed to be small enough for machine compliance to be irrelevant. Instead, we obtained load and displacement values from the Instron Testing machine. However, this could have been a mistaken assumption. In future, we will attempt to keep the stress-strain methodology consistent across all types of samples.

The tensile testing on C-Fabric reinforced composites of the FVER-1 was performed to compare its strength and modulus with the composites prepared using only Derakane resin. Composites with formulated resin exhibited higher tensile modulus and slight lower tensile strength compared with composites of pure Derakane as shown in Figure 176. It suggests that addition of 20 wt. % GVER to Derakane is improving tensile properties of the resin.

The tensile testing on C-Fabric reinforced composites of the formulate GVER was performed to compare its strength and modulus with the composites prepared using Derakane resin as shown in Table 45. We have prepared samples for GVER with different weight % of styrene content and analyzed their tensile strength and modulus. Composites with formulated resin exhibited similar tensile modulus and tensile strength compared with composites of pure Derakane as shown in Figure 177. The VER with different amount of green resin and commercial resin almost have similar tensile properties. We have not demonstrated samples until their failure, as the sample were prepared with the intention to show the tightness properties of the green resin with the commercial material. The tensile strength and tensile modulus of the composites remained almost same upon mixing commercial resin with green resin in a different amount or by even reducing the amount of styrene in pure green resin. The stress vs. strain profile of Br-VER and VER composites that describes the ultimate tensile strength, elastic modulus and strain to failure data of the both VER and Br-VER composite specimen. To investigate the tensile properties of neat resin material the panels were manufactured using open faced silicone molds. The tensile properties were measured using ASTM D638 and 4.5” Gauge Length. The dimensions of each specimen of VER and Br-VER neat resin panels has average width ~ 0.518 and 0.511, and thickness of 0.129 and 0.131, respectively.

Table 45. Tensile Properties of C-Fabric Reinforced Composites of Formulated Non-brominated GVER

Specimen	Tensile Strength (MPa)	Tensile Modulus (GPa)
	Derakane Momentum 411-350	
CVER-1	736	55.3
CVER-2	635	52.3
CVER-3	459	52.3
CVER-4	702	53.2
Average	691 ± 41	53 ± 1.2
	20 wt. % GVER and 80 wt. % Derakane Momentum 411 350	
FVER-1-1	671	65.4
FVER-1-2	651	58.9
FVER-1-3	686	59.8
Average	669 ± 14.3	61.4 ± 2.9
	50 wt. % GVER and 50 wt. % Derakane Momentum 411 350	
FVER-2-1	665	59.2
FVER-2-2	714	59.8
FVER-2-3	669	62.5
Average	683 ± 22	60.5 ± 1.4
	80 wt. % GVER and 20 wt. % Derakane Momentum 411 350	
FVER-3-1	709	57.4
FVER-3-2	695	63.6
FVER-3-3	648	58.2
Average	684 ± 26	59.7 ± 2.8
	GVER with 40 wt. % of Styrene	
FVER-4-1	658	58.2
FVER-4-2	655	58.1
FVER-4-3	730	60.7
Average	681 ± 35	59 ± 1.2
	GVER with 30 wt. % of Styrene	
FVER-5-1	676	55.9
FVER-5-2	718	59.1
FVER-5-3	681	58.6
Average	692 ± 18.9	57.9 ± 1.4
	GVER with 20 wt. % of Styrene	
FVER-6-1	576	50.3
FVER-6-2	553	53.6
FVER-6-3	544	53.1
Average	558 ± 13.5	52.3 ± 1.8

Similarly, we have prepared different formulation of brominated resin with different amount of styrene and commercial Derakane resin as shown in Table 46. The test of tensile strength and tensile modulus of such composites has been performed as shown in Figure 177. The tensile strength of the brominated GVER remained almost same upon mixing commercial resin with green resin in different amount or by even reducing the amount of styrene in pure green resin.

However, a sharp increase in tensile modulus was observed as amount of styrene decreased in the brominated green VER. The composites of Br-GVER with 20 wt. % of styrene exhibited tensile modulus of ~75 GPa.

Table 46. Tensile Properties of C-Fabric Reinforced Composites of Formulated Brominated GVER.

Specimen	Tensile Strength (MPa)	Tensile Modulus (GPa)
	C-Fabric Reinforced Derakane 510 40A	
Br-CVER-1	762	52.0
Br-CVER-2	751	47.5
Br-CVER-3	598	56.1
Average	704 ± 74	52 ± 3.5
	20 wt. % Br-GVER and 80 wt. % Derakane 510 40A	
FVER-7-1	702	65.4
FVER-7-2	754	58.9
FVER-7-3	690	59.8
Average	715 ± 26	61.4 ± 2.9
	50 wt. % Br-GVER and 50 wt. % Derakane 510 40A	
FVER-8-1	785	69.6
FVER-8-2	830	79.3
FVER-8-3	797	76.5
Average	804 ± 19	75.2 ± 1.4
	80 wt. % Br-GVER and 20 wt. % Derakane 510 40A	
FVER-9-1	653	58.0
FVER-9-2	781	71.7
FVER-9-3	685	65.1
Average	706 ± 54	64.9 ± 5.6
	Br-GVER with 40 wt. % of Styrene	
FVER-10-1	670	57.1
FVER-10-2	747	59.3
FVER-10-3	780	64.7
Average	733 ± 46	60.4 ± 3.2
	Br-GVER with 30 wt. % of Styrene	
FVER-11-1	730	86.2
FVER-11-2	735	64.1
FVER-11-3	730	71.7
Average	732 ± 2	74.0 ± 9.2
	Br-GVER with 20 wt. % of Styrene	
FVER-12-1	714	80.7
FVER-12-2	705	70.3
FVER-12-3	723	75.2
Average	714 ± 7	75.4 ± 4.2

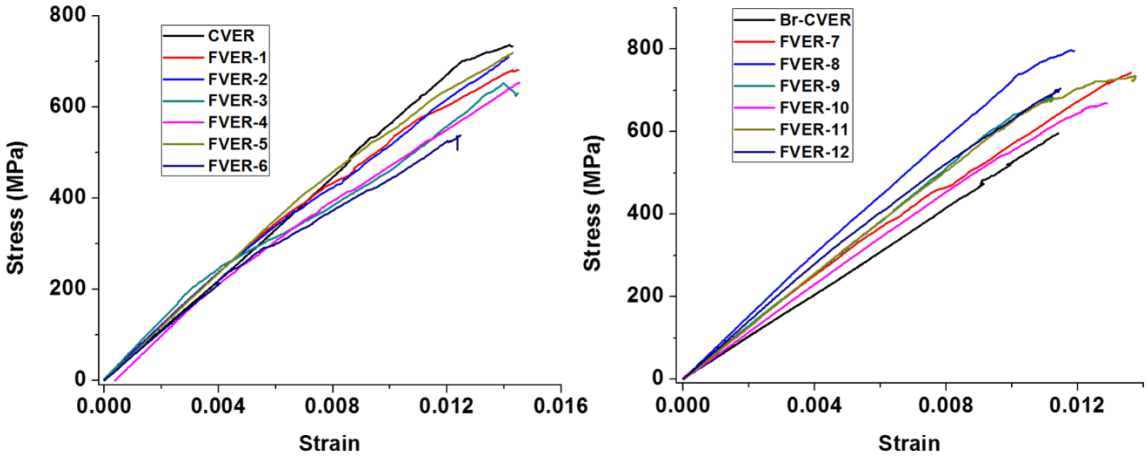


Figure 177. Stress vs. Strain Plot for C-Fabric Reinforced Composites of Non-brominates /Brominates Resin Made-up Using different formulations.

The vinyl ester prepolymer is monodisperse (polydispersity index (PDI) = 1.0) with low molecular weight (MW = 512.60 g mol^{-1}). Within polydisperse systems, the polymer fraction with higher molecular weights dominates the melt viscosity either as $\eta \propto M^2$ or $\eta \propto M^{3.4}$ if below or above the entanglement molecular weight, respectively. La Scala et al. have reported power-law exponents as high as 5 to 10 due to interactions with the styrene monomer. As compared to the typical polydispersity PDI ~ 2 for commercial polyester resins, the monodisperse vinyl ester prepolymer possesses a significantly lower viscosity than commercial polyesters.

Resin infusion times during composites processing is directly related to the formulation viscosity, which is typical ~500 cps. Commercial resins commonly contain 40-50 wt. % of the reactive diluent styrene to achieve this viscosity range; the baseline commercial resin was chosen for this project – Derakane Momentum 411-350 – is a BPA-based vinyl ester resin that contains 40 wt. % styrene.

The large vinyl ester resin market and the difficulties of quickly scaling bio-sourced production make it imperative to investigate resin blends of bio-sourced and traditional petroleum-based materials. The GVER formulated with 40 wt. % of styrene was blended with the commercial resin Derakane Momentum 411-350 in ratios of 20 to 80 wt. % for structural equivalence testing.

3.6.2.2. Flexure Testing.

We have investigated flexure testing of brominated & non-brominated composite specimens. The flexural test was analyzed using ASTM D790, which is also called three-point bend test. In the main parameter for testing: the span length: thickness ratio = 20:1, span length for brominated carbon fiber = 2.70”, span length for non-brominated carbon fiber = 3.60”, specimen dimensions is 5” x 0.5” x 0.16”.

Flexural strength is also known as modulus of rupture, bend strength, or fracture strength. It is used to be defined as a material's ability to resist deformation under load. In the test, a specimen having either a circular or rectangular cross-section is bent until fracture or yielding takes place. The flexural strength represents the highest stress experienced within the material at its moment of rupture. It is measured in terms of stress. The specimen dimensions for the flexural testing are of the VER and Br-VER's carbon fabric based composite had an average width of 0.502 and 0.406, and thickness of 0.181 and 0.1358 respectively. The setup for the flexural testing is described in Figure 178.

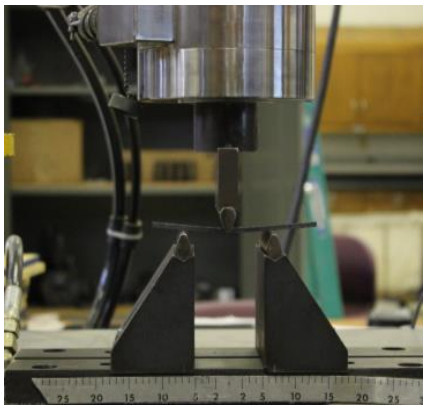


Figure 178. Loading of VER and Br-VER specimens for flexure testing.

We have investigated neat brominated & non-brominated specimen for their flexure testing. The material was investigated following ASTM D790. In the main parameter of the three-point bend test: the span length: thickness ratio = 20:1, span length: 2.7", and specimen dimensions were 5" x 0.5" x 0.16". The specimen dimensions of the VER and Br-VER samples have an average width of 0.497 and 0.496, and thickness of 0.121 and 0.134 respectively. The specimens of the neat Br-VER for flexural testing are shown in Figure 179. The specimen is slightly yellowish in color due to the nature of Br-VER.

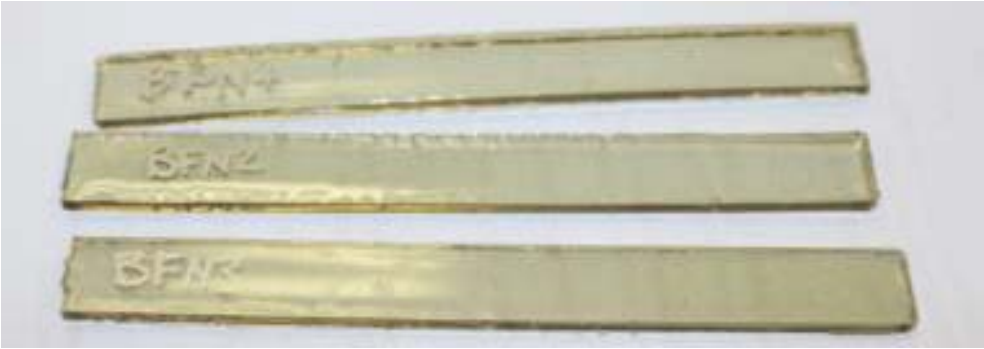


Figure 179. A specimen of near Br-VER for flexure testing.

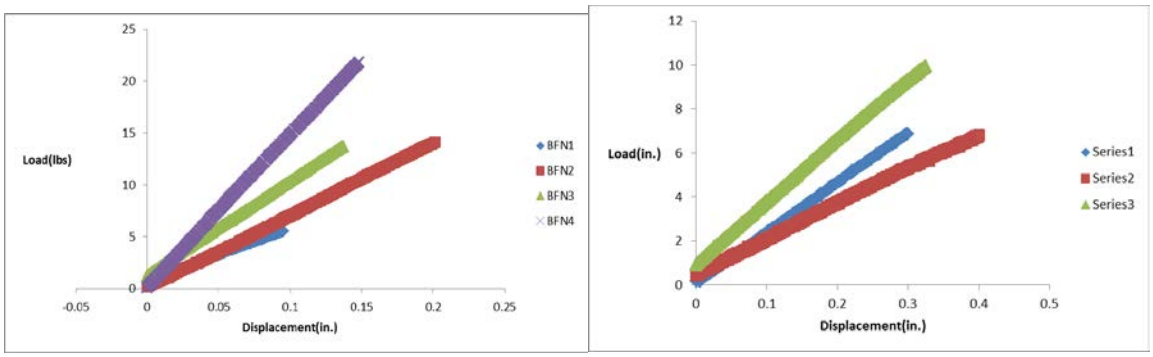


Figure 180. Load vs. Displacement of VER and Br-VER neat resin samples.

The load vs displacement plots of VER and Br-VER neat resin samples are shown in Figure 180. The flexural strength and flexural modulus of the VER and Br-VER neat resin are discussed in Table 47.

Table 47. Flexural modulus and strength of neat VER and Br-VER specimens.

Br-VER neat resin specimen				
Sample	Flexural Modulus (Brominated Neat) E		Flexural Strength (FS)	
	psi	MPa	psi	MPa
1	257525	1775	1452	10
2	384167	2648	2835	16
3	396744	2735	3238	22
4	397229	2738	3760	26
AVERAGE	393000 ± 6000	2700 ± 42	3300 ± 380	21 ± 4
VER neat resin specimen				
1	340587	2348	4792	33
2	193467	1333	3173	22
3	354809	2446	4741	33
AVERAGE	±	±	±	±

The flexural testing on C-Fabric reinforced composites of the formulated nonbrominated GVER was performed to compare its strength and modulus with the composites prepared using only Derakane resin. Composites with formulated resin exhibited similar flexural modulus and flexural strength compared with composites of pure Derakane. FVER-2 with 50 wt. % of GVER exhibited slightly higher flexural modulus and strength compared with commercial resin. FVER-3 with 80 wt. % GVER had poor flexural strength and modulus compared with commercial resin. Similarly, the GVER with 40 wt. % styrene had the lower flexural strength and flexural modulus. GVER with 30 wt. % of styrene had similar flexural performance compared with commercial resin. The flexural property of FVER-6 that is 20 wt. % Br-GVER and 80 wt. % of Derakane 510 40A

was similar to 100 % commercial resin as shown in Table 48. Flexural Properties of C-Fabric Reinforced Composites of Formulated GVER..

Table 48. Flexural Properties of C-Fabric Reinforced Composites of Formulated GVER.

Specimen	Flexural Strength (MPa)	Flexural Modulus (GPa)
Derakane Momentum 411-350		
VER-1	410	32.4
VER-2	420	35.4
VER-3	424	33.0
VER-4	428	35.1
VER-5	428	34.4
Average	422 ± 8	34.1 ± 1.3
20 wt. % GVER and 80 wt. % Derakane Momentum 411 350 (Retested)		
FVER-1-1	381	49.8
FVER-1-2	419	49.0
FVER-1-3	395	50.3
Average	398 ± 15	49.7 ± 0.54
50 wt. % GVER and 50 wt. % Derakane Momentum 411 350		
FVER-2-1	435	52
FVER-2-2	471	46.1
FVER-2-3	432	50.3
Average	446 ± 17.7	49.5 ± 2.48
80 wt. % GVER and 20 wt. % Derakane Momentum 411 350		
FVER-3-1	257	46.5
FVER-3-2	257	45.2
FVER-3-3	275	47.5
Average	263 ± 8.5	46.4 ± 0.94
GVER with 40 wt. % of Styrene		
FVER-4-1	186	46.7
FVER-4-2	181	45.1
FVER-4-3	202	41.9
Average	189.6 ± 8.96	44.6 ± 2.0
GVER with 30 wt. % of Styrene		
FVER-5-1	409	52
FVER-5-2	327	50.1
FVER-5-3	352	47.2
Average	362.7 ± 34.3	49.8 ± 1.97
GVER with 20 wt. % of Styrene		
FVER-6-1	397	61.6
FVER-6-2	360	65.9
FVER-6-3	361	62.3
Average	373 **± 17.4**	63.3 **± 1.9**

Table 49. Flexural Properties of C-Fabric Reinforced Composites of Formulated Br-GVER.

Specimen	Flexural Strength (MPa)	Flexural Modulus (GPa)
C-Fabric Reinforced Derakane 510 40A		
Br-CVER-1	406	45.4
Br-CVER-2	472	58.0
Br-CVER-3	422	48.6
Br-CVER-4	368	45.8
Br-CVER-5	388	48.4
Average	412 ± 36	49 ± 4.5
20 wt. % Br-GVER and 80 wt. % Derakane 510 40A		
FVER-7-1	335	45.3
FVER-7-2	341	48.8
FVER-7-3	362	49.5
Average	346 ± 11.6	47.9 ± 1.84
50 wt. % Br-GVER and 50 wt. % Derakane 510 40A		
FVER-8-1	518	56.8
FVER-8-2	609	60.2
FVER-8-3	589	58.5
Average	572 ± 40.0	58.5 ± 1.38
80 wt. % Br-GVER and 20 wt. % Derakane 510 40A		
FVER-9-1	529	56.7
FVER-9-2	503	56.5
FVER-9-3	568	55.6
Average	533 ± 26.6	56.3 ± 0.46
Br-GVER with 40 wt. % of Styrene		
FVER-10-1	545	59.4
FVER-10-2	616	57.4
FVER-10-3	535	56.8
FVER-10-4	608	60.6
FVER-10-5	508	56.1
Average	562 ± 42.2	58.1 ± 1.68
Br-GVER with 30 wt. % of Styrene		
FVER-11-1	474	57.2
FVER-11-2	423	54.5
FVER-11-3	456	58.1
FVER-11-4	493	55.9
Average	461.3 ± 25.8	56.4 ± 1.37
Br-GVER with 20 wt. % of Styrene		
FVER-12-1	651	64.5
FVER-12-2	601	58.4
FVER-12-3	579	64.1
FVER-12-4	565	58.4

Average	599 ± 32.5	61.3 ± 2.95

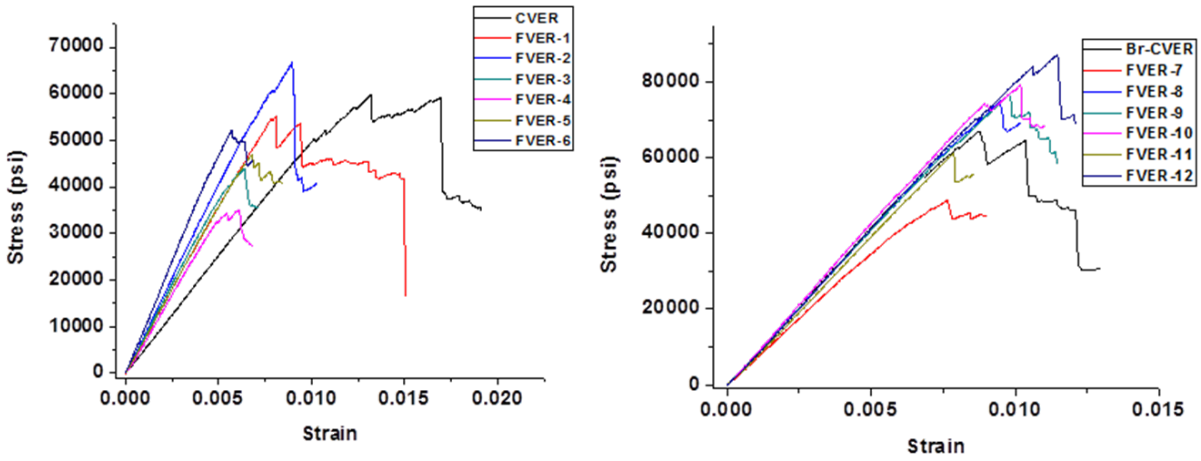


Figure 181. Stress vs. Strain Plot for Flexural Testing C-Fabric Reinforced Composites of Brominates Resin

The flexural property of FVER-6 that is 20 wt. % Br-GVER and 80 wt. % of Derakane 510 40A was similar to 100 % commercial resin. The VER and Br-VER data for the composite specimens turned out to be very similar with the exception of the flexural modulus. This could be due to the fact that the region of the plate from which the specimens were extracted from the non-brominated specimen had a lower fiber volume fraction. Similarly, we have prepared a different formulation of brominated resin with a different amount of styrene and commercial resin. The flexural strength and flexural modulus of such composites have been prepared as shown in Figure 181 and Table 49. The tensile strength of the brominated GVER remained almost same upon mixing commercial resin with green resin in a different amount or by even reducing the amount of styrene in pure green resin.

3.6.2.3. Short-Beam Strength Testing.

Short beam strength testing was performed on VER and Br-VER composite specimens following ASTM D2344. In the testing the span length was 1” and the targeted specimen dimensions was 1.5” x 0.5” x 0.25”.

Figure 182. Short-Beam Strength Testing (Brominated & Non-Brominated Composite Specimens).

The short beam strength testing equipment is shown in Figure 182. The VER and Br-VER's carbon fabric composite's short beam shear strength test data are discussed in Table 50 and Table 51. Both material VER and Br-VER's composite exhibited similar laminate properties during short beam shear strength testing. The flexural testing on C-Fabric reinforced composites of the Derakane/GVER 80/20 was performed to compare its strength and modulus with the composites prepared using only Derakane resin. Composites with formulated resin exhibited higher flexural modulus and flexural strength compared with composites of pure Derakane as shown in Error! Reference source not found.**.** It suggests that addition of 20 wt. % GVER to Derakane is improving flexural properties of the resin significantly.

Table 50. Short Beam Shear Strength of C-Fabric Reinforced Composites of Formulated GVER.

Specimen	Short Beam Shear Strength (MPa)
Derakane Momentum 411-350	
CVER-1	36
CVER-2	30
CVER-3	28
CVER-4	33
CVER-5	27
Average	32 ± 3
20 wt. % GVER and 80 wt. % Derakane Momentum 411 350	
FVER-1-1	31.6
FVER-1-2	28.5
FVER-1-3	33.7
FVER-1-4	33.6
FVER-1-5	30.5
Average	31.6 ± 1.96

50 wt. % GVER and 50 wt. % Derakane Momentum 411 350	
FVER-2-1	36.1
FVER-2-2	34.6
FVER-2-3	35
Average	35 ± 0.63
80 wt. % GVER and 20 wt. % Derakane Momentum 411 350	
FVER-3-1	22.6
FVER-3-2	22.7
FVER-3-3	25.8
Average	23.7 ± 1.5
GVER with 40 wt. % of Styrene	
FVER-4-1	18.2
FVER-4-2	18.2
FVER-4-3	19.1
Average	18.5 ± 0.42
GVER with 30 wt. % of Styrene	
FVER-5-1	27.8
FVER-5-2	32.4
FVER-5-3	32.2
Average	30.8 ± 2.12
GVER with 20 wt. % of Styrene	
FVER-6-1	31.6
FVER-6-2	32.3
FVER-6-3	30.2
Average	31.4 ± 0.89

Table 51. Short Beam Shear Strength of C-Fabric Reinforced Composites of Formulated Br-GVER.

Specimen	**Short Beam Shear Strength (MPa)**
C-Fabric Reinforced Derakane 510 40A	
Br-VER-1	31
Br-VER-2	32
Br-VER-3	33
Br-VER-4	31
Br-VER-5	34
Average	32 ± 0.81
20 wt. % Br-GVER and 80 wt. % Derakane 510 40A	
FVER-7-1	28.6
FVER-7-2	28.9
FVER-7-3	30.1
Average	29.2 ± 0.65

50 wt. % Br-GVER and 50 wt. % Derakane 510 40A	
FVER-8-1	42.6
FVER-8-2	44.6
FVER-8-3	43.1
FVER-8-4	44.6
FVER-8-5	45.8
Average	44.1 ± 1.16
80 wt. % Br-GVER and 20 wt. % Derakane 510 40A	
FVER-9-1	42.8
FVER-9-2	36.6
FVER-9-3	36.3
FVER-9-4	40.6
FVER-9-5	41.2
Average	39.5 ± 2.56
Br- GVER with 40 wt. % of Styrene	
FVER-10-1	47.0
FVER-10-2	45.6
FVER-10-3	43.9
FVER-10-4	45.1
FVER-10-5	44.2
Average	45.2 ± 1.08
Br-GVER with 30 wt. % of Styrene	
FVER-11-1	39.4
FVER-11-2	43.0
FVER-11-3	45.7
FVER-11-4	45.6
FVER-11-5	43.9
Average	43.5 ± 2.32
GVER with 20 wt. % of Styrene	
FVER-12-1	50.5
FVER-12-2	49.1
FVER-12-3	49.5
FVER-12-4	50.2
FVER-12-5	51.9
Average	50.3 ± 0.98

Formulated GVER with different amount of styrene has slight lower short beam strength compared with commercial resin, as the amount of styrene increased that Short-Beam Strength (SBS) decreases a bit as shown in Table 50. However, in GVER upon reducing the amount of styrene, the SBS has improved significantly as shown in Table 51. Formulated Br-GVER exhibited SBS compared with commercial resin.

3.6.2.4. Short Beam Shear Testing (NAVAIR)

NAVAIR constantly provided technical support in guiding UML to prepare the setup for VARTM and for fluid uptake study. The results obtained at UML with the composite materials

needed to be verified by NAVAIR. UML send various formulated resin to NAVAIR for composite preparation followed by mechanical testing as shown in Figure 183. Ashland also sends their Derakane brominated and nonbrominated resin to NAVAIR for study. Each resin has recommended catalyst ratios given in parts per hundred resin molding compound (phr), according to its technical datasheet, shown in Appendices 1 and 2. In total, there were three chemicals used to catalyze each of these resin systems: Hipoint 90 (MEKP catalyst), acetylacetone, and 6% cobalt octoate were used with both resin systems to provide the necessary gel times for each infusion. Derakane Momentum 411-350 was mixed with 1.00 phr MEKP, 0.05 phr Co-Naph, and 0.015 phr acetylacetone, according to the lab conditions and gel time required. After the resin was infused into the required number of AS4 plies, the resulting panels were green cured overnight and post-cured at 215 ˚F for three hours. Similarly, Derakane 510A-40 was mixed with 1.25 phr MEKP, 0.20 phr Co-Naph, and 0.05 phr acetylacetone before infusing and curing at room temperature, then postcuring at 215 ˚F for three hours.

Figure 183. Formulated Resin Sent to NAVAIR for Composite Fabrication and Mechanical Testing.

The infusion of each resin type was carried out according to the VARTM infusion process, with a few deviations: distribution medium was used across the surface of the panel in order to facilitate wetting, and the panel was green cured at room temperature, eliminating the need for a heat blanket and thermocouples. After the necessary number of 32-ply panels was produced, two panels from each resin system were cut into coupons for flammability testing by Usman Sorathia at NAVSEA. Additional panels of 16 plies were produced for mechanical and thermal testing, specifically short beam shear (SBS) testing according to ASTM D2344 and dynamical mechanical analysis (DMA) according to ASTM D7028. The results from the short beam shear tests can be

seen in Table 52, where it appears that the two resin systems yield very similar short beam shear strengths. From a preliminary analysis, the two appear comparable.

Table 52. Short Beam Shear Test Results of VER and Br-VER composite samples prepared at NAVAIR.

Derakane Momentum 411-350 SBS Results		
Specimen	**Load (lbf)**	**SBS (ksi)**
1	166.919	4.23
2	155.091	3.96
3	171.045	4.38
4	143.584	3.63
5	180.536	4.57
6	164.957	4.15
Mean	**163.689**	**4.15**
Standard Deviation	**12.869**	**0.33**
Coefficient of Variation	**0.0786**	**0.08**
Derakane 510A-40 SBS Results		
Specimen	**Load (lbf)**	**SBS (ksi)**
1	157.034	4.08
2	156.986	4.02
3	163.683	4.33
4	163.082	4.19
5	162.147	4.14
6	162.725	4.26
Mean	**160.943**	**4.17**
Standard Deviation	**3.087**	**0.11**
Coefficient of Variation	**0.019**	**0.03**

Table 53. SBS testing on FVER 1, FVER-7 and FVER-8

Method	**ASTM D7264**			
Sample ID	**CT-2782 FVER-1**			
Specimen	**Width (in)**	**Thickness (in)**	**Peak Load (lbf)**	**3 Pt Max Flex Stress (ksi)**
1	0.5010	0.2010	240.219	73.88
2	0.5030	0.2010	228.236	69.91
3	0.5025	0.1975	237.722	75.50
4	0.5025	0.2020	234.623	71.23
5	0.5035	0.2010	241.746	73.98
6	0.5020	0.2020	211.979	64.42
Mean	**0.5024**	**0.2008**	**232.421**	**71.49**
Std Dev	**0.0009**	**0.0017**	**11.100**	**4.01**
% COV	**0.17**	**0.83**	**4.78**	**5.61**

Method	**ASTM D7264**			
Sample ID	**CT-2783 FVER-7**			
Specimen	**Width (in)**	**Thickness (in)**	**Peak Load (lbf)**	**3 Pt Max Flex Stress (ksi)**
1	0.5040	0.1410	89.691	55.72
2	0.5020	0.1410	83.661	52.18
3	0.5030	0.1400	84.166	53.14
4	0.5025	0.1400	84.976	53.71
5	0.5025	0.1400	85.878	54.28
6	0.5035	0.1400	82.278	51.90
Mean	**0.5029**	**0.1403**	**85.108**	**53.49**
Std Dev	**0.0007**	**0.0005**	**2.553**	**1.41**
% COV	**0.15**	**0.37**	**3.00**	**2.64**

Method	**ASTM D7264**			
Sample ID	**CT-2784 FVER-8**			
Specimen	**Width (in)**	**Thickness (in)**	**Peak Load (lbf)**	**3 Pt Max Flex Stress (ksi)**
1	0.5030	0.1305	77.312	56.18
2	0.5040	0.1305	78.469	56.91
3	0.5030	0.1300	76.726	56.19
4	0.5030	0.1295	87.840	64.82
5	0.5035	0.1295	76.226	56.20
6	0.5030	0.1305	87.949	63.91
Mean	**0.5032**	**0.1301**	**80.754**	**59.03**
Std Dev	**0.0004**	**0.0005**	**5.582**	**4.15**
% COV	**0.08**	**0.38**	**6.91**	**7.03**

We described in task 5 that specimen with different thickness were prepared by VARTM. We have performed a series of testing in order to determine the performance of formulated GVER with Derakane Momentum 411-350. Flexural Testing from NAVAIR, Dr. John Brennan (NAVAIR-Patuxent River, MD) is supporting UML team with their technical expertise and helping us in the expansion of the work by providing various troubleshooting pathways. We have sent 400 g FVER-7 with 20 wt. % Br-GVER + 80 % Derakane 510 40A and 400 g of FVER-8 with 50 wt. % GVER + 50 % Derakane 510 40A to NAVAIR as shown in Table 53. They are in process of fabricating C-Fabric reinforced composites and sending us SBS results.

Table 54. Dynamical Mechanical Analysis Results of the VER and Br-VER composite specimen.

Derakane Momentum 411-350 Tg		Derakane 510A-40 Tg	
Specimen	**Glass Transition Temp.**	**Specimen**	**Glass Transition Temp.**
1	118.28˚C	1	118.65˚C
2	116.34˚C	2	119.30˚C

**Tg measured from the knee of storage modulus curve.

The DMA allowed us to use storage modulus measurements to compare the glass transition temperature (Tg) of the two resin systems as shown in Table 54. The results of the DMA testing shows that the two resin systems have equivalent Tg. From the testing performed to date, Derakane Momentum 411-350 and Derakane 510A-40 seem to perform similarly after curing, although their rate of infusion and gel time are different.

3.6.3. Fluid Uptake Studies

This study seeks to compare the fluid uptake properties of two commercially available composite resins, Derakane Momentum 411-350 and Derakane 510A-40. The kind of fluid studied includes common solvents and chemicals frequently used in aerospace applications.

Beginning with panels of composite already fabricated according to the VARTM process, small specimens were cut, dried, and weighed to establish baseline moisture content. Then, three specimens of each resin type (for a total of 36 specimens) were immersed in a jar of each fluid. The fluids used included deionized (DI) water, toluene, mineral spirits, isopropanol, hydraulic fluid (MIL-PRF-5606), and lubricating oil (MIL-PRF-7808). The baseline specimens were weighed after immersion for 24 hours, 7 days, and 14 days. The resulting weights were recorded and percent weight gain calculated based on the baseline measurements. These results are shown as averages of the three specimens for each condition.

After two weeks, the weight-gain of each resin type ranged from 0.02% to almost 7%, depending on the fluid used. The results can be seen in the following six charts, one for each fluid type, contrasting the weight gain of Derakane Momentum 411-350 with that of Derakane 510A-40. In general, it appears that Derakane 510A-40 tends to absorb more fluid than Derakane Momentum 411-350, but the effects of this tendency on the resin's mechanical properties are unknown.

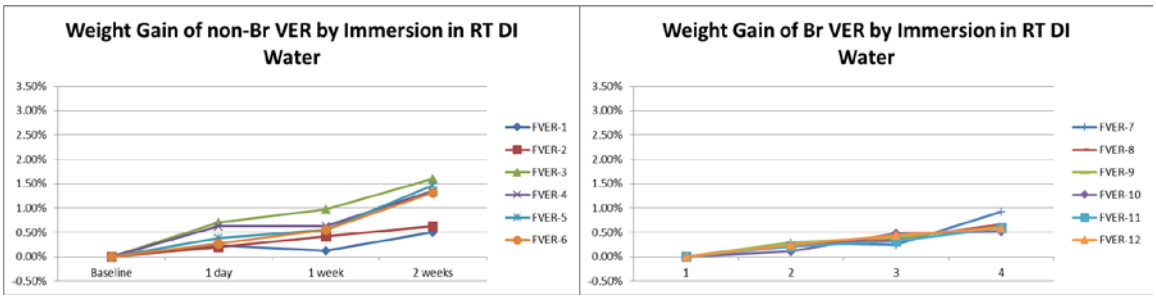


Figure 184. Weight Gain of Composites by Immersion in DI Water.

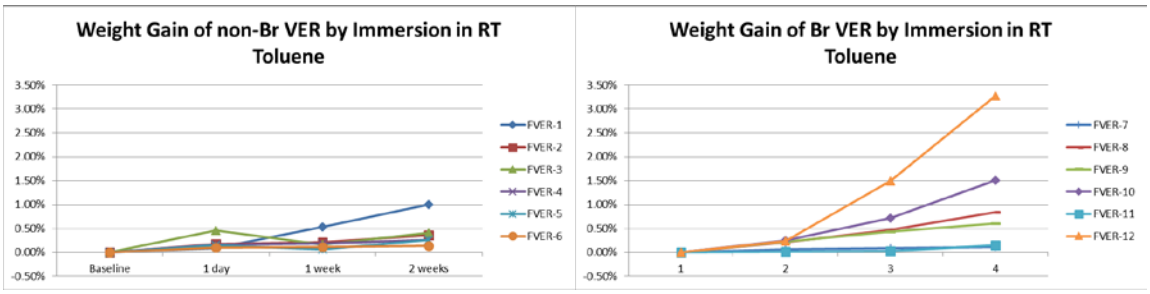


Figure 185. Weight Gain of Composites by Immersion in Toluene.

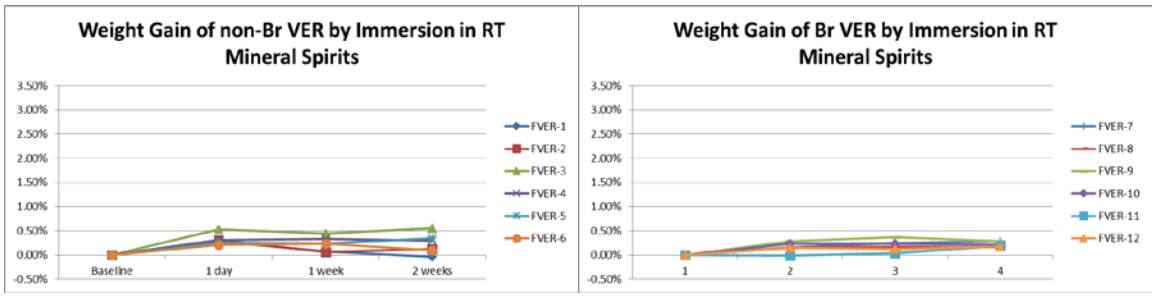


Figure 186. Weight Gain of Composites by Immersion in Mineral Spirits.

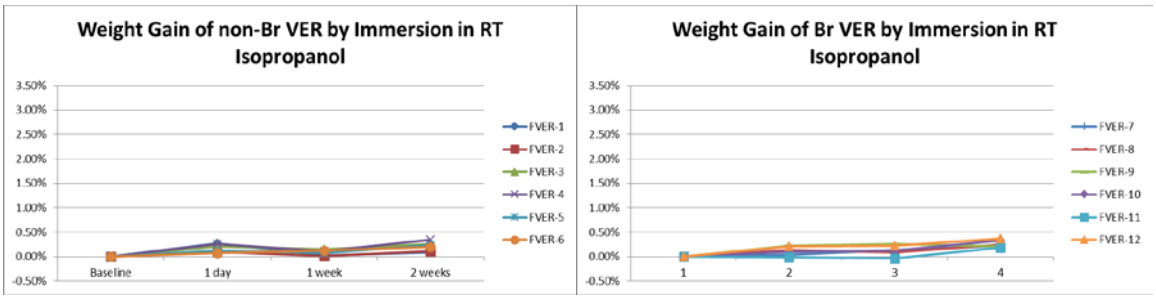


Figure 187. Weight Gain of Composites by Immersion in Isopropanol.

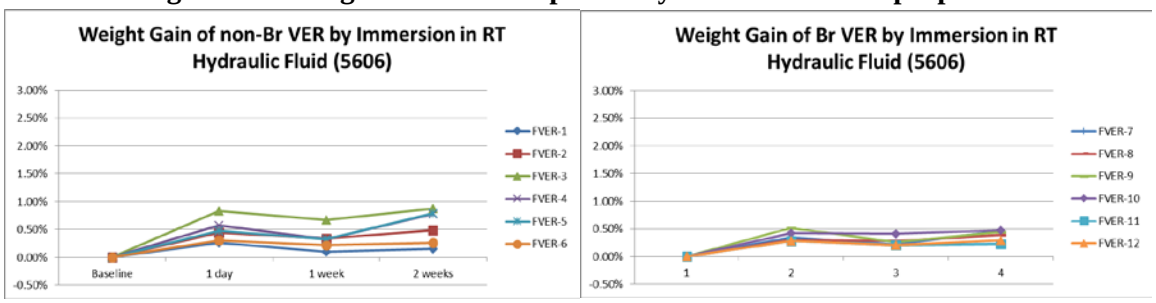


Figure 188. Weight Gain of Composites by Immersion in Hydraulic Fluid.

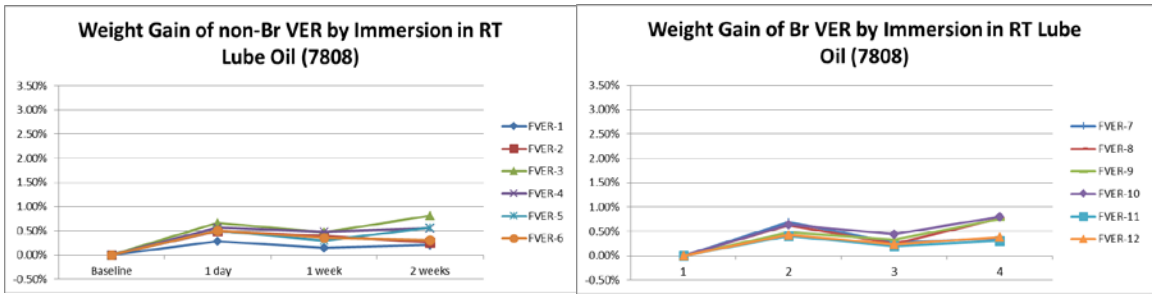


Figure 189. Weight Gain of Composites by Immersion in Lube Oil.

The fluid uptake with different solvents was summarized in Figure 184, Figure 185, Figure 186, Figure 187, Figure 188, and Figure 189, which represents uptake of DI water, toluene, mineral spirit, isopropanol, hydraulic fluids, and lube oil respectively. The graphs are quite obvious and easy to understand for relative study data. In all cases and among all solvents, formulated GVER and Br-GVER with 20 wt. % of styrene exhibited the highest resistance to all fluids compared with all other formulations. In order to further determine the fluid uptake properties of these VERs, the immersion studies will be continued until 30 days have elapsed in total. Additional studies recommended include measuring moisture saturation in a humid environment and conducting further immersion studies in which the fluids are heated to speed diffusion. To establish the impact of fluid uptake on resin properties, mechanical testing could also be performed. This mechanical testing should include a batch of short beam shear testing of the dried specimens prior to fluid conditioning, as well as a batch of testing after a defined fluid exposure.

3.6.4. Marine Applications of VHER.

The newly developed VHER was investigated for their performance for marine applications. The glass transition temperature (Tg) of the obtained sample was determined from the peak in Tan δ values using DMA. The sample displayed a Tg of 119 °C compared to a reported 135 ºC Tg for Derakane 441-400 as shown in Figure 190. The flexural storage modulus of the sample was observed to be around 2.4 GPA at room temperature. The thermal stability of the cured VHER was determined using thermogravimetric analysis (TGA). As seen in Figure 191, the onset temperature for degradation cured VHER (T_o) was observed at 417 °C, and the highest rate of degradation (T_{max}) was observed at 453 °C. In comparison for Derakane 441-400 the T_o and T_{max} were observed at 412 °C and 446 °C respectively. Without being bound by theory, this higher stability of VHER to thermal degradation can be attributed to the presence of ether moieties as opposed to ester groups in the case of Derakane. A higher char yield of 10 wt. % was also observed for VHER as opposed to 3 wt. % for Derakane. The cured VHER coupons in shown in Figure 192.

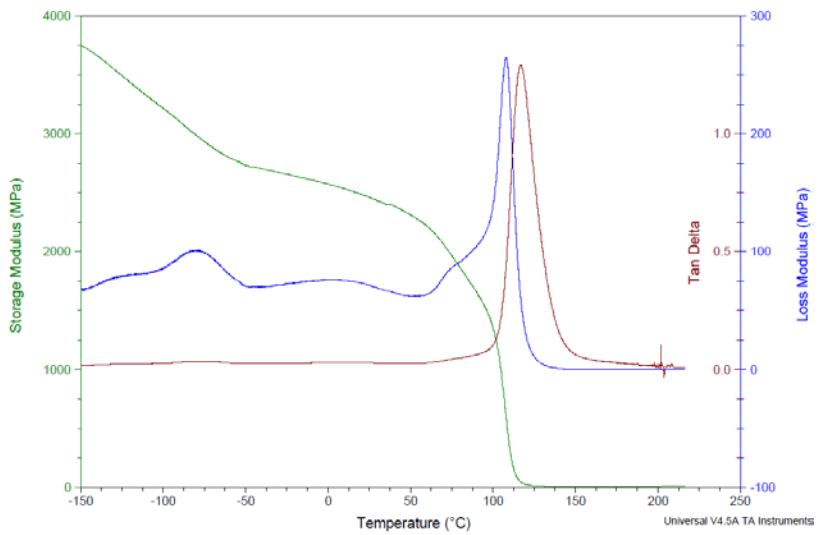


Figure 190. DMA of VHER and Derakane resin

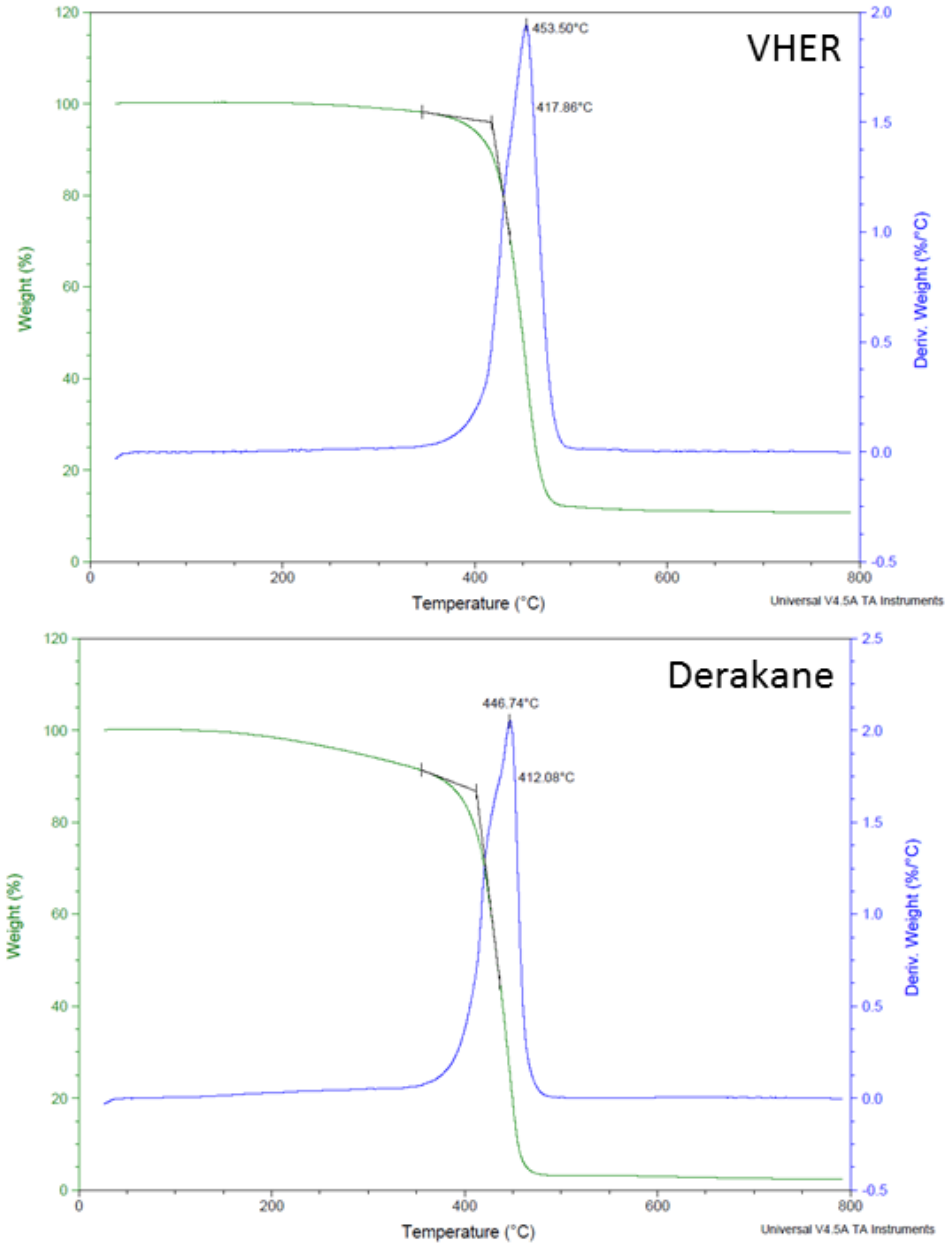


Figure 191. TGA of VHER and Derakane resin.

Using the formulations coatings of VHER and Derakane were processed on Aluminum Q-panels. The coated panels were then immersed in conc. H_2SO_4 for 48 hours to determine their hydrolytic stability. As seen in Figure 193, the Derakane coatings displayed a significant change in color as well as cracking and erosion of the coating. VHER coatings, in contrast, displayed a slight change in color and the film integrity is retained. This indicates that VHER is more stable to hydrolysis as compared to Derakane. This can be attributed to the ether moieties present in VHER as compared to the hydrolysable ester moieties in Derakane. Barcol hardness measurements were performed according to ASTM D-2583 and a Barcol hardness of 32 was observed for the cured samples, which is comparable to the Barcol hardness of 35 reported for Derakane 441-400.

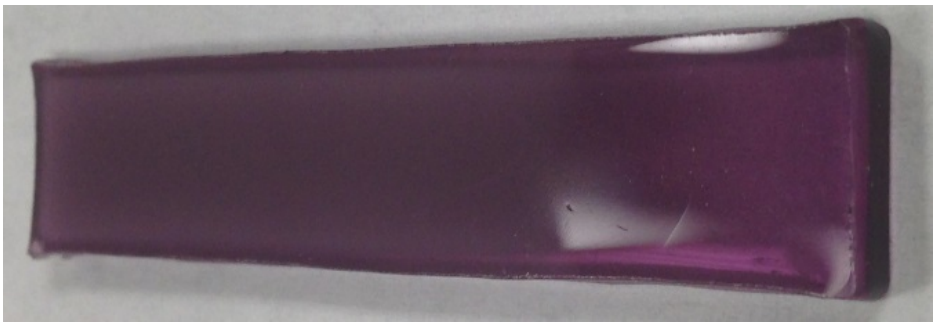


Figure 192. VHER after curing

In marine applications, continuous contact with an aqueous environment can cause osmotic blistering in boat hulls, which can have detrimental effects on the properties and reduce lifetime. In order to assess their affinity for water, cured Derakane and VHER samples with dimensions 40.2 mm x 12.4 mm x 3.1 mm, and 40.5 mm x 12.2 mm x 3.4 mm respectively were selected. The samples were immersed in deionized water at 60 °C for 30 days. Prior to immersion in water, the samples were placed under vacuum at 80 °C for 48 hours and cooled under vacuum to remove and absorbed moisture under ambient conditions, then weighed carefully using an analytical balance. For each subsequent measurement, before weighing the samples were allowed to cool to room temperature and patted dry. The resultant data on weight increase as a function of time is displayed in Figure 194. As the data shows, there is a steady increase in the weight of both materials due to the diffusion of deionized water into the samples, followed by saturation after about 20 days. Due to the greater polarity of the ester moieties in the VER than the ether moieties in the VHER, the equilibrium water uptake of the former (0.6 wt. %) substantially exceeded that of the latter (0.2 wt. %). The lower water uptake observed in the VHER is an advantage of the VHER material for long-term durability of parts in marine applications.

Figure 193. Coating of VHER and Derakane on different surfaces.

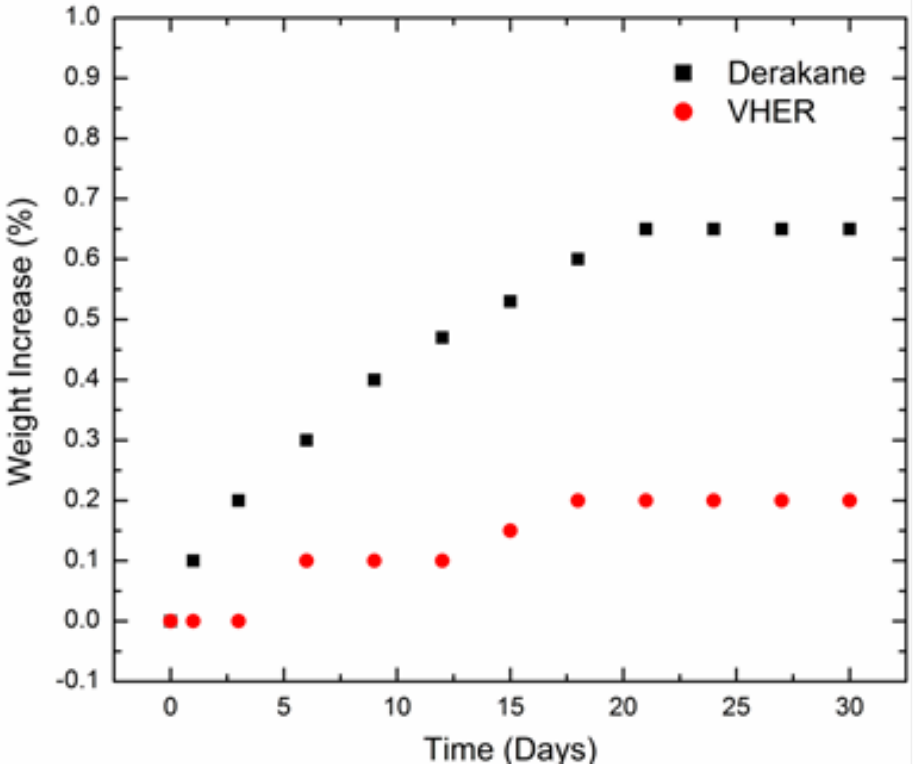


Figure 194. Water uptake measurements for cured Derakane 411-400 (black) and VHER (red).

Gardco wet film applicators (wire size 6, S6) were utilized for processing VHER and Derakane 441-400 VER coatings on Q-panel uncoated 3” x 6” aluminum test panels. The aluminum substrates were cleaned first by immersion in a pH 2 aqueous sulfuric acid bath for 5 minutes at 25°C. The panels were then washed with deionized water and dried at 110°C in a convection oven for 5 min. The panels were cooled to room temperature, after which the VHER and Derakane 441-400 VER formulations with 1.5 phr MEKP (Norox MEKP-925H), 0.2 phr cobalt naphthenate (6% in mineral spirits, Sigma-Aldrich), and in the case of VHER 0.15 phr of dimethyl aniline (DMA), were applied using the S6 wet film applicator. In a convection oven, the Derakane 441-400 VER coating cured in 1 hour at 220 °C. For coatings, the VHER formulation containing 33 % Styrene and DMA as the secondary accelerator, cure time was increased to 6 hours for complete curing at 220 °C. Using this procedure, continuous, tack-free, clear, coatings of were obtained. In adhesion testing, the results are obtained by visual examination of the marked area. In order to aid in this process, trace quantities of a luminescent dye, carboxyfluorescein, were introduced into the formulations.

To determine coating stability vs. solvent attack, the obtained coatings were characterized via the MEK double rub test (ASTM D5402) using cheese cloth and commercially available methyl ethyl ketone (Sigma-Aldrich). In a typical test, a doubled-over piece of cheese cloth was placed in a beaker containing MEK and saturated until dripping wet. The MEK-wetted cheesecloth was then placed on the test sample and pressed firmly with the index finger at a 45° angle and 100 double rubs were performed on the central area of each coating, after which they were visually inspected. No visual changes were observed in any of the coatings after the MEK double rub test. The coatings on which the MEK double rub test was performed were then utilized for ASTM D3359 adhesion testing. A Gardco Paint Adhesion Test Kit with an 11 tooth 1.0 mm cutter (PA-2053) was utilized for screening the obtained coatings via ASTM D3359 (Standard Method for Measuring Adhesion by Tape Test, a.k.a. “Crosshatch Adhesion Test”), Test Method B, recommended for coatings with dry thicknesses below 50 µm. The presence of the fluorescent dye in the coatings significantly improved the evaluation of coatings following adhesion testing. After cross-hatching, tape application and peeling, the samples were observed under 365 nm UV illumination to evaluate the degree of coating removal from the substrate. **Figure** 195 displays photographs of the samples after adhesion testing; neither coating experienced any loss of material from the substrate after the adhesion tape test, meaning both are classified as 5B coatings (the highest level of performance indicated by this testing standard). These results confirm that the equally high performance of both the VHER and Derakane 441-400 VER coatings.

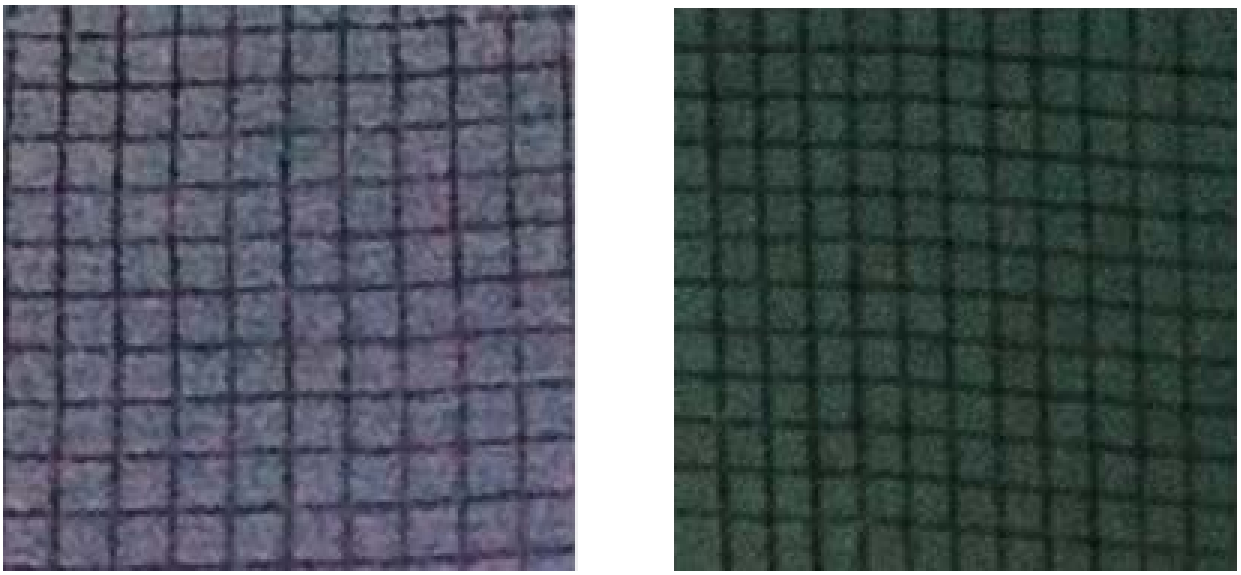


Figure 195. Photographs of VHER (left) and Derakane (right) coatings after ASTM D3359 Adhesion Tape test.

A T-Bend tester was used to perform 0T, 1T, and 2T coating flexibility bend tests (ASTM D4145) on all coated samples following MEK double rub testing (ASTM D5402). This test is important as it determines the flexibility and adhesion of the coatings on substrates that are deformed by bending. In this test, coated samples were bent using a T-Bend tester procured from Qualtech Products Industry. 0T, 1T, and 2T bends were produced, after which the coatings were inspected for damage. The pressure-sensitive tape provided in the ASTM D3359 Gardco Paint Adhesion Test Kit was used to determine the adhesion/pickoff of the coatings at the bent edge. The 0T bend test is the most challenging test to pass, as the radius of curvature at the T-bend is lowest, in this case, nevertheless, neither the VHER nor the Derakane 441-400 VER coatings displayed any damage or removal of coated material following this test as shown in Figure 196. Hence, both can be classified as 0T coatings. For use in applications such as chemical storage tanks, desulfurization flue stacks etc. enhanced chemical stability is desired. To determine the chemical stability of the processed VHER and Derakane 441-400 VER coatings, the coated panels were immersed in concentrated H_2SO_4 for 48 hours. As seen in Figure 193, the Derakane coatings displayed a significant change in color as well as cracking and erosion of the coating. VHER coatings, in contrast, displayed only a slight change in color and experienced no changes in film integrity. This indicates that VHER is more stable vs. hydrolysis, as compared to a Derakane, 441-400 VER. This can be attributed to the stable ether moieties present in the VHER coating as compared to the hydrolytically unstable ester moieties in the Derakane 441-400 coating.

Figure 196. Coating flexibility bend test (ASTM D4145)

Following immersion in concentrated H_2SO_4 for 48 hours, 0T bends were produced to determine the effect of hydrolysis on the flexibility and adhesion of the coatings. The pressure-sensitive tape provided in the ASTM D3359 Gardco Paint Adhesion Test Kit was used to assess the adhesion/pickoff of the coatings at the bent edge. Even after immersion in concentrated $H2SO_4$ for 48 hours, the VHER coatings displayed no damage or coating removal following the adhesion test as shown in Figure 197. In contrast, Derakane 441-400 VER coatings failed the test due to the loss of a considerable portion of the coating at the 0T bend as seen in Figure 197. The terms and expressions that have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the embodiments of the present invention. Thus, it should be understood that although the present invention has been specifically disclosed by specific embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those of ordinary skill in the art, and that such modifications and variations are considered to be within the scope of embodiments of the present invention.

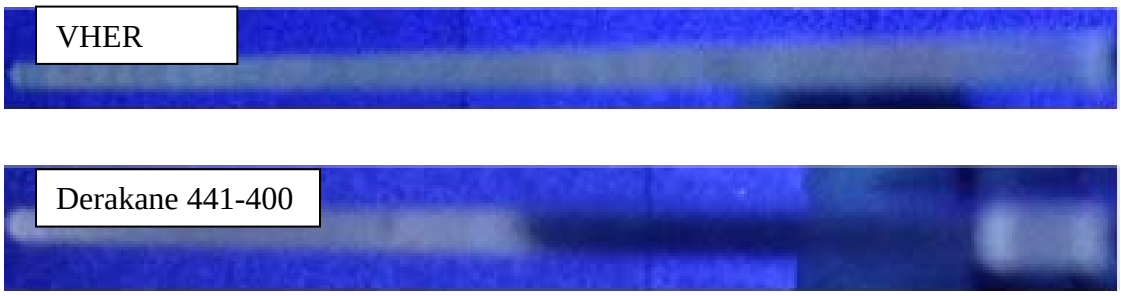


Figure 197. Coating at the 0T bend after immersion in acid for 16 h.

4. Conclusions and Implications for Future Research/Implementation

During the project years, we have collaborated with various company and manufacturer to procure the source materials. This led us to complete our tasks such as 'refinement of phenol from lignin', 'glycidyl methacrylate from biowaste glycerin', 'scale-up of GVER' and 'formulation of GVER' successfully. Synthesis of GVER from biowaste materials was successfully demonstrated as shown in Figure 198. In addition to that, two other new approached for the synthesis of GVER through reduced step synthesis were proposed and filled for the preliminary patent application. An alternative route for the synthesis of VER using different transformative reactions have produced many other high-value chemical products. Synthesis and scale-up of GVER were continued to support the remaining tasks of investigating the formulation, mechanical and flammability performance of various compositions of GVER. The synthesis of GVER has multiple synthesis steps to produce various intermediate.

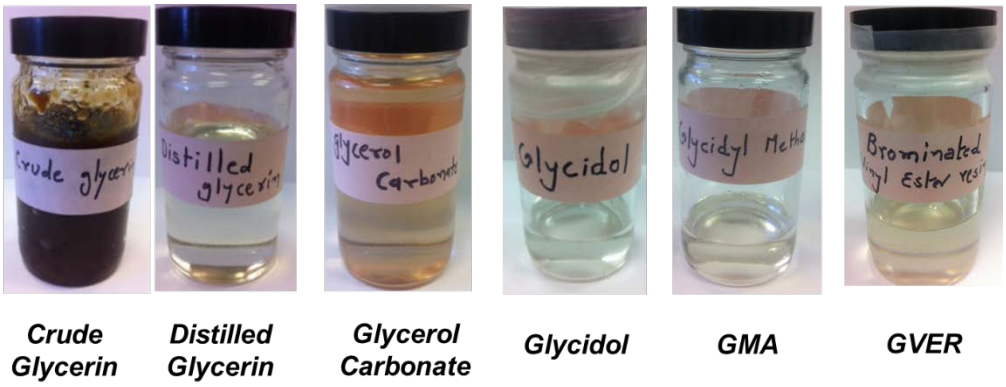


Figure 198. Successful demonstration of the development of GVER from biodiesel-based glycerin.

The procurement of phenol (the simplest form of phenolics) out of all phenolic compounds of pyrolysate was very challenging during the whole periods. Not only for the multiple steps of refinement from the crude pyrolysis products but also we had to try multiple times of pyrolysis on a daily basis for scale-up. The pilot size of the reactor with fluid bed system might be an alternative set up for large scale preparation for a future research for scale up.

Bio-derived resins showed similar or better mechanical properties than the commercially available resin. All bio-derived resins have a significantly longer pot life than the commercial resin (CVER). The processing for manufacturing composites using VARTM becomes easier as the Green vinyl ester resin (GVER) contents increases. The improved flammability properties were found in GVER compared with the commercial resin (CVER).

During this project (SERDP WP 2317), we have been a focus on the phenol, simplest form of phenolic compounds, production to produce BPA (Bisphenol A). There has been an increasing

demand to find the alternative chemicals in industry because BPA has been known as endocrine-disrupting chemicals. There has been a gradual shift of analogs such as BPS (Bisphenol S) and BPF (Bisphenol F). However, these chemicals were also reported as hormonally active as BPA with endocrine-disrupting effects based on many literature reports. Most recent interest is on BGF (Bisguaiacol F) leading market trend so-called "BPA-free" to comply the demand of new safe alternative to BPA. The precursor vanillyl alcohol and guaiacol could be derived from lignin. It is also produced more than phenol among the phenolic compounds during pyrolysis. This could be the alternative resin materials to be developed in the future.

Our successful results led us to prepare four manuscripts for publication (some of them are in progress). We prepared the summary of work performed during the project, WP 2317 below.

- **Novel Synthetic Procedures of Vinyl Ester Resin using waste glycerin**

A novel environmentally benign protocol for the synthesis of vinyl ester resin (VER) was developed. Our synthetic strategies were designed to use a commercial waste material, glycerin, from biodiesel manufacturing and convert it into a widely utilized resin. The VER was first synthesized using bisphenol A (BPA) and glycidyl methacrylate (GMA) as precursors. GMA was synthesized *via* a multistep synthetic protocol using glycerin obtained from a biodiesel manufacturing waste stream, while current synthetic protocols for the manufacture of VER employed petroleum feedstock, which reduces the sustainability, and used epichlorohydrin, a known environmentally hazardous material that produces acute toxicity in case of inhalation. Our synthesis of the green vinyl ester resins (GVER) was launched from renewable sources using three steps: (1) synthesis of GMA from waste glycerin; (2) conversion of phenol into BPA using environmentally benign conditions, and (3) synthesis of GVER from BPA and GMA. During the novel synthetic protocol, other valuable intermediates, such as glycerol carbonate and glycidol, were also obtained. The second precursor, bisphenol A was synthesized by the reaction of phenol and acetone using an environmentally benign synthetic protocol. The Green VER was synthesized by reaction of BPA and GMA. This synthetic strategy opens avenues for obtaining this valuable resin using sustainable environmentally benign routes.

- **Green Bisphenol A: A High Valued Building Block Isolated from Lignin Biowaste**

Isolation of high-value chemicals from bio-waste material has been a field of interest over the last few decades driven by growing environmental concerns. Lignin, a by-product of pulping and agro-based industries, has long been considered a source of renewable chemicals such as phenolics. In our fast pyrolysis studies, it was demonstrated that the pyrolysates of lignin were isolated and purified, and used in synthesis of Bisphenol A (BPA), a high-value building block employed in a wide range of plastic materials. A relationship between the pyrolysis conditions of three different lignin feedstocks and phenol yields were studied. Phenolics were extracted and purified from the pyrolysate and then used for Bisphenol A synthesis. The synthesis of green BPA was demonstrated from pyrolyzed lignin, a renewable biomass waste stream. Initially, lignin was pyrolyzed in a primary reactor to create pyrolysis vapors that were swept into a secondary reactor and allowed to react further before condensing and collecting the product oil. As expected, the oil was comprised of a variety of phenolic compounds. The

phenolics were extracted and distilled to concentrate green phenol. From green phenol, sustainable bisphenol A (BPA) was synthesized. In addition, other products of lignin pyrolysis have a potential value such as the char, which could be used for process energy, and the remaining oil fractions which could contain valuable chemicals or a blend of chemicals that could be upgraded and used as a fuel.

- **Green GVER Composites**

A green vinyl ester resin (GVER) and its composites were investigated as a route for bio-based resin use in structural applications. The GVER was formulated using a monodisperse vinyl ester created via a novel synthetic route capable of using bio-waste material from paper and biodiesel industries. The GVER was used either as a neat resin or as blended with a commercial vinyl ester resin. The processing viscosity and gel times were investigated. The GVER reaches a similar viscosity as the commercial resin with only half the styrene monomer content, thereby reducing the volatile organic compounds (VOC) associated with manufacturing. Composites of the GVER matrix reinforced by carbon fabric were tested for their tensile and flexural properties. Initial flammability properties were measured by cone calorimetry and smoke density tests. The mechanical and flammability performance of the GVER compare favorably with commercial resin and provide a route for composites manufacturing from sustainably sourced vinyl ester matrix. The synthesis of Green Vinyl Ester Resin was successfully scaled to formulate vinyl ester resins suitable for infusion of carbon-fiber reinforced composites. A series of resins were formulated by combining the GVER with 0 to 80% commercial resin (Derakane Momentum 411 350). A similar processing viscosity to the commercial VER (40 wt. % styrene) was achieved for the GVER with 20 wt. % styrene, thereby reducing the styrene content by up to half. The activated resin rheology shows an extended pot life at room temperature which can be shortened on demand with minimal 20°C temperature increase. Resin formulations ranging from 20 to 80 wt. % GVER, and pure GVER with 30-40 wt. % styrene content, exhibited similar tensile strength, flexural strength, and short beam strength to those of the commercial resin. Moreover, resin formulations with 50 to 100 wt. % of GVER exhibited an improved flammability and smoke density performance compared to the commercial resin. However, GVER formulated with only 20 wt. % styrene demonstrated compromised mechanical properties, as well as flaming smoke density performance comparable to the commercial resin. These results provide a pathway to transition from petroleum-based vinyl ester resins to their bio-based counterparts while maintaining existing processing conditions and comparable mechanical and flammability performance.

- **Flame Retardant Vinyl Ester Resin (FRVER) Composites**

Brominated vinyl ester resins (Br-VER) are economically viable, high performance materials that are widely utilized in specialty applications such as the fabrication of hulls in naval vessels because the modification of polymeric materials with additives such as halogens can slow the rapid proliferation of damage at any one of these stages and in doing so suppress the likelihood of a fire. In particular, the addition of bromine to the polymeric chain significantly improves the flammability performance of the material as it captures the free oxygen radical and retards the ability of the flames to propagate. In this work, Br-VER was synthesized using tetrabromobisphenol A (TBBPA) and glycidyl methacrylate (GMA) as precursors, both of which can be isolated from biowaste materials. The pure di-functional Br-VER was dried and mixed with 40 wt. % of styrene. The brominated vinyl ester pre-polymer was

successfully synthesized by solvent free reaction of TBBPA and GMA and purified by column chromatography. Rheological studies on resin formulations showed that the bio-derived GVER has a significantly lower viscosity and a longer pot life than the commercial resin (Derakane 510A-40) which are both critical parameters for end use applications like resin infusion. All of the bio-derived formulations with varying wt. % of GVER showed improved thermo-mechanical properties such as storage modulus and glass transition temperature. The newly formulated brominated VER and green composites must be able to retain its economic value by entering the market at a similar price point to the current resin system without having its chemical, thermal and mechanical performance compromised.

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6. Appendices

A1. Patent Applications.

1. Provisional Patent Application-VER Synthesis- Docket No.Docket No. SLW 4724.005WO1 UML 2015-038 & 039.

2. Provisional Patent Application-VHER Synthesis- Docket No.Docket No. UML 2015-041-4724.007WO1.

A2. Invention Disclosures.

3. UMass Lowell Invention Disclosure BABDHPE VER cID.

4. UMass Lowell Invention Disclosure 2015-039 VER cID.

5. UMass Lowell Invention Disclosure 2015-040 BADGE cID.

6. UMass Lowell Invention Disclosure_GCMA_GVER_2016-020.

7. UMass Lowell Invention-Disclosure_Pyrolysis_2015-007.

8. UMass Lowell Invention Disclosure_VER_Synthesis_2015-008.

A3. Published Articles.

9. Published Research Article-2016-Journal_of_Applied_Polymer_Science.

10. Published Research Article-2015-RSC Advances.

A4. Manuscripts in Preparation.

11. In preparation Manuscript-2017-Bioresources.

12. In preparation Manuscript-2017-Polymer.

A5. Presentation at Conferences and IPR meetings.

13. NERM 2016-YLee presentation.

14. AIChE-SPS Conference 2016-YLee_Properties of Bio-derived Vinyl Ester Resin based Composites.

15. 250th ACS Poster presentation.

16. NERM_062015_presentation.

17. IPR_102014_presentation.

18. IPR_042015_presentation.

19. IPR_042016-presentation.

A6. Nondisclosure Agreements.

20. NDA with Maine Standard Biofuels.

21. NDA with Maine Seed Company.

22. NDA Ashland-UMass Lowell 02-05-16.

23. NDA UML-Dixie-final version.

A7. Response to Action Items.

24. Action Item-I, Justification of Bromination of Bisphenol A.

25. Action Item-II, Uptake of Water, Hydrocarbon Fuel and Hydraulic Fluid by VER.

26. Action Item-III, White Paper on Possible Approaches of Increasing Yield of Phenol and Other High Value Phenolic.

27. Action item-IV_BPA alternative.

A8. Standard Operating Procedures.

28. SOP for handling cobalt naphthenate.

29. SOP for handling Styrene.

30. SOP of Synthesis of GMA.

31. SOP of fast pyrolysis of lignin using helium gas.

32. SOP for Phenol refinement from crude product of lignin pyrolysis.

A9. Important Meeting Summary

33. Meeting Summary at Maine Forum.

34. Weekly Newsletter at The Ashland PA Plant_06052014.

35. Technical Meeting Summary Ashland Dublin OH 06232014

Appendix A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re **PROVISIONAL** Patent Application of: Akshay Kokil et al.

Title: METHODS OF MAKING BIS(HYDROXYHYDROCARBYL)ETHER BISPHENOL AND VINYL ESTER RESIN

Docket No.: 4724.005PRV

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

We are transmitting herewith the following attached items (as indicated with an "X"):

X PROVISIONAL Patent Application comprising:
  X Specification (25 pgs.).
  X 3 Sheets of Colored Drawings.
X Provisional Application Cover Sheet (1 pg.).
X Authorization to charge Deposit Account 19-0743 in the amount of $130.00 to cover the provisional filing fee and any applicable application size fee.
X Small entity status claimed under 37 C.F.R. 1.27.
X Authorization to Permit Access (PTO/SB/39) (1 pg.).
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Please charge any additional required fees or credit overpayment to Deposit Account No. 19-0743.

SCHWEGMAN LUNDBERG & WOESSNER, P.A.
Customer Number: 21186

By: /Nicholas P. Lanzatella/
Nicholas P. Lanzatella
Reg. No. 63,803

Express Mail mailing label number: EM167936272US
Date of Deposit: December 23, 2015
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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail mailing label number: EM167936272US

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Akshay	Kokil	Dracut, MA
Yongwoo	Lee	Salem, MA
Priyank N.	Shah	Lowell, MA

TITLE OF THE INVENTION (500 characters max):

METHODS OF MAKING BIS(HYDROXYHYDROCARBYL)ETHER BISPHENOL AND VINYL ESTER RESIN

CORRESPONDENCE ADDRESS

Direct all correspondence to: The address corresponding to Customer Number:	21186

ENCLOSED APPLICATION PARTS *(check all that apply)*

	Application Data Sheet. See 37 CFR 1.76		CD(s), Number of CDs: _____
X	Colored Drawing(s) *Number of Sheets* (3)	X	Other (specify): Authorization to Permit Access (PTO/SB/39) (1 pg.)
X	Specification *Number of Pages* (25)		

Fees Due: Filing Fee of $260 ($130 for small entity) ($65 for micro entity). If the specification and drawings exceed 100 sheets of paper, an application size fee is also due, which is $400 ($200 for small entity) ($100 for micro entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

METHOD OF PAYMENT OF THE FILING FEE AND APPLICATION SIZE FEE FOR THIS PROVISIONAL APPLICATION FOR PATENT

X	Applicant asserts small entity status. See 37 CFR 1.27.
	Applicant certifies micro entity status. See 37 CFR 1.29. *Applicant must attach form PTO/SB/15A or B or equivalent.*
	A check or money order made payable to the *Director of the United States Patent and Trademark Office* is enclosed to cover the filing fee and application size fee (if applicable).
	Payment by credit card. Form PTO-2038 is attached
X	The Director is hereby authorized to charge the filing fee and application size fee (if applicable), as well as any additional required fees, or credit any overpayment to Deposit Account Number: 19-0743.
	TOTAL FEE AMOUNT $ $130.00

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

	No.
	Yes, the invention was made by an agency of the U.S. Government. The U.S. Government agency name is:
X	Yes, the invention was made under a contract with an agency of the U.S. Government. The name of the U.S. Government agency and Government contract number are: Strategic Environmental Research and Development, SERDP WP-2317

SIGNATURE: /Nicholas P. Lanzatella/

Date: December 23, 2015

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DOCKET NUMBER: 4724.005PRV

In re Patent Application of: Akshay Kokil et al.
Title: METHODS OF MAKING BIS(HYDROXYHYDROCARBYL)ETHER BISPHENOL AND VINYL ESTER RESIN
Attorney Docket No.: 4724.005PRV

Receipt is hereby acknowledged for the following in the United States Patent and Trademark Office:

CONTENTS: PROVISIONAL PATENT APPLICATION: Specification (25 pgs); 3 Sheets of Colored Drawings; Authorization to charge Deposit Account 19-0743 in the amount of $130.00 to cover the provisional filing fee and any applicable application size fee.; small entity status claimed under 37 C.F.R. 1.27; Authorization to Permit Access (PTO/SB/39) (1 pg.); Provisional Application Cover Sheet (1 pg) and Transmittal Sheet.

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In re Patent Application of: Akshay Kokil et al.

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AUTHORIZATION TO PERMIT ACCESS TO APPLICATION BY PARTICIPATING OFFICES Send completed form to: Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450	Application Number	Unknown
	Filing Date	Herewith
	Atty Docket Number	4724.005PRV
	First Named Inventor	Akshay Kokil et al.
	Title(Required)	METHODS OF MAKING BIS(HYDROXYHYDROCARBYL)ETHER BISPHENOL AND VINYL ESTER RESIN

The undersigned hereby grants the USPTO authority to provide access to the above-identified patent application by the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), and the World Intellectual Property Office (WIPO), and any other foreign intellectual property offices participating with the USPTO in a bilateral or multilateral priority document exchange agreement, in which a foreign application claiming priority to the above-identified patent application is filed. See 37 CFR 1.14(c) and (h).

In accordance with 37 CFR 1.14(h)(3) and the respective priority document exchange agreement, access to the above-identified application will be provided with respect to: 1) the above-identified patent application-as-filed, 2) any foreign application to which the above-identified patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the above-identified patent application, and 3) any U.S. application-as-filed from which benefit is sought in the above-identified patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing the Authorization to Permit Access to Application by Participating Offices.
This written authorization should be submitted prior to the filing of a subsequent foreign application, in which priority is claimed to the above-identified patent application, with any participating intellectual property office (e.g., the EPO, JPO, KIPO, SIPO, or DAS Accessing Office). However, if applicant does not wish the EPO, JPO, KIPO, SIPO, WIPO, or other participating intellectual property office in which a foreign application claiming priority to the above-identified patent application is filed to have access to the above-identified patent application, this written authorization should not be filed.

No fee will be charged under 37 CFR 1.19(b)(1) for providing a participating intellectual property office with an electronic copy of the above-identified patent application.

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/ Nicholas P. Lanzatella /	12/23/2015
Signature	Date
Nicholas P. Lanzatella	(612) 349-9580
Typed or printed name	Telephone Number
Registered Practitioner	Reg No. 63,803
Title	Registration Number, if applicable

This collection of information is required by 37 CFR 1.14(h). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process an application). Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 6 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

PROVISIONAL PATENT APPLICATION

METHODS OF MAKING BIS(HYDROXYHYDROCARBYL)ETHER BISPHENOL AND VINYL ESTER RESIN

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METHODS OF MAKING BIS(HYDROXYHYDROCARBYL)ETHER BISPHENOL AND VINYL ESTER RESIN

STATEMENT OF GOVERNMENT SUPPORT

[0001] This invention was made with Government support under SERDP WP-2317 awarded by Strategic Environmental Research and Development Program. The U.S. Government has certain rights in this invention.

BACKGROUND

[0002] Vinyl ester resins (VERs) are high performance unsaturated resins with exceptional mechanical strength and corrosion resistance. In addition to their superior performance, these resins display lower viscosities than conventional epoxy resins resulting in significantly improved processability. Due to their superior properties and excellent processability, VERs find use, either in pure form or as a matrix in fiber reinforced composites, in diverse industries, such as, ship building, automotive part construction, infrastructure polymer concrete reinforcements, corrosion resistance coatings (on chemical storage tanks, pipes and ducting, fume extraction systems, gas cleaning units), top-coat materials (with excellent adhesion to plastics, steel and concrete), optical fiber coating, UV curing inks and printed circuit board manufacture (*Jaswal, S.; Gaur, B. 'New trends in vinyl ester resins' Rev. Chem. Eng. 2014, DOI 10.1515/revce-2014-0012*). The versatility of these resins for diverse applications has resulted in a huge global market and ever increasing potential.

[0003] VERs are currently synthesized by addition reaction of epoxide resins with unsaturated carboxylic acids. A variety of chemical compounds containing the epoxy groups have been used for synthesis of VERs. Particularly bisphenol-A (BPA) based VER resins are widely utilized due to their exceptional mechanical strength and chemical resistance. Currently for BPA based VER synthesis, the epoxy containing bisphenol-A diglycidyl ether (BADGE) is reacted with either methacrylic acid or methyl methacylate. These resins were first commercialized as Epocryl resins by Shell Chemical Company and later as Derakane resins by Dow Chemical Company. Currently these resins are produced predominantly by Ashland, DSM and Reichold.

[0004] BADGE is currently synthesized using BPA and epichlorohydrin as starting materials. Patents issued for the synthesis of BADGE using BPA and epichlorohydrin, include U.S. Pat. No. 3121727 A to Baliker et al. assigned to Shell Oil Co. and U.S. Pat. No. 4877857 A to Shirtum et al. assigned to The Dow Chemical Company.

[0005] BPA-based VER is synthesized from BADGE by the addition reaction of its epoxy groups with acrylic acid based monomers. Patents issued for the synthesis of VER using this synthetic protocol include U.S. Pat. No. 3256226 to Fekete et al., and No. 3317465 to Doyle et al., both assigned to H. H. Robertson Co.; No. 3345401 to May; No. 3373221 to May; No. 3377406 to Newey; and No. 3432478 to May, all assigned to Shell Oil Co.; No. 3548030 to Jernigan; and No. 3564074 to Swisher et al., both assigned to Dow Chemical Co.; No. 3634542 to Dowd et al.; and No. 3637618 to May, both assigned to Shell Oil Co.

[0006] The production of VER is still performed using the synthetic protocols reported more than 3 decades ago. Even though the synthetic protocol used is efficient, it requires the use of epichlorohydrin, which performs the dual role of a solvent and reactant. Epichlorohydrin however, has been identified by the U.S. Environmental Protection Agency (EPA) as a hazardous air pollutant and it also features on the list of controlled chemicals by the EPA. Hence, to ensure continued environmental sustainability and improved work place safety an alternative route for the synthesis of VER is required.

[0007] Most of the chemicals used for the synthesis of VER are derived from petroleum based feedstocks, which introduces price volatility. In 2014 all the major manufacturers of VER, namely Ashland, DSM and Reichold, announced an increase in the VER price due to the increased cost of raw materials derived from petroleum feedstocks. Hence, an alternate route for improved sustainability and reduced cost volatility of this commercially important resin is required.

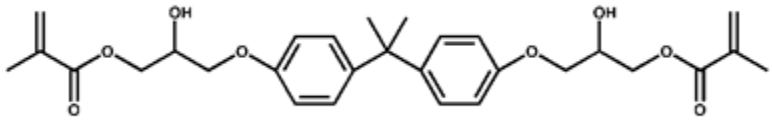
[0008] A typical VER composition consists of styrene as a reactive diluent. However, styrene is a highly carcinogenic chemical and has been identified as a hazardous air pollutant by the EPA. Hence, alternatives for styrene as reactive diluent in VER compositions are required.

SUMMARY OF THE INVENTION

[0009] In various embodiments, the present invention provides a method for producing a vinyl ester resin (VER). The method includes reacting a bisphenol with a (C_1-

C_{10})hydrocarbylpolyol to form a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol. The method also includes reacting the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with a vinyl carboxylic acid or a salt, ester, or acid halide thereof to form the VER.

[0010] In various embodiments, the present invention provides a method for producing a vinyl ester resin (VER). The method includes reacting bisphenol A with glycerin to form bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE). The method includes reacting the BABDHPE with methyl methacrylate to form the VER. The VER has the structure:



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[0011] In various embodiments, the present invention provides a method for producing a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of a bisphenol. The method includes reacting a bisphenol with a (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol.

[0012] In various embodiments, the present invention provides a method for producing bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE). The method includes reacting bisphenol A with a glycerin to form the BABDHPE.

[0013] In various embodiments, the present invention has advantages over other methods of making VER, at least some of which are unexpected. For example, in various embodiments, the present invention provides an environmentally benign methodology for obtaining VER formulations with “green” reactive diluent. In various embodiments, the present invention provides an environmentally benign “green” methodology for the synthesis of BABDHPE and VER. In various embodiments, the present invention provides a novel two-step or single pot synthetic protocol. In various embodiments, the present invention provides a method that eliminates or decreases the amount of toxic chemicals in VER synthesis and VER formulations, such as epichlorohydrin and styrene. In various embodiments, the use of a single pot synthetic method eliminates and/or significantly reduces the use of other chemical reagents required for purification of the VER. In various embodiments, the present invention provides a method that utilizes starting materials derived from bio-waste streams, which can improve the environmental and cost sustainability of the procedure.

BRIEF DESCRIPTION OF THE FIGURES

[0014] The drawings illustrate generally, by way of example, but not by way of limitation, various embodiments discussed in the present document.

[0015] FIG. 1 illustrates a proton NMR of isolated BABDHPE in DMSO-d^6.

[0016] FIG. 2 illustrates a proton NMR of a VER in DMSO-d^6, in accordance with various embodiments.

[0017] FIG. 3 illustrates a proton NMR of the VER product in DMSO d^6.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Reference will now be made in detail to certain embodiments of the disclosed subject matter, examples of which are illustrated in part in the accompanying drawings. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that the exemplified subject matter is not intended to limit the claims to the disclosed subject matter.

[0019] Throughout this document, values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of "about 0.1% to about 5%" or "about 0.1% to 5%" should be interpreted to include not just about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement "about X to Y" has the same meaning as "about X to about Y," unless indicated otherwise. Likewise, the statement "about X, Y, or about Z" has the same meaning as "about X, about Y, or about Z," unless indicated otherwise.

[0020] In this document, the terms "a," "an," or "the" are used to include one or more than one unless the context clearly dictates otherwise. The term "or" is used to refer to a nonexclusive "or" unless otherwise indicated. The statement "at least one of A and B" has the same meaning as "A, B, or A and B." In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document

and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section. All publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety, as though individually incorporated by reference. In the event of inconsistent usages between this document and those documents so incorporated by reference, the usage in the incorporated reference should be considered supplementary to that of this document; for irreconcilable inconsistencies, the usage in this document controls.

[0021] In the methods described herein, the acts can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited. Furthermore, specified acts can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed act of doing X and a claimed act of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

[0022] The term “about” as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range, and includes the exact stated value or range.

[0023] The term “substantially” as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more, or 100%.

[0024] The term “organic group” as used herein refers to any carbon-containing functional group. Examples can include an oxygen-containing group such as an alkoxy group, aryloxy group, aralkyloxy group, oxo(carbonyl) group; a carboxyl group including a carboxylic acid, carboxylate, and a carboxylate ester; a sulfur-containing group such as an alkyl and aryl sulfide group; and other heteroatom-containing groups. Non-limiting examples of organic groups include OR, OOR, $OC(O)N(R)_2$, CN, CF_3, OCF_3, R, C(O), methylenedioxy, ethylenedioxy, $N(R)_2$, SR, SOR, SO_2R, $SO_2N(R)_2$, SO_3R, C(O)R, C(O)C(O)R, $C(O)CH_2C(O)R$, C(S)R, C(O)OR, OC(O)R, $C(O)N(R)_2$, $OC(O)N(R)_2$, $C(S)N(R)_2$, $(CH_2)_{0-2}N(R)C(O)R$, $(CH_2)_{0-2}N(R)N(R)_2$, N(R)N(R)C(O)R, N(R)N(R)C(O)OR, $N(R)N(R)CON(R)_2$, $N(R)SO_2R$, $N(R)SO_2N(R)_2$, N(R)C(O)OR, N(R)C(O)R, N(R)C(S)R, $N(R)C(O)N(R)_2$, $N(R)C(S)N(R)_2$, N(COR)COR, N(OR)R, $C(=NH)N(R)_2$, C(O)N(OR)R, C(=NOR)R, and substituted or unsubstituted $(C_1\text{-}C_{100})$hydrocarbyl, wherein R can be hydrogen (in examples that include other

carbon atoms) or a carbon-based moiety, and wherein the carbon-based moiety can be substituted or unsubstituted.

[0025] The term "substituted" as used herein in conjunction with a molecule or an organic group as defined herein refers to the state in which one or more hydrogen atoms contained therein are replaced by one or more non-hydrogen atoms. The term "functional group" or "substituent" as used herein refers to a group that can be or is substituted onto a molecule or onto an organic group. Examples of substituents or functional groups include, but are not limited to, a halogen (e.g., F, Cl, Br, and I); an oxygen atom in groups such as hydroxy groups, alkoxy groups, aryloxy groups, aralkyloxy groups, oxo(carbonyl) groups, carboxyl groups including carboxylic acids, carboxylates, and carboxylate esters; a sulfur atom in groups such as thiol groups, alkyl and aryl sulfide groups, sulfoxide groups, sulfone groups, sulfonyl groups, and sulfonamide groups; a nitrogen atom in groups such as amines, hydroxyamines, nitriles, nitro groups, N-oxides, hydrazides, azides, and enamines; and other heteroatoms in various other groups. Non-limiting examples of substituents that can be bonded to a substituted carbon (or other) atom include F, Cl, Br, I, OR, $OC(O)N(R)_2$, CN, NO, NO_2, ONO_2, azido, CF_3, OCF_3, R, O (oxo), S (thiono), C(O), S(O), methylenedioxy, ethylenedioxy, $N(R)_2$, SR, SOR, SO_2R, $SO_2N(R)_2$, SO_3R, C(O)R, C(O)C(O)R, $C(O)CH_2C(O)R$, C(S)R, C(O)OR, OC(O)R, $C(O)N(R)_2$, $OC(O)N(R)_2$, $C(S)N(R)_2$, $(CH_2)_{0-2}N(R)C(O)R$, $(CH_2)_{0-2}N(R)N(R)_2$, N(R)N(R)C(O)R, N(R)N(R)C(O)OR, $N(R)N(R)CON(R)_2$, $N(R)SO_2R$, $N(R)SO_2N(R)_2$, N(R)C(O)OR, N(R)C(O)R, N(R)C(S)R, $N(R)C(O)N(R)_2$, $N(R)C(S)N(R)_2$, N(COR)COR, N(OR)R, $C(=NH)N(R)_2$, C(O)N(OR)R, and C(=NOR)R, wherein R can be hydrogen or a carbon-based moiety; for example, R can be hydrogen, $(C_1\text{-}C_{100})$hydrocarbyl, alkyl, acyl, cycloalkyl, aryl, aralkyl, heterocyclyl, heteroaryl, or heteroarylalkyl; or wherein two R groups bonded to a nitrogen atom or to adjacent nitrogen atoms can together with the nitrogen atom or atoms form a heterocyclyl.

[0026] The term "alkyl" as used herein refers to straight chain and branched alkyl groups and cycloalkyl groups having from 1 to 40 carbon atoms, 1 to about 20 carbon atoms, 1 to 12 carbons or, in some embodiments, from 1 to 8 carbon atoms. Examples of straight chain alkyl groups include those with from 1 to 8 carbon atoms such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, iso-butyl, sec-butyl, t-butyl, neopentyl, isopentyl, and 2,2-

dimethylpropyl groups. As used herein, the term "alkyl" encompasses n-alkyl, isoalkyl, and anteisoalkyl groups as well as other branched chain forms of alkyl. Representative substituted alkyl groups can be substituted one or more times with any of the groups listed herein, for example, amino, hydroxy, cyano, carboxy, nitro, thio, alkoxy, and halogen groups.

[0027] The term "alkenyl" as used herein refers to straight and branched chain and cyclic alkyl groups as defined herein, except that at least one double bond exists between two carbon atoms. Thus, alkenyl groups have from 2 to 40 carbon atoms, or 2 to about 20 carbon atoms, or 2 to 12 carbon atoms or, in some embodiments, from 2 to 8 carbon atoms. Examples include, but are not limited to vinyl, $-CH=CH(CH_3)$, $-CH=C(CH_3)_2$, $-C(CH_3)=CH_2$, $-C(CH_3)=CH(CH_3)$, $-C(CH_2CH_3)=CH_2$, cyclohexenyl, cyclopentenyl, cyclohexadienyl, butadienyl, pentadienyl, and hexadienyl among others.

[0028] The term "aryl" as used herein refers to cyclic aromatic hydrocarbon groups that do not contain heteroatoms in the ring. Thus aryl groups include, but are not limited to, phenyl, azulenyl, heptalenyl, biphenyl, indacenyl, fluorenyl, phenanthrenyl, triphenylenyl, pyrenyl, naphthacenyl, chrysenyl, biphenylenyl, anthracenyl, and naphthyl groups. In some embodiments, aryl groups contain about 6 to about 14 carbons in the ring portions of the groups. Aryl groups can be unsubstituted or substituted, as defined herein. Representative substituted aryl groups can be mono-substituted or substituted more than once, such as, but not limited to, a phenyl group substituted at any one or more of 2-, 3-, 4-, 5-, or 6-positions of the phenyl ring, or a naphthyl group substituted at any one or more of 2- to 8-positions thereof.

[0029] The terms "halo," "halogen," or "halide" group, as used herein, by themselves or as part of another substituent, mean, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom.

[0030] The term "hydrocarbon" or "hydrocarbyl" as used herein refers to a molecule or functional group, respectively, that includes carbon and hydrogen atoms. The term can also refer to a molecule or functional group that normally includes both carbon and hydrogen atoms but wherein all the hydrogen atoms are substituted with other functional groups.

[0031] As used herein, the term "hydrocarbyl" refers to a functional group derived from a straight chain, branched, or cyclic hydrocarbon, and can be alkyl, alkenyl, alkynyl, aryl, cycloalkyl, acyl, or any combination thereof. Hydrocarbyl groups can be shown as (C_a-C_b)hydrocarbyl, wherein a and b are integers and mean having any of a to b number of carbon

atoms. For example, (C_1-C_4)hydrocarbyl means the hydrocarbyl group can be methyl (C_1), ethyl (C_2), propyl (C_3), or butyl (C_4), and (C_0-C_b)hydrocarbyl means in certain embodiments there is no hydrocarbyl group.

[0032] The term "solvent" as used herein refers to a liquid that can dissolve a solid, liquid, or gas. Non-limiting examples of solvents are silicones, organic compounds, water, alcohols, ionic liquids, and supercritical fluids.

[0033] The term "room temperature" as used herein refers to a temperature of about 15 °C to 28 °C.

[0034] The term "standard temperature and pressure" as used herein refers to 20 °C and 101 kPa.

[0035] As used herein, the term "polymer" refers to a molecule having at least one repeating unit and can include copolymers.

[0036] In various embodiments, salts having a positively charged counterion can include any suitable positively charged counterion. For example, the counterion can be ammonium(NH_4^+), or an alkali metal such as sodium (Na^+), potassium (K^+), or lithium (Li^+). In some embodiments, the counterion can have a positive charge greater than +1, which can in some embodiments complex to multiple ionized groups, such as Zn^{2+}, Al^{3+}, or alkaline earth metals such as Ca^{2+} or Mg^{2+}.

[0037] In various embodiments, salts having a negatively charged counterion can include any suitable negatively charged counterion. For example, the counterion can be a halide, such as fluoride, chloride, iodide, or bromide. In other examples, the counterion can be nitrate, hydrogen sulfate, dihydrogen phosphate, bicarbonate, nitrite, perchlorate, iodate, chlorate, bromate, chlorite, hypochlorite, hypobromite, cyanide, amide, cyanate, hydroxide, permanganate. The counterion can be a conjugate base of any carboxylic acid, such as acetate or formate. In some embodiments, a counterion can have a negative charge greater than -1, which can in some embodiments complex to multiple ionized groups, such as oxide, sulfide, nitride, arsenate, phosphate, arsenite, hydrogen phosphate, sulfate, thiosulfate, sulfite, carbonate, chromate, dichromate, peroxide, or oxalate.

[0038] The polymers described herein can terminate in any suitable way. In some embodiments, the polymers can terminate with an end group that is independently chosen from a suitable polymerization initiator, -H, -OH, a substituted or unsubstituted (C_1-C_{20})hydrocarbyl

(e.g., (C_1-C_{10})alkyl or (C_6-C_{20})aryl) interrupted with 0, 1, 2, or 3 groups independently selected from -O-, substituted or unsubstituted -NH-, and -S-, a poly(substituted or unsubstituted (C_1-C_{20})hydrocarbyloxy), and a poly(substituted or unsubstituted (C_1-C_{20})hydrocarbylamino).

Method for producing a vinyl ester resin (VER).

[0039] In various embodiments, the present invention provides a method for producing a vinyl ester resin (VER). The method can include reacting a bisphenol with a (C_1-C_{10})hydrocarbylpolyol to form a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol. The method can also include reacting the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with a vinyl carboxylic acid or a salt, ester, or acid halide thereof to form the VER. As used herein, an "acid halide" of a carboxylic acid -C(O)-OH is -C(O)-X, wherein -X is -Cl, -Br, -F, or -I, such as -Cl or -Br.

[0040] The method can further include polymerizing the obtained VER, such as polymerizing via the terminal vinyl groups. The polymerizing can include forming a homopolymer or copolymer. The polymerizing can include polymerizing the VER with a vinyl-substituted organic compound. The vinyl-substituted organic compound can be styrene. The vinyl-substituted organic compound can be a vinyl ester formed from the (C_1-C_{10})hydrocarbylpolyol and the vinyl carboxylic acid or the salt, ester, or acid halide thereof that is reacted with the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol to form the VER. In some embodiments, polymerizing with the vinyl ester formed from the (C_1-C_{10})hydrocarbylpolyol and the vinyl carboxylic acid or the salt, ester, or acid halide thereof that is reacted with the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol to form the VER can result in elimination or reduction in use of styrene as the reactive diluent.

[0041] In some embodiments, the present invention provides a two-step method of forming VER from bisphenol. The reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol can occur in single reaction vessel. The reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER can occur in a single reaction vessel.

[0042] The bisphenol can be any suitable bisphenol (e.g., a compound containing two hydroxyphenyl functionalities). The bisphenol can be chosen from bisphenol A (2,2-bis(4-

hydroxyphenyl)propane), bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl-ethane), bisphenol AF (2,2-bis(4-hydroxyphenyl)hexafluoropropane), bisphenol B (2,2-bis(4-hydroxyphenyl)butane), bisphenol BP (bis-(4-hydroxyphenyl)diphenylmethane), bisphenol C (2,2-bis(3-methyl-4-hydroxyphenyl)propane), bisphenol E (1,1-bis(4-hydroxyphenyl)ethane), bisphenol F (bis(4-hydroxydiphenyl)methane), bisphenol G (2,2-bis(4-hydroxy-3-isopropyl-phenyl)propane), bisphenol PH (5,5'-(1-methylethyliden)-bis[1,1'-(bisphenyl)-2-ol]propane), bisphenol TMC (1,1-bis(4-hydroyphenyl)-3,3,5-trimethyl-cyclohexane), bisphenol Z (1,1-bis(4-hydroxyphenyl)-cyclohexane), and combinations thereof. The bisphenol can be bisphenol A (2,2-bis(4-hydroxyphenyl)propane).

[0043] The (C_1-C_{10})hydrocarbylpolyol can be any suitable (C_1-C_{10})hydrocarbylpolyol. The (C_1-C_{10})hydrocarbylpolyol can be a (C_1-C_{10})hydrocarbyltriol. The (C_1-C_{10})hydrocarbylpolyol can include at least two terminal hydroxy groups. The (C_1-C_{10})hydrocarbylpolyol can be a propanetriol. The (C_1-C_{10})hydrocarbylpolyol can be glycerol (1,2,3-trihydroxypropane).

[0044] The reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol can be performed in the presence of one or more etherification catalysts. The reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol can be performed in the presence of a base. The base can be a carbonate salt. The carbonate salt can be potassium carbonate.

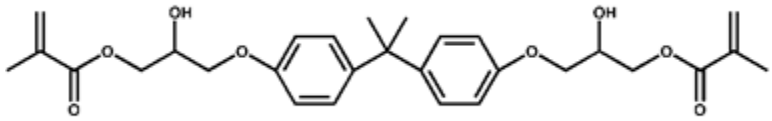
[0045] The reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol can be performed in the presence of an ester. The ester can be any suitable (C_1-C_{10})alkyl ester of a (C_1-C_{10})carboxylic acid. The ester can be diethyl carbonate.

[0046] The bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol can be bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE).

[0047] The vinyl carboxylic acid or the salt, ester, or acid halide thereof that is reacted with the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol to form the VER can be any suitable vinyl carboxylic acid or salt, ester, or acid halide thereof. The vinyl carboxylic acid or salt, ester, or acid halide thereof can be a substituted or unsubstituted (C_1-C_{10})hydrocarbyl ester of (C_3-C_{10})vinylcarboxylic acid. The vinyl carboxylic acid or salt, ester, or acid halide thereof can be a substituted or unsubstituted (C_1-C_{10})hydrocarbyl ester of methacrylic acid. The vinyl carboxylic acid or salt, ester, or acid halide thereof can be methyl methacrylate.

[0048] The reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or salt, ester, or acid halide thereof to form the VER can be performed in the presence of one or more esterification or transesterification catalysts. The reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or salt, ester, or acid halide thereof to form the VER can be performed in the presence of a base. The base can be a carbonate salt. The carbonate salt can be potassium carbonate.

[0049] The VER can have the structure:



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[0050] The VER can be purified using any suitable method, such as column chromatography or precipitation (e.g., from methanol/water).

[0051] The yield of the VER from the bisphenol can be any suitable yield, such as about 10% to about 100%, or such as about 10% or less, or less than, equal to, or greater than about 12%, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 82, 84, 86, 88, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 99.9, or about 99.99% or more. The conversion of the bisphenol can be any suitable conversion, such as 10% to about 100%, or such as about 10% or less, or less than, equal to, or greater than about 12%, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 82, 84, 86, 88, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 99.9, or about 99.99% or more. The yield of the VER from the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol can be any suitable yield, such as about 10% or less, or less than, equal to, or greater than about 12%, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 82, 84, 86, 88, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 99.9, or about 99.99% or more. The conversion of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol can be any suitable conversion, such as about 10% to about 100%, or such as about 10% or less, or less than, equal to, or greater than about 12%, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 82, 84, 86, 88, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 99.9, or about 99.99% or more.

[0052] In some embodiments, the present invention provides a one pot method of forming VER from bisphenol. Both the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol, and

the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or salt, ester, or acid halide thereof to form the VER, are performed in a single reaction vessel without any purification or work up between the reactions.

Method for producing a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of a bisphenol.

[0053] In various embodiments, the present invention provides a method for producing a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of a bisphenol. The method can include any embodiment of reacting a bisphenol with a (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol described herein. The reaction can occur in a single reaction vessel.

[0054] The method can be a method for producing bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE) including reacting bisphenol A with a glycerin to form the BABDHPE.

Examples

[0055] Various embodiments of the present invention can be better understood by reference to the following Examples which are offered by way of illustration. The present invention is not limited to the Examples given herein.

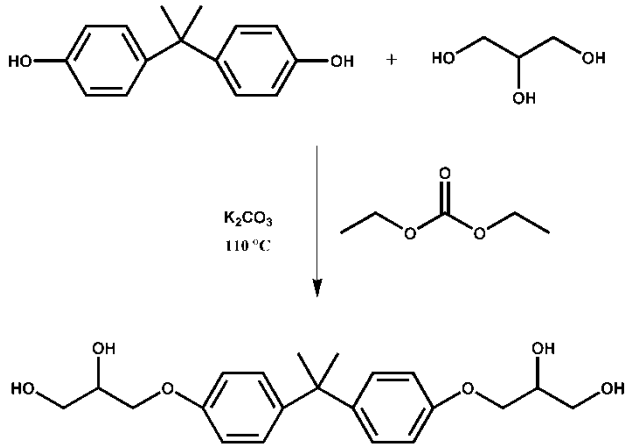
Example 1. One pot synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE).

[0056] Materials: Bisphenol A, diethylene carbonate and potassium carbonate were procured from Sigma Aldrich and utilized without further purification. Crude glycerol as a bio-waste was procured from Maine Standard Biofuels. Glycerol in pure from was obtained using vacuum distillation.

[0057] In a single necked round bottom flask bisphenol A (10 g, 43.80 mmol), glycerol (24.20 g, 262.82 mmol), diethyl carbonate (15.52 g, 131.4 mmol) and potassium carbonate (3 g, 21.70 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 110 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethylether and the ethanol byproduct. The hot reaction mixture was then added to a beaker containing 500 mL deionized water. A viscous reaction product was allowed to settle over time and the supernatant water removed. The crude

reaction product was washed twice with 500 mL water to remove any unreacted glycerol. The 99% pure Bisphenol A bis(2,3-dihydroxypropyl)ether was isolated in quantitative yields. The reaction is illustrated in Scheme 1.

[0058] Scheme 1. Reaction scheme for synthesis of bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE).



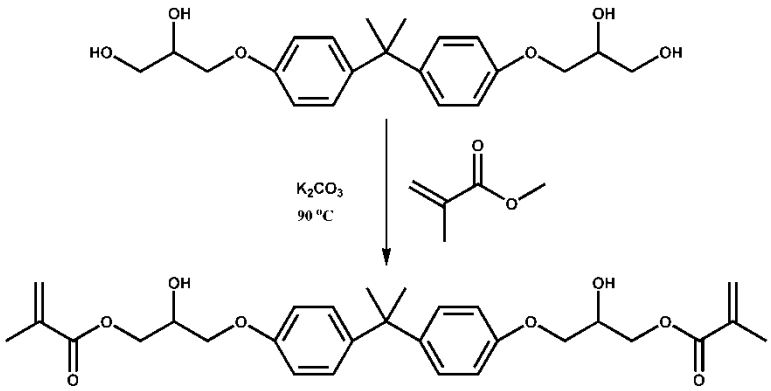
[0059] The purity of the reaction product was determined using proton NMR. FIG. 1 illustrates a proton NMR of isolated BABDHPE in DMSO-d^6. This solvent free reaction occurs through *in-situ* formation of glycerol carbonate as described in literature. The reaction can also be performed using commercially available glycerol carbonate instead of glycerol and diethyl carbonate.

Example 2. Synthesis of VER.

[0060] Materials: Methyl methacrylate and Potassium Carbonate were procured from Sigma Aldrich and utilized without further purification. The isolated BABDHPE was utilized for the reaction.

[0061] In a single necked round bottom flask Bisphenol A bis(2,3-dihydroxypropyl)ether (1 g, 2.65 mmol), as received Methyl methacrylate (1.32 g, 13.28 mmol) and Potassium Carbonate (300 mg, 2.17 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 90 °C. After 18 h the reaction was stopped by applying vacuum to remove any unreacted methyl methacrylate and the methanol byproduct. The reaction is illustrated in Scheme 2.

[0062] Scheme 2. Reaction scheme for synthesis of VER by transesterification of BABDHPE.



[0063] FIG. 2 illustrates a proton NMR of the synthesized VER in DMSO-d^6. Potassium carbonate was selected as an example here to demonstrate the feasibility of the reaction protocol. A 25% conversion was obtained in the current reaction protocol as evidenced by the presence of vinyl protons around 6.04 and 5.61 ppm.

[0064] The experiment was re-performed using a reaction temperature of 110 °C and using low vacuum, obtaining a conversion of about 99%.

Example 3. Single pot synthesis of VER.

[0065] The catalyst (potassium carbonate) utilized for the reactions described in Examples 1 and 2 is the same and it is used in same concentrations. Hence, the above two reactions can be combined to obtain VER.

[0066] Materials: Bisphenol A, diethylene carbonate, potassium carbonate, and methyl methacrylate were procured from Sigma Aldrich and utilized without further purification. Crude glycerol as a bio-waste was procured from Maine Standard Biofuels. Glycerol in pure from was obtained using vacuum distillation.

[0067] Procedure: In a single necked round bottom flask Bisphenol A (1 g, 4.38 mmol), Glycerol (2.42 g, 26.28 mmol), Diethyl carbonate (1.552 g, 1.314 mmol) and Potassium Carbonate (300 mg, 2.17 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 110 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethyl carbonate, glycerol, and ethanol byproduct.

[0068] To the crude reaction mixture 5 mL of dimethyl sulfoxide was added to reduce the viscosity of the reaction mixture and 3 mL of methyl methacrylate was added. The transesterification reaction was performed at 110 °C with the application of mild vacuum to remove the azeotrope formed by methanol and methyl methacrylate. After 12 hours the vacuum was increased to remove any unreacted methyl methacrylate and methanol byproduct. The crude reaction mixture in dimethyl sulfoxide was then introduced into 1:8 mixture of methanol:deionized water to precipitate the product and centrifuged to obtain a viscous precipitate. The precipitate was washed 3 times with 1:8 mixture of methanol:deionized water to remove any trapped methyl methacrylate and glycerol derivative. The resulting crude product was analyzed by proton NMR and a 99% conversion was observed. The purification of the product was done by column chromatography on silica gel with a mixture of 3:7 hexanes:ethyl acetate as the eluent. The first fraction contained the VER product. A proton NMR of the VER product in DMSO d^6 is shown in FIG. 3.

[0069] The terms and expressions that have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the embodiments of the present invention. Thus, it should be understood that although the present invention has been specifically disclosed by specific embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those of ordinary skill in the art, and that such modifications and variations are considered to be within the scope of embodiments of the present invention.

<u>Additional Embodiments.</u>

[0070] The following exemplary embodiments are provided, the numbering of which is not to be construed as designating levels of importance:

[0071] Embodiment 1 provides a method for producing a vinyl ester resin (VER), the method comprising:

reacting a bisphenol with a (C_1-C_{10})hydrocarbylpolyol to form a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol; and

reacting the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with a vinyl carboxylic acid or a salt, ester, or acid halide thereof, to form the VER.

[0072] Embodiment 2 provides the method of Embodiment 1, further comprising polymerizing the VER.

[0073] Embodiment 3 provides the method of any one of Embodiments 1-2, further comprising polymerizing the VER with a vinyl-substituted organic compound.

[0074] Embodiment 4 provides the method of Embodiment 3, wherein the vinyl-substituted organic compound is styrene.

[0075] Embodiment 5 provides the method of any one of Embodiments 3-4, wherein the vinyl-substituted organic compound is a vinyl ester formed from the (C_1-C_{10})hydrocarbylpolyol and the vinyl carboxylic acid or the salt, ester, or acid halide thereof.

[0076] Embodiment 6 provides the method of any one of Embodiments 1-5, wherein the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol occurs in single reaction vessel.

[0077] Embodiment 7 provides the method of any one of Embodiments 1-6, wherein the bisphenol is chosen from bisphenol A (2,2-bis(4-hydroxyphenyl)propane), bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl-ethane), bisphenol AF (2,2-bis(4-hydroxyphenyl)hexafluoropropane), bisphenol B (2,2-bis(4-hydroxyphenyl)butane), bisphenol BP (bis-(4-hydroxyphenyl)diphenylmethane), bisphenol C (2,2-bis(3-methyl-4-hydroxyphenyl)propane), bisphenol E (1,1-bis(4-hydroxyphenyl)ethane), bisphenol F (bis(4-hydroxydiphenyl)methane), bisphenol G (2,2-bis(4-hydroxy-3-isopropyl-phenyl)propane), bisphenol PH (5,5'-(1-methylethyliden)-bis[1,1'-(bisphenyl)-2-ol]propane), bisphenol TMC (1,1-bis(4-hydroyphenyl)-3,3,5-trimethyl-cyclohexane), bisphenol Z (1,1-bis(4-hydroxyphenyl)-cyclohexane), and combinations thereof.

[0078] Embodiment 8 provides the method of any one of Embodiments 1-7, wherein the bisphenol is bisphenol A (2,2-bis(4-hydroxyphenyl)propane).

[0079] Embodiment 9 provides the method of any one of Embodiments 1-8, wherein the (C_1-C_{10})hydrocarbylpolyol is a (C_1-C_{10})hydrocarbyltriol.

[0080] Embodiment 10 provides the method of any one of Embodiments 1-9, wherein the (C_1-C_{10})hydrocarbylpolyol comprises at least two terminal hydroxy groups.

[0081] Embodiment 11 provides the method of any one of Embodiments 1-10, wherein the (C_1-C_{10})hydrocarbylpolyol is a propanetriol.

[0082] Embodiment 12 provides the method of any one of Embodiments 1-11, wherein the (C_1-C_{10})hydrocarbylpolyol is glycerol.

[0083] Embodiment 13 provides the method of any one of Embodiments 1-12, wherein the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol is performed in the presence of one or more etherification catalysts.

[0084] Embodiment 14 provides the method of any one of Embodiments 1-13, wherein the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol is performed in the presence of a base.

[0085] Embodiment 15 provides the method of Embodiment 14, wherein the base is a carbonate salt.

[0086] Embodiment 16 provides the method of Embodiment 15, wherein the carbonate salt is potassium carbonate.

[0087] Embodiment 17 provides the method of any one of Embodiments 1-16, wherein the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol is performed in the presence of an ester.

[0088] Embodiment 18 provides the method of Embodiment 17, wherein the ester is diethyl carbonate.

[0089] Embodiment 19 provides the method of any one of Embodiments 1-18, wherein the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol is bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE).

[0090] Embodiment 20 provides the method of any one of Embodiments 1-19, wherein the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER occurs in a single reaction vessel.

[0091] Embodiment 21 provides the method of any one of Embodiments 1-20, wherein the vinyl carboxylic acid or salt, ester, or acid halide thereof is a substituted or unsubstituted (C_1-C_{10})hydrocarbyl ester of (C_3-C_{10})vinylcarboxylic acid.

[0092] Embodiment 22 provides the method of Embodiment 21, wherein the vinyl carboxylic acid or the salt, ester, or acid halide thereof is a substituted or unsubstituted (C_1-C_{10})hydrocarbyl ester of methacrylic acid.

[0093] Embodiment 23 provides the method of any one of Embodiments 1-22, wherein the vinyl carboxylic acid or the salt, ester, or acid halide thereof is methyl methacrylate.

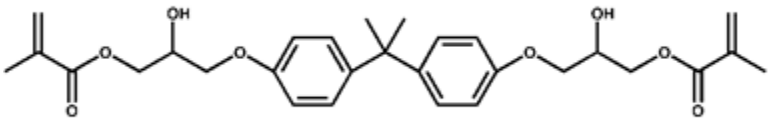
[0094] Embodiment 24 provides the method of any one of Embodiments 1-23, wherein the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER is performed in the presence of one or more esterification or transesterification catalysts.

[0095] Embodiment 25 provides the method of any one of Embodiments 1-24, wherein the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER is performed in the presence of a base.

[0096] Embodiment 26 provides the method of Embodiment 25, wherein the base is a carbonate salt.

[0097] Embodiment 27 provides the method of Embodiment 26, wherein the carbonate salt is potassium carbonate.

[0098] Embodiment 28 provides the method of any one of Embodiments 1-27, wherein the VER has the structure:



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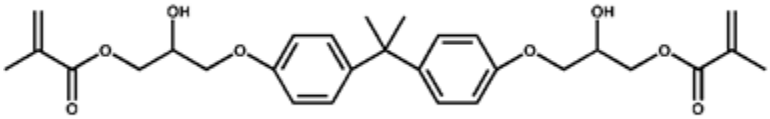
Embodiment 29 provides the method of any one of Embodiments 1-28, wherein both the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol, and the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER, are performed in a single reaction vessel without any purification or work up between the reactions.

[0099] Embodiment 30 provides a method for producing a vinyl ester resin (VER), the method comprising:

reacting bisphenol A with glycerin to form bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE); and

reacting the BABDHPE with methyl methacrylate to form the VER, wherein the VER has the structure:



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[00100] Embodiment 31 provides a method for producing a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of a bisphenol, the method comprising:

reacting a bisphenol with a (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol.

[00101] Embodiment 32 provides a method for producing bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE), the method comprising:

reacting bisphenol A with a glycerin to form the BABDHPE.

[00102] Embodiment 33 provides the method of any one or any combination of Embodiments 1-32 optionally configured such that all elements or options recited are available to use or select from.

CLAIMS

What is claimed is:

1. A method for producing a vinyl ester resin (VER), the method comprising:

reacting a bisphenol with a (C_1-C_{10})hydrocarbylpolyol to form a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol; and

reacting the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with a vinyl carboxylic acid or a salt, ester, or acid halide thereof, to form the VER.

2. The method of claim 1, further comprising polymerizing the VER.

3. The method of claim 1, further comprising polymerizing the VER with a vinyl-substituted organic compound.

4. The method of claim 3, wherein the vinyl-substituted organic compound is styrene.

5. The method of claim 3, wherein the vinyl-substituted organic compound is a vinyl ester formed from the (C_1-C_{10})hydrocarbylpolyol and the vinyl carboxylic acid or the salt, ester, or acid halide thereof.

6. The method of claim 1, wherein the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol occurs in single reaction vessel.

7. The method of claim 1, wherein the bisphenol is chosen from bisphenol A (2,2-bis(4-hydroxyphenyl)propane), bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl-ethane), bisphenol AF (2,2-bis(4-hydroxyphenyl)hexafluoropropane), bisphenol B (2,2-bis(4-hydroxyphenyl)butane), bisphenol BP (bis-(4-hydroxyphenyl)diphenylmethane), bisphenol C (2,2-bis(3-methyl-4-hydroxyphenyl)propane), bisphenol E (1,1-bis(4-hydroxyphenyl)ethane), bisphenol F (bis(4-hydroxydiphenyl)methane), bisphenol G (2,2-bis(4-hydroxy-3-isopropyl-phenyl)propane), bisphenol PH (5,5'-(1-methylethyliden)-bis[1,1'-(bisphenyl)-2-ol]propane),

bisphenol TMC (1,1-bis(4-hydroyphenyl)-3,3,5-trimethyl-cyclohexane), bisphenol Z (1,1-bis(4-hydroxyphenyl)-cyclohexane), and combinations thereof.

8. The method of claim 1, wherein the bisphenol is bisphenol A (2,2-bis(4-hydroxyphenyl)propane).

9. The method of claim 1, wherein the (C_1-C_{10})hydrocarbylpolyol is a (C_1-C_{10})hydrocarbyltriol.

10. The method of claim 1, wherein the (C_1-C_{10})hydrocarbylpolyol comprises at least two terminal hydroxy groups.

11. The method of claim 1, wherein the (C_1-C_{10})hydrocarbylpolyol is a propanetriol.

12. The method of claim 1, wherein the (C_1-C_{10})hydrocarbylpolyol is glycerol.

13. The method of claim 1, wherein the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol is performed in the presence of one or more etherification catalysts.

14. The method of claim 1, wherein the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol is performed in the presence of a base.

15. The method of claim 14, wherein the base is a carbonate salt.

16. The method of claim 15, wherein the carbonate salt is potassium carbonate.

17. The method of claim 1, wherein the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol is performed in the presence of an ester.

18. The method of claim 17, wherein the ester is diethyl carbonate.

19. The method of claim 1, wherein the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol is bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE).

20. The method of claim 1, wherein the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER occurs in a single reaction vessel.

21. The method of claim 1, wherein the vinyl carboxylic acid or salt, ester, or acid halide thereof is a substituted or unsubstituted (C_1-C_{10})hydrocarbyl ester of (C_3-C_{10})vinylcarboxylic acid.

22. The method of claim 21, wherein the vinyl carboxylic acid or the salt, ester, or acid halide thereof is a substituted or unsubstituted (C_1-C_{10})hydrocarbyl ester of methacrylic acid.

23. The method of claim 1, wherein the vinyl carboxylic acid or the salt, ester, or acid halide thereof is methyl methacrylate.

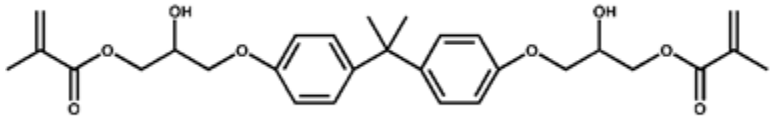
24. The method of claim 1, wherein the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER is performed in the presence of one or more esterification or transesterification catalysts.

25. The method of claim 1, wherein the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER is performed in the presence of a base.

26. The method of claim 25, wherein the base is a carbonate salt.

27. The method of claim 26, wherein the carbonate salt is potassium carbonate.

28. The method of claim 1, wherein the VER has the structure:



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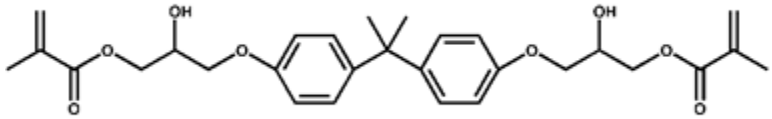
29. The method of claim 1, wherein both the reaction of the bisphenol with the (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol, and the reaction of the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with the vinyl carboxylic acid or the salt, ester, or acid halide thereof to form the VER, are performed in a single reaction vessel without any purification or work up between the reactions.

30. A method for producing a vinyl ester resin (VER), the method comprising:

reacting bisphenol A with glycerin to form bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE); and

reacting the BABDHPE with methyl methacrylate to form the VER, wherein the VER has the structure:



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31. A method for producing a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of a bisphenol, the method comprising:

reacting a bisphenol with a (C_1-C_{10})hydrocarbylpolyol to form the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol.

32. A method for producing bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE), the method comprising:

reacting bisphenol A with a glycerin to form the BABDHPE.

ABSTRACT

Various embodiments of the present invention relate to methods of making bis(hydroxyhydrocarbyl)ether bisphenol and vinyl ester resin. In various embodiments, the present invention provides a method for producing a vinyl ester resin (VER). The method can include reacting a bisphenol with a (C_1-C_{10})hydrocarbylpolyol to form a bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol. The method can include reacting the bis(hydroxy((C_1-C_{10})hydrocarbyl)ether of the bisphenol with a vinyl ester to form the VER.

FIGURES

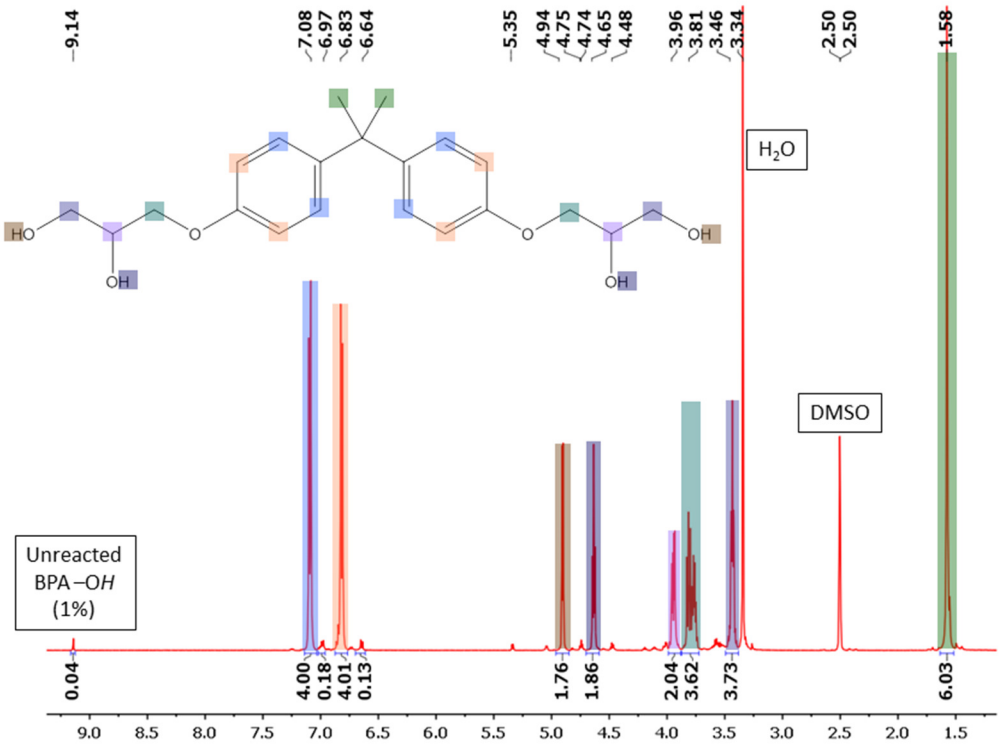

FIG. 1.

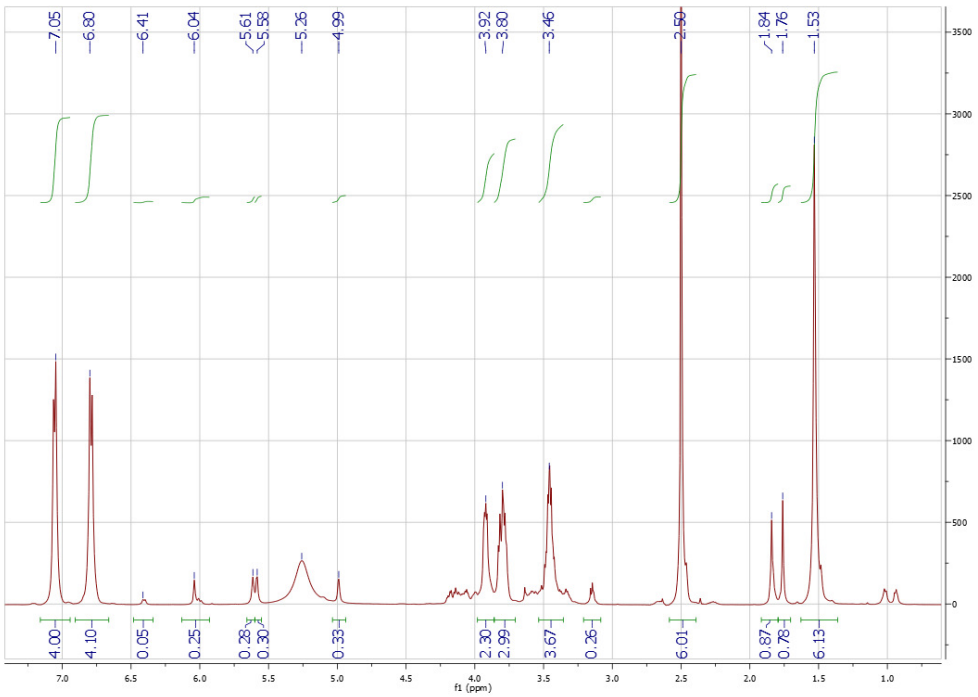
7.05
6.80
6.41
6.04
5.61
5.58
5.26
4.99
3.92
3.80
3.46
2.50
1.84
1.76
1.53
4.00
4.10
0.05
0.25
0.28
0.30
0.33
2.30
2.99
3.67
0.26
6.01
0.87
0.78
6.13
f1 (ppm)

FIG. 2.

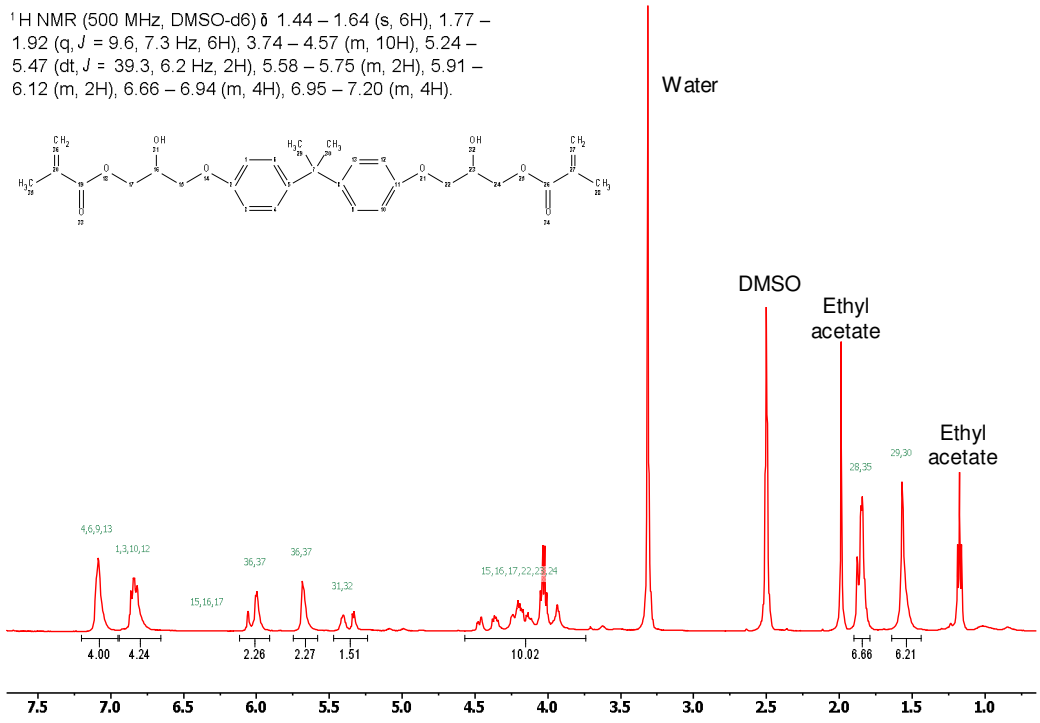
1 H NMR (500 MHz, DMSO-d6) δ 1.44 – 1.64 (s, 6H), 1.77 – 1.92 (q, J = 9.6, 7.3 Hz, 6H), 3.74 – 4.57 (m, 10H), 5.24 – 5.47 (dt, J = 39.3, 6.2 Hz, 2H), 5.58 – 5.75 (m, 2H), 5.91 – 6.12 (m, 2H), 6.66 – 6.94 (m, 4H), 6.95 – 7.20 (m, 4H).
Water
DMSO
Ethyl acetate
Ethyl acetate
4,6,9,13
1,3,10,12
15,16,17
36,37
36,37
31,32
15,16,17,22,23,24
28,35
29,30
4.00
4.24
2.26
2.27
1.51
10.02
6.66
6.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

FIG. 3.

Appendix B

PCT PATENT APPLICATION

VINYL HYDROXYL ETHER RESINS

INVENTORS:

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Docket No.: SLW 4724.007WO1, UML 2015-041

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Minneapolis, MN 55402

VINYL HYDROXYL ETHER RESINS

CROSS-REFERENCE TO RELATED APPLICATION

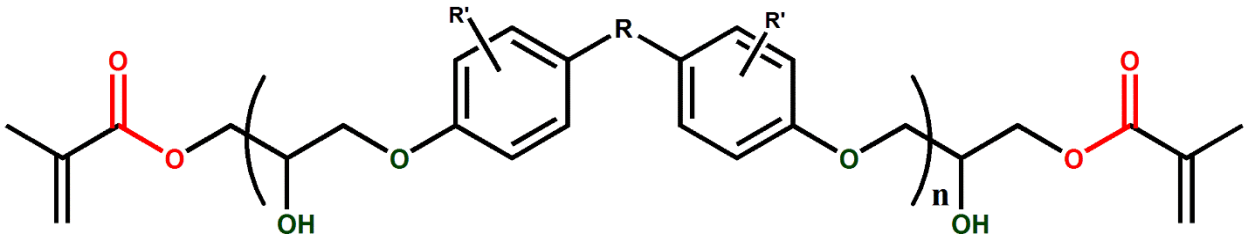
[0001] This application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 62/303,724, filed March 4, 2016, the disclosure of which is incorporated herein in its entirety by reference.

BACKGROUND

[0002] Vinyl ester resins (VERs) are high performance unsaturated resins with exceptional mechanical strength and corrosion resistance. In addition to their superior performance, these resins display lower viscosities than conventional epoxy resins resulting in significantly improved processability. Due to their superior properties and excellent processability, VERs find use, either in pure form or as a matrix in fiber reinforced composites, in diverse industries, such as, ship building, automotive part construction, infrastructure polymer concrete reinforcements, corrosion resistance coatings (on chemical storage tanks, pipes and ducting, fume extraction systems, gas cleaning units), top-coat materials (with excellent adhesion to plastics, steel and concrete), optical fiber coating, UV curing inks and printed circuit board manufacture (*Jaswal, S.; Gaur, B. 'New trends in vinyl ester resins' Rev. Chem. Eng. 2014, DOI 10.1515/revce-2014-0012*). The versatility of these resins for diverse applications has resulted in a huge global market and ever increasing potential.

[0003] VERs are currently synthesized by addition reaction of epoxide resins with unsaturated carboxylic acids. A variety of chemical compounds containing the epoxy groups have been used for synthesis of VERs. Particularly bisphenol-A (BPA) based VER resins are widely utilized due to their exceptional mechanical strength and chemical resistance. Currently for BPA based VER synthesis, the epoxy containing bisphenol-A diglycidyl ether (BADGE) is reacted with either methacrylic acid or methyl methacylate. These resins were first commercialized as Epocryl resins by Shell Chemical Company and later as Derakane resins by Dow Chemical Company. Currently these resins are produced predominantly by Ashland, DSM and Reichold.

[0004] VERs typically have the following structure:

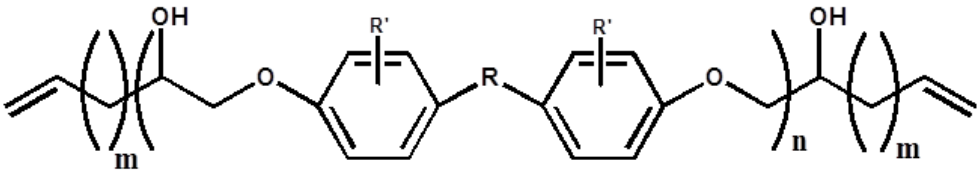


[0005] Although VERs are widely utilized, the structure still contains ester linkages which are susceptible to chemical and thermal degradation. The hydroxyl group present in the VER, however, is vital for its interaction with a variety of substrates and fiber reinforcements.

[0006] Hence, a structure containing the hydroxyl group and no ester linkages would result in significantly more stable class of resins. A compound displaying these structural motifs has not been reported yet.

SUMMARY OF THE INVENTION

[0007] In various embodiments, the present invention provides a vinyl hydroxyl ether resin (VHER) having the general structure:



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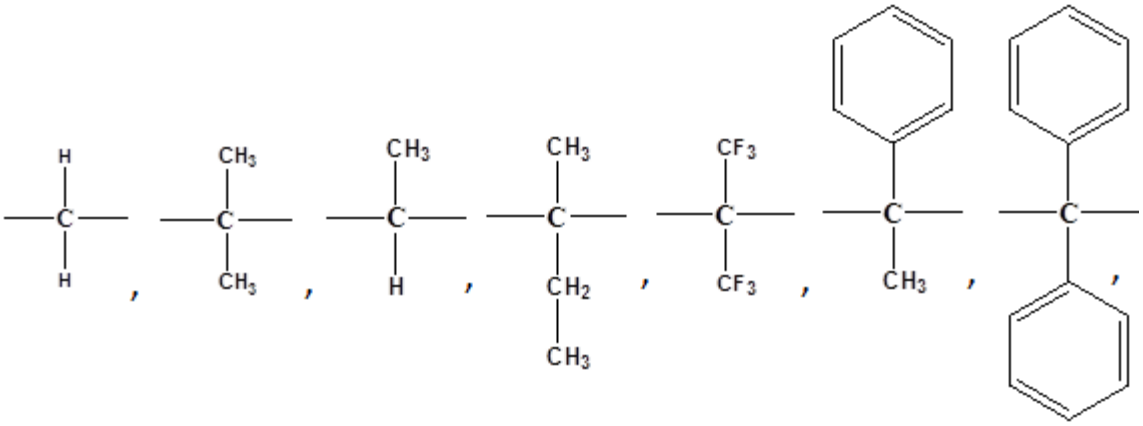
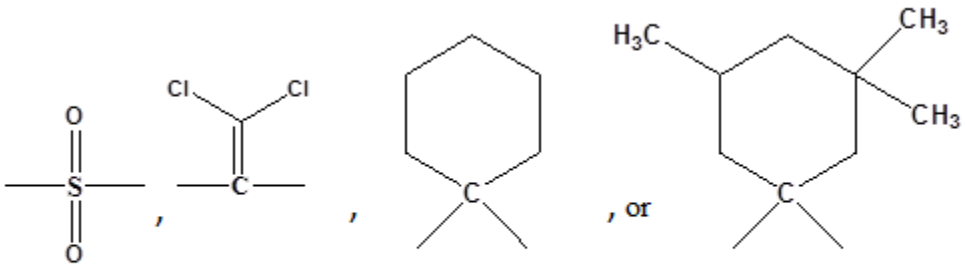
in which m and n are integers. The end groups can be either be an allyl alcohol where m = 0 or comprised of multiple aliphatic repeating units where m ≥ 1. In various embodiments, m ranges from 0 to 100, and n ranges from 1 to 100. At each occurrence, R' independently represents hydrogen, or mono-, di-, or tri-substitution of (C_1-C_{10})hydrocarbyl. The variable R represents O, SO_2, or $C(R^1)_2$. Each occurrence of R^1 is independently chosen from hydrogen, phenyl, and substituted or unsubstituted (C_1-C_{10})hydrocarbyl. In one embodiment, R^1 is (C_1-C_{10})hydrocarbyl substituted with one or more halogens selected from F, Cl, and Br. In some embodiments R is:





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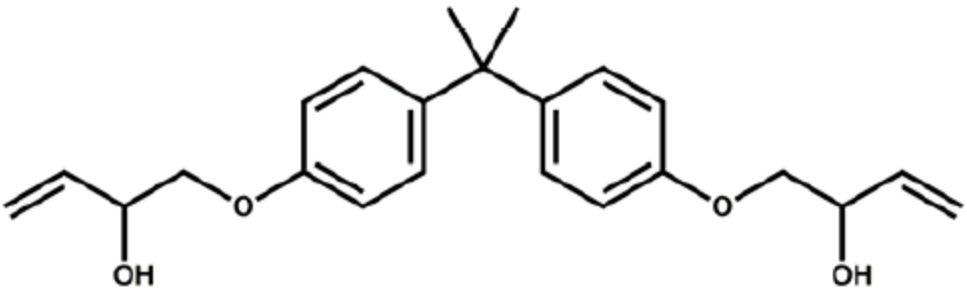
[0008] In one embodiment, R' is CH_3 or $CH(CH_3)_2$.

[0009] In various embodiments, the present invention provides a vinyl hydroxyl ether resin (VHER) having the structure:



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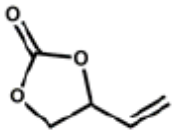
Some embodiments provide a polymerization product of a starting material composition that includes the VHER. Some embodiments provide a method of making the VHER including combining Bisphenol A:

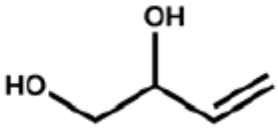
,

with vinyl ethylene carbonate:



,

or with 3-butene-(1,2-diol):



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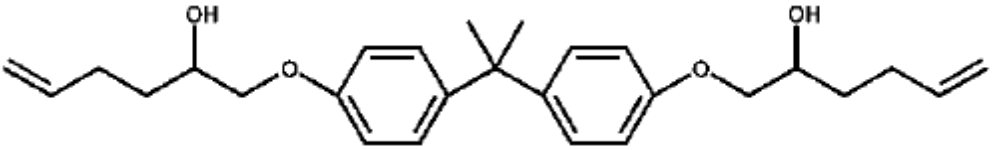
under conditions sufficient to give the VHER

[0010] Various embodiments provide a vinyl hydroxyl ether resin (VHER) having the structure:



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Some embodiments provide a polymerization product of a starting material composition, the starting material composition including the VHER. Some embodiments provide a method of making the VHER including combining Bisphenol A:

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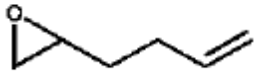
with 3-butene-(1,2-diol):



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under conditions sufficient to give the VHER.

[0011] Various embodiments include a new class of resins, vinyl hydroxyl ether resin (VHER). Various embodiments including an environmentally benign "green" methodology for the synthesis of the VHERs. Various embodiments provide a novel single-step synthetic protocol for the synthesis of the VHERs.

[0012] In some embodiments, the retention of hydroxyl moieties in the structure of the VHERs would introduce stronger interactions with a variety of substrates and fiber reinforcements, as compared to other resins. In various embodiments, the elimination of ester moieties in the structure of the VHERs can provide improved stability towards chemical and thermal degradation of the resin. In various embodiments, the VHER can be cured to produce a thermoset polymer with reduced polar ester groups, compared to polymer made from VERs. This can advantageously reduce or minimize blistering-type defects, often observed in long term use of VER polymers in aquatic environments. In various embodiments, the VHER has improved chemical stability compared to other resins, which can be used to produce thinner corrosion resistant coatings. Thinner coatings can help in lowering the environmental footprint of the materials.

[0013] In some embodiments a reactive diluent (e.g., styrene) can be used in formulations for reduction of VHER viscosity. The reduction in viscosity can aid in efficient processing of the resin. However, styrene is a carcinogenic compound, and hence a reduced amount in the formulations is desired for safer work environment. VHER displays lower viscosity than vinyl epoxy resin (VER), which would reduce the amount of required reactive diluent (e.g., styrene) in the formulations, resulting in "greener" formulations.

[0014] In various embodiments, the VHER can be a more stable alternative to widely utilized resins used in diverse industries, such as, ship building, automotive part construction, infrastructure polymer concrete reinforcements, corrosion resistance coatings (e.g., on chemical storage tanks, pipes and ducting, fume extraction systems, gas cleaning units), top-coat materials (e.g., with excellent adhesion to plastics, steel and concrete), optical fiber coating, UV curing inks, printed circuit board manufacture, and fiber-reinforced composites.

BRIEF DESCRIPTION OF THE FIGURES

[0015] The drawings illustrate generally, by way of example, but not by way of limitation, various embodiments of the present invention.

[0016] FIG.1 is a reaction scheme for synthesis of model compound Bisphenol A bis(2-hydroxypropyl)ether (BABHPE)

[0017] FIG. 2 is the proton NMR spectrum of BABHPE in DMSO-d^6.

[0018] FIG. 3 is a reaction scheme for synthesis of VHER by employing vinyl ethylene carbonate.

[0019] FIG. 4 is the proton NMR of a VHER in DMSO-d^6.

[0020] FIG. 5 is a reaction scheme for the synthesis of VHER by employing 3-butene-(1,2-diol).

[0021] FIG. 6 is a reaction scheme for synthesis of VHER by employing 1,2-epoxy-5-hexene.

[0022] FIG. 7 shows photographs of Derakane and VHER formulations (top row). Cured formulations and solid tack-free thermoset products (bottom row).

[0023] FIG. 8 is the proton NMR and FTIR spectra of a VHER. FIG. 8A is the proton NMR of VHER in DMSO d^6. FIG. 8B is FTIR spectra for a VHER (upper line, red) and BPA (lower line, black).

[0024] FIG. 9 is a photograph of cured one pot synthesized VHER with 33% styrene.

[0025] FIG. 10 is a plot of Storage Modulus, Loss Modulus and Tan Delta traces obtained using the cured one pot synthesized VHER with 33% styrene.

[0026] FIG. 11 is a plot of TGA traces for cured VHER (top) and Derakane 411-400 (bottom).

[0027] FIG. 12 is photographs of cured coatings of VHER (left) and Derakane 411-400 (right) after immersion in conc. H_2SO_4 for 48 hours.

[0028] FIG. 13 is a plot of water uptake measurements for cured Derakane 411-400 (top, black) and VHER (bottom, red).

[0029] FIG. 14 is photographs of VHER (left) and Derakane (right) coatings after the ASTM D3350 Adhesion Tape test.

[0030] FIG. 15 is photographs of the 0T, 1T, and 2T bend test results for VHER and Derakane 441-400 VER coatings after MEK double rub testing.

[0031] FIG. 16 is 0T bend test results for VHER (top) and Derakane (bottom) coatings after immersion in concentrated H_2SO_4 for 48 hours.

DETAILED DESCRIPTION OF THE INVENTION

[0032] Reference will now be made in detail to certain embodiments of the disclosed subject matter, examples of which are illustrated in part in the accompanying drawings. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that the exemplified subject matter is not intended to limit the claims to the disclosed subject matter.

[0033] Throughout this document, values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of "about 0.1% to about 5%" or "about 0.1% to 5%" should be interpreted to include not just about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement "about X to Y" has the same meaning as "about X to about Y," unless indicated otherwise. Likewise, the statement "about X, Y, or about Z" has the same meaning as "about X, about Y, or about Z," unless indicated otherwise.

[0034] In this document, the terms "a," "an," or "the" are used to include one or more than one unless the context clearly dictates otherwise. The term "or" is used to refer to a nonexclusive "or" unless otherwise indicated. The statement "at least one of A and B" has the same meaning as "A, B, or A and B." In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section

[0035] In the methods described herein, the acts can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is

explicitly recited. Furthermore, specified acts can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed act of doing X and a claimed act of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

[0036] The term “about” as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range, and includes the exact stated value or range.

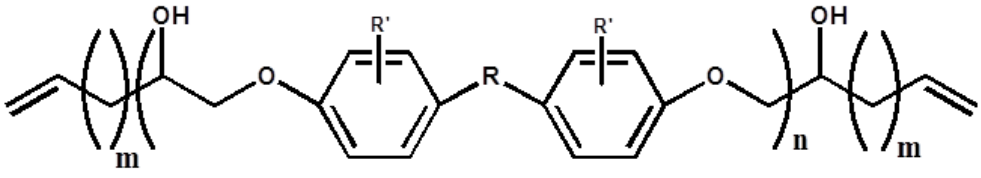
[0037] The term “substantially” as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more, or 100%.

[0038] As used herein, the term “polymer” refers to a molecule having at least one repeating unit and can include copolymers.

[0039] The polymers described herein can terminate in any suitable way. In some embodiments, the polymers can terminate with an end group that is independently chosen from a suitable polymerization initiator, -H, -OH, a substituted or unsubstituted (C_1-C_{20})hydrocarbyl (e.g., (C_1-C_{10})alkyl or (C_6-C_{20})aryl) interrupted with 0, 1, 2, or 3 groups independently selected from -O-, substituted or unsubstituted -NH-, and -S-, a poly(substituted or unsubstituted (C_1-C_{20})hydrocarbyloxy), and a poly(substituted or unsubstituted (C_1-C_{20})hydrocarbylamino).The term “hydrocarbon” or “hydrocarbyl” as used herein refers to a molecule or functional group that includes carbon and hydrogen atoms. The term can also refer to a molecule or functional group that normally includes both carbon and hydrogen atoms but wherein all the hydrogen atoms are substituted with other functional groups.

[0040] As used herein, the term “substituted” as used herein in conjunction with a molecule or an organic group as defined herein refers to the state in which one or more hydrogen atoms contained therein are replaced by one or more non-hydrogen atoms.

[0041] In one embodiment the present invention provides a vinyl hydroxyl ether resin (VHER) having the structure:



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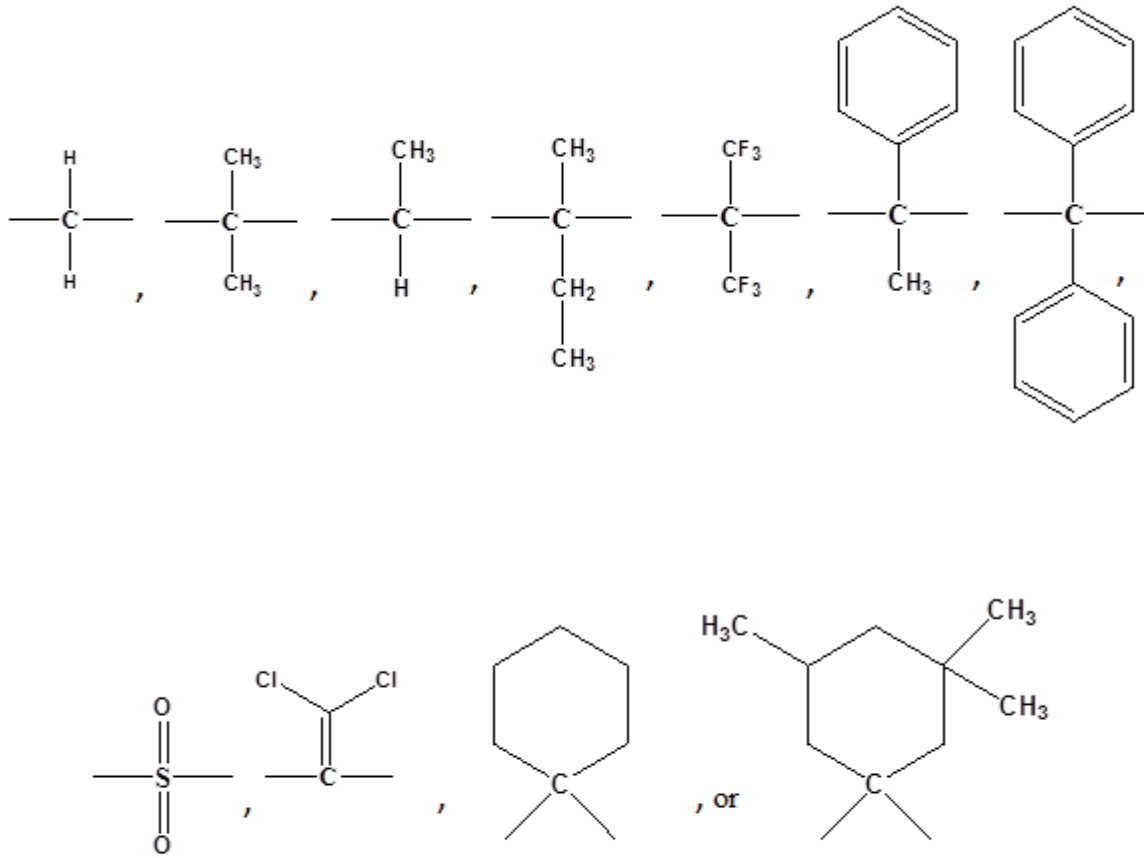
in which m and n are integers. The end groups can be either be an allyl alcohol where m = 0 or comprised of multiple aliphatic repeating units where m ≥ 1. In various embodiments, m ranges from 0 to 100, and n ranges from 1 to 100. At each occurrence, R' independently represents hydrogen, or mono-, di-, or tri-substitution of (C_1-C_{10})hydrocarbyl. The variable R represents O, SO_2, or $C(R^1)_2$. Each occurrence of R^1 is independently chosen from hydrogen, phenyl, and substituted or unsubstituted (C_1-C_{10})hydrocarbyl. In one embodiment, R^1 is (C_1-C_{10})hydrocarbyl substituted with one or more halogens selected from F, Cl, and Br. In some embodiments R is



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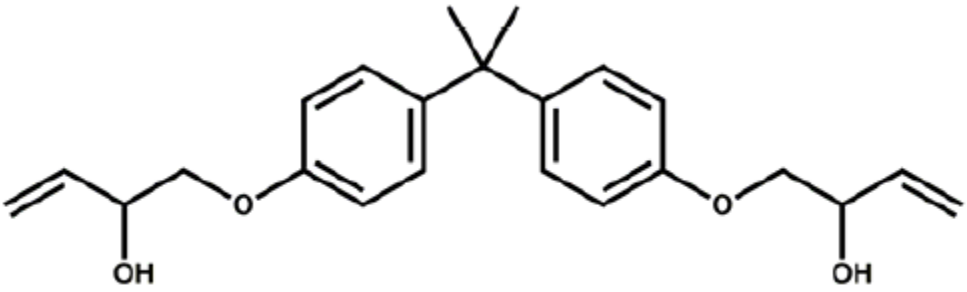
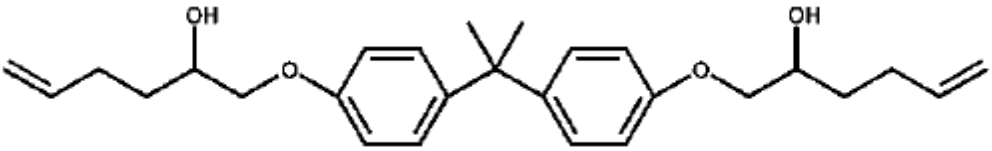
[0042] In one embodiment, R' is CH_3 or $CH(CH_3)_2$.

[0043] In some embodiments the VHER has the structure



,

or the structure:



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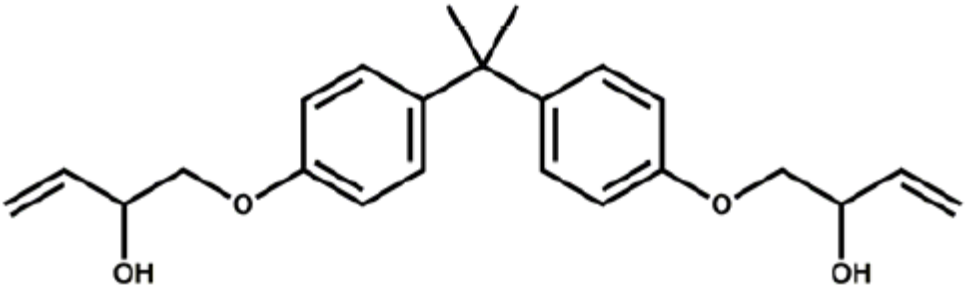
[0044] In one embodiment, a method of making the VHER with the structure



includes combining Bisphenol A:

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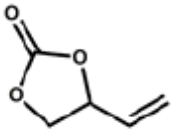
with vinyl ethylene carbonate:



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under conditions sufficient to give the VHER. In some embodiments, the reaction is carried out under basic conditions. The base can be any suitable base that is capable of deprotonating the

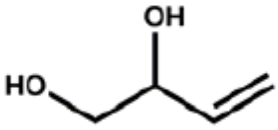
phenolic starting material. Suitable bases include, but are not limited to, lithium carbonate, sodium carbonate, potassium carbonate, lithium hydride, sodium hydride, and potassium hydride. The reaction is typically conducted by heating the reagents neat (without solvent). A suitable reaction temperature can be between 50-200 ºC, or between 100-150 ºC.

[0045] Suitable phenols for the reaction are not limited to Bisphenol A. Other suitable phenols include, but are not limited to, bisphenol AP (1,1-bis(4-hydroxyphenyl)-1-phenyl-ethane), bisphenol AF (2,2-bis(4-hydroxyphenyl)hexafluoropropane), bisphenol B (2,2-bis(4-hydroxyphenyl)butane), bisphenol BP (bis-(4-hydroxyphenyl)diphenylmethane), bisphenol C (2,2-bis(3-methyl-4-hydroxyphenyl)propane), bisphenol E (1,1-bis(4-hydroxyphenyl)ethane), bisphenol F (bis(4-hydroxydiphenyl)methane), bisphenol G (2,2-bis(4-hydroxy-3-isopropyl-phenyl)propane), bisphenol PH (5,5'-(1-methylethyliden)-bis[1,1'-(bisphenyl)-2-ol]propane), bisphenol TMC (1,1-bis(4-hydroyphenyl)-3,3,5-trimethyl-cyclohexane), bisphenol Z (1,1-bis(4-hydroxyphenyl)-cyclohexane), and combinations thereof.

[0046] In one embodiment, the VHER can be made by a method including:
combining Bisphenol A:

,

with 3-butene-(1,2-diol):



,

under conditions sufficient to give the VHER, according to the conditions described above.

[0047] In another embodiment, a method of making the VHER includes
combining Bisphenol A:

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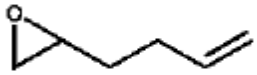
with 1,2-epoxy-5-hexene:



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under conditions sufficient to give the VHER. Advantageously, when epoxide starting materials are used, an environmentally friendly solvent-free reaction single pot reaction can be conducted. Other suitable epoxides include, but are not limited to, 2-epoxy-6-heptene, 1,2-epoxy-7-octene, 1,2-epoxy-8-nonene, 1,2-epoxy-9-decene, or combinations thereof. Suitable reaction conditions for reacting a phenol and an epoxide and a phenol are described in, for example, Lee et al. RSC Adv. 2015, 5, 38673-38679.

Examples

[0048] Various embodiments of the present invention can be better understood by reference to the following Examples which are offered by way of illustration. The present invention is not limited to the Examples given herein.

Example 1. One step protocol used for synthesis of a model compound bisphenol A bis(2-hydroxypropyl)ether (BABHPE).

[0049] Following is the detailed one step protocol used for synthesis of a model compound Bisphenol A bis(2-hydroxypropyl)ether (BABHPE).

[0050] Materials. Bisphenol A, propylene glycol, diethylene carbonate and potassium carbonate were procured from Sigma Aldrich and utilized without further purification.

[0051] In a single necked round bottom flask bisphenol A (1 g, 4.38 mmol), propylene glycol (1.99 g, 26.28 mmol), diethyl carbonate (1.55 g, 13.14 mmol), and potassium carbonate (0.302 g, 2.19 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 115 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethylether and the ethanol byproduct. The hot reaction mixture was then added to a beaker containing 500 mL deionized water. A viscous reaction product was allowed to settle over time and the supernatant water removed. The 85% pure Bisphenol A bis(2-hydroxypropyl)ether (BABHPE) was isolated in quantitative yields. The purity of the reaction product was determined using proton NMR shown herein at Figure 2. This

solvent free reaction occurs through *in-situ* formation of glycerol carbonate as described in literature (Truscello A. M. et al. Green Chemistry 2013, 15, 625).

Example 2. Synthesis of VHER.

[0052] The model reaction procedure given in Example 1 establishes the synthetic procedure for VHER. As in-situ formation of the cyclic carbonate occurs, two different synthesis strategies can be used as presented below (Figure 3 and 4). The reactions thus performed will be single step and single pot procedures. Investigations on these concepts are underway and the results will be included here. By changing the length of the alkyl segments (e.g., hexyl, octyl etc.) used the viscosity and other properties of the final product can be tailored. The use of longer alkyl chains would also provide non-allylic product. This can be performed by using longer chain 1,2-diols, for example by using 5-hexene-(1,2-diol), as a reactant with Bisphenol A.

[0053] Materials. Bisphenol A, vinyl ethylene carbonate, and potassium carbonate were procured from Sigma Aldrich and utilized without further purification.

[0054] In a single necked round bottom flask Bisphenol A (1 g), as received Vinyl ethylene carbonate (1.5 mL) and potassium carbonate (300 mg) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 115 °C. After 18 h the reaction was stopped by applying vacuum to remove any unreacted vinyl ethylene carbonate. The obtained product was dissolved in 3 mL of dimethyl sulfoxide and added dropwise to 40 mL deionized water. The isolated precipitate, in quantitative yield, was analyzed using proton NMR (Figure 4). As seen in the NMR a quantitative conversion of BPA to VHER was obtained.

[0055] A large scale synthesis of VHER can be also performed according to the following protocol as one embodiment of the invention.

[0056] Materials. Bisphenol A, vinyl ethylene carbonate, and potassium carbonate were procured from Sigma Aldrich and utilized without further purification.

[0057] The reaction scheme utilized for the synthesis of VHER is displayed in Figure 2. Bisphenol A (50 g), as received vinyl ethylene carbonate (75 mL) and potassium carbonate (5 g) were introduced in a single necked round bottom flask. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 115 ºC. After 18 h the

reaction was stopped by applying vacuum to remove any unreacted vinyl ethylene carbonate. The obtained product was dissolved in 30 mL of dimethyl sulfoxide and added dropwise to 400 mL deionized water.

[0058] The isolated precipitate, in quantitative yield, was analyzed using proton NMR (Figure 8A) and FTIR (Figure 8B). As seen in the NMR spectrum in Figure 8A, a quantitative conversion of BPA to VHER was obtained. In the FTIR spectrum (Figure 8B), a strong peak around 930 cm^{-1} (boxed region in Figure 8A) was observed for the VHER but was absent in the bisphenol A (BPA) spectrum. This peak is attributed to the bending of the vinyl groups. The absorption band associated with the ether moieties present in the VHER appears in the same region as the C-O stretch centered around 1200 cm^{-1} from the parent BPA.

[0059] Using the reaction procedure shown herein for BABHPE, VHER can also be synthesized using 3-butene-(1,2-diol) according to the reaction scheme presented in Figure 5.

[0060] In an alternate synthetic protocol VHER can be synthesized using cheaper commercially available starting materials (e.g. 1,2-epoxy-5-hexene) through an environmentally benign solvent free single pot reaction methodology as conceptualized in Figure 6. The reaction between an epoxy group and the BPA hydroxyl moiety has been reported (Lee et al. RSC Adv. 2015, 5, 38673-38679).

Example 3. Curing of VHER.

[0061] Preliminary curing experiments were performed with formulations containing the synthesized VHER, styrene (40 % w/w), methyl ethyl ketone peroxide (as free radical initiator) and cobalt naphthenate (promoter). These chemicals were chosen since they are used in all commercial VER formulations. As a control commercially available VER (Derakane from Ashland) was cured using the same conditions as the VHER.

[0062] The curing reactions were performed at 25 °C for 24 hours. As seen from Figure 7, curing of Derakane was successful with these reaction conditions. Importantly, curing of VHER was also successful with these curing conditions – typically used in the industry. The cured VHER formulation resulted in a solid and tack-free thermoset. These preliminary results indeed demonstrate the successful synthesis and curing of VHER.

Example 4. VHER Formulations and Characterization.

[0063] The synthesized VHER was mixed with 20, 33 and 40 wt% styrene to give formulations analogous to commercially available Derakane VERs. These mixtures were stored at room temperature in a dark location, and were stable under these conditions for over 6 months, with no gelation or precipitation.

[0064] In one embodiment, the synthesized VHER was mixed with 33 wt% styrene, which is similar to the commercially available Derakane 441-400. For curing, 1.5 phr methyl ethyl ketone peroxide (MEKP, Norox MEKP-925H) was used as the initiator and 0.2 phr cobalt naphthenate (6% in mineral spirits, Sigma Aldrich) was used as the accelerator. In a typical formulation step, the MEKP was first added to the VHER solution in Styrene and mixed at 1000 rpm for 1 min using a FlackTek Speedmixer. The accelerator was then introduced to the formulation and mixed at 1000 rpm for 1 min using a FlackTek Speedmixer. The formulation was then cured at 60°C for 16 hours followed by post curing at 110°C for 4 hours. In order to reduce the cure time of this formulation, 0.15 phr of dimethyl aniline (DMA) was added to the above VHER formulation as a secondary accelerator and mixed at 1000 rpm for 1 min using a FlackTek Speedmixer. In order to reduce the curing time 0.15 phr dimethyl aniline was added to the above described VHER formulation as an accelerator.

[0065] The resulting formulation was then cured at 60 °C for 10 hours followed by post curing at 110 °C for 1 hour. At the end of which a stiff non-tacky cured VER sample was obtained Figure 9. The Derakane 411-400 formulations were obtained using same procedure used for VHER, and contained the same amounts of initiator and accelerator. The Derakane formulations were then cured at 60°C for 3 hours followed by post curing at 110°C for 1 hour.

[0066] The glass transition temperature (Tg) of the obtained sample was determined from the peak in Tan δ values using Dynamic Mechanical Analysis. The sample displayed a Tg of 119 ºC (Figure 10) compared to a reported 135 ºC Tg for Derakane 441-400. The flexural storage modulus of the sample was observed to be around 2.4 GPA at room temperature.

[0067] The thermal stability of the cured VHER was determined using thermogravimetric analysis (TGA). As seen in Figure 11, the onset temperature for degradation cured VHER (T_o) was observed at 417 °C, and the highest rate of degradation (T_{max}) was observed at 453 °C. In comparison for Derakane 441-400 the T_o and T_{max} were observed at 412 °C and 446 °C respectively. Without being bound by theory, this higher stability of VHER to thermal degradation can be attributed to the presence of ether moieties as opposed to ester groups in the

case of Derakane. A higher char yield of 10 wt% was also observed for VHER as opposed to 3 wt% for Derakane.

[0068] Using the formulations coatings of VHER and Derakane were processed on Aluminum Q panels. The coated panels were then immersed in conc. H_2SO_4 for 48 hours to determine their hydrolytic stability. As seen in Figure 12, the Derakane coatings displayed significant change in color as well as cracking and erosion of the coating. VHER coatings in contrast displayed slight change in color and the film integrity is retained. This indicates that VHER is more stable to hydrolysis as compared to Derakane. This can be attributed to the ether moieties present in VHER as compared to the hydrolysable ester moieties in Derakane.

[0069] Barcol hardness measurements were performed according to ASTM D-2583 and a Barcol hardness of 32 was observed for the cured samples, which is comparable to the Barcol hardness of 35 reported for Derakane 441-400.

Example 5: Marine Applications of VHER.

[0070] In marine applications continuous contact with an aqueous environment can cause osmotic blistering in boat hulls, which can have detrimental effects on the properties and reduce lifetime. In order to assess their affinity for water, cured Derakane and VHER samples with dimensions 40.2 mm x 12.4 mm x 3.1 mm, and 40.5 mm x 12.2 mm x 3.4 mm respectively were selected. The samples were immersed in deionized water at 60°C for 30 days according to the procedure reported in Sobrinho, L.L. et al., *Materials Research*, Vol. 12, No. 3, 353-361, 2009. Prior to immersion in water, the samples were placed under vacuum at 80°C for 48 hours and cooled under vacuum to remove and absorbed moisture under ambient conditions, then weighed carefully using an analytical balance. For each subsequent measurement, before weighing the samples were allowed to cool to room temperature and patted dry. The resultant data on weight increase as a function of time is displayed in Figure 13. As the data shows, there is a steady increase in the weight of both materials due to the diffusion of deionized water into the samples, followed by saturation after about 20 days. Due to the greater polarity of the ester moieties in the VER than the ether moieties in the VHER, the equilibrium water uptake of the former (0.6 wt%) substantially exceeded that of the latter (0.2 wt%). The lower water uptake observed in the VHER is an advantage of the VHER material for long-term durability of parts in marine applications.

[0071] Gardco wet film applicators (wire size 6, S6) were utilized for processing VHER and Derakane 441-400 VER coatings on Q-panel uncoated 3” x 6” aluminum test panels. The aluminum substrates were cleaned first by immersion in a pH 2 aqueous sulfuric acid bath for 5 minutes at 25°C. The panels were then washed with deionized water and dried at 110°C in a convection oven for 5 min. The panels were cooled to room temperature, after which the VHER and Derakane 441-400 VER formulations with 1.5 phr MEKP (Norox MEKP-925H), 0.2 phr cobalt naphthenate (6% in mineral spirits, Sigma Aldrich), and in the case of VHER 0.15 phr of dimethyl aniline (DMA), were applied using the S6 wet film applicator. In a convection oven the Derakane 441-400 VER coating cured in 1 hour at 220°C. For coatings the VHER formulation containing 33% Styrene and DMA as the secondary accelerator, cure time was increased to 6 hours for complete curing at 220°C. Using this procedure, continuous, tack-free, clear, coatings of were obtained. In adhesion testing the results are obtained by visual examination of the marked area. In order to aid in this process, trace quantities of a luminescent dye, carboxyfluorescein, were introduced into the formulations.

[0072] To determine coating stability vs. solvent attack, the obtained coatings were characterized via the MEK double rub test (ASTM D5402) using cheese cloth and commercially available methyl ethyl ketone (Sigma Aldrich). In a typical test a doubled-over piece of cheese cloth was placed in a beaker containing MEK and saturated until dripping wet. The MEK-wetted cheese cloth was then placed on the test sample and pressed firmly with the index finger at a 45° angle, and 100 double rubs were performed on the central area of each coating, after which they were visually inspected. No visual changes were observed in any of the coatings after the MEK double rub test.

[0073] The coatings on which the MEK double rub test was performed were then utilized for ASTM D3359 adhesion testing. A Gardco Paint Adhesion Test Kit with an 11 tooth 1.0 mm cutter (PA-2053) was utilized for screening the obtained coatings via ASTM D3359 (Standard Method for Measuring Adhesion by Tape Test, a.k.a. “Crosshatch Adhesion Test”), Test Method B, recommended for coatings with dry thicknesses below 50 µm. The presence of the fluorescent dye in the coatings significantly improved the evaluation of coatings following adhesion testing. After cross-hatching, tape application and peeling, the samples were observed under 365 nm UV illumination to evaluate the degree of coating removal from the substrate. Figure 13 displays photographs of the samples after adhesion testing; neither coating experienced any loss of

material from the substrate after the adhesion tape test, meaning both are classified as 5B coatings (the highest level of performance indicated by this testing standard). These results confirm that the equally high performance of both the VHER and Derakane 441-400 VER coatings.

[0074] A T-Bend tester was used to perform 0T, 1T, and 2T coating flexibility bend tests (ASTM D4145) on all coated samples following MEK double rub testing (ASTM D5402). This test is important as it determines the flexibility and adhesion of the coatings on substrates that are deformed by bending. In this test, coated samples were bent using a T-Bend tester procured from Qualtech Products Industry. 0T, 1T, and 2T bends were produced, after which the coatings were inspected for damage. The pressure-sensitive tape provided in the ASTM D3359 Gardco Paint Adhesion Test Kit was used to determine the adhesion/pickoff of the coatings at the bent edge. The 0T bend test is the most challenging test to pass, as the radius of curvature at the T-bend is lowest in this case, nevertheless, neither the VHER nor the Derakane 441-400 VER coatings displayed any damage or removal of coated material following this test (Figure 15). Hence, both can be classified as 0T coatings.

[0075] For use in applications such as chemical storage tanks, desulfurization flue stacks etc. enhanced chemical stability is desired. To determine the chemical stability of the processed VHER and Derakane 441-400 VER coatings, the coated panels were immersed in concentrated H_2SO_4 for 48 hours. As seen in Figure 12, the Derakane coatings displayed a significant change in color as well as cracking and erosion of the coating. VHER coatings in contrast displayed only a slight change in color and experienced no changes in film integrity. This indicates that VHER is more stable vs. hydrolysis as compared to a Derakane 441-400 VER. This can be attributed to the stable ether moieties present in the VHER coating as compared to the hydrolytically unstable ester moieties in the Derakane 441-400 coating.

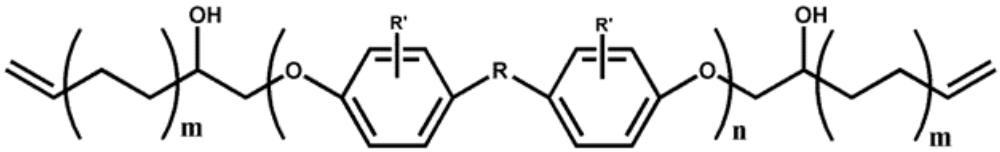
[0076] Following immersion in concentrated H_2SO_4 for 48 hours, 0T bends were produced to determine the effect of hydrolysis on the flexibility and adhesion of the coatings. The pressure-sensitive tape provided in the ASTM D3359 Gardco Paint Adhesion Test Kit was used to assess the adhesion/pickoff of the coatings at the bent edge. Even after immersion in concentrated H2SO4 for 48 hours, the VHER coatings displayed no damage or coating removal following the adhesion test (Figure 16). In contrast, Derakane 441-400 VER coatings failed the test due to the loss of a considerable portion of the coating at the 0T bend as seen in Figure 16.

[0077] The terms and expressions that have been employed are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the embodiments of the present invention. Thus, it should be understood that although the present invention has been specifically disclosed by specific embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those of ordinary skill in the art, and that such modifications and variations are considered to be within the scope of embodiments of the present invention.

Exemplary Embodiments.

[0078] The following exemplary embodiments are provided, the numbering of which is not to be construed as designating levels of importance:

[0079] Embodiment 1 provides a vinyl hydroxyl ether resin (VHER) having the structure:



,

wherein

m is an integer ranging from 0 to 100,

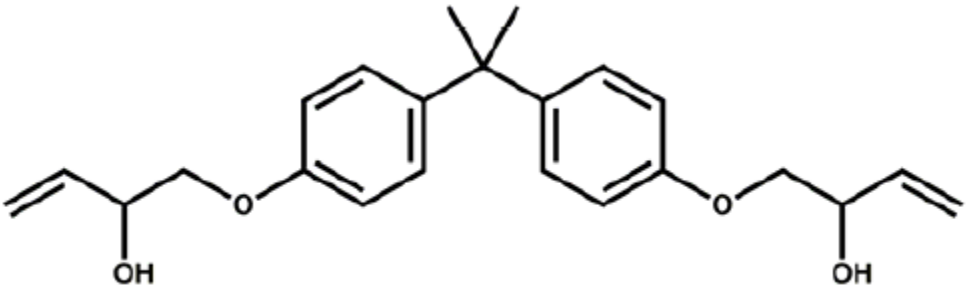
n is an integer ranging from 1 to 100,

at each occurrence R' is independently a substituted or unsubstituted (C_1-C_{10})hydrocarbyl,

R is O, SO_2, or $C(R^1)_2$, and,

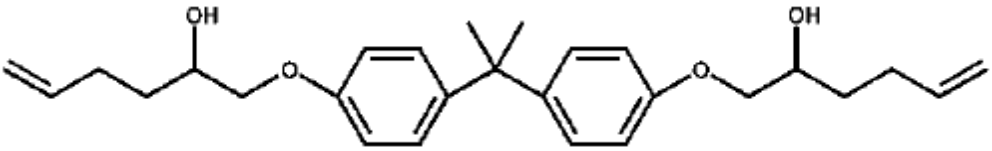
R^1 is independently hydrogen, phenyl, or substituted or unsubstituted (C_1-C_{10})hydrocarbyl.

[0080] Embodiment 2 provides the vinyl hydroxyl ether resin (VHER) of embodiment 1 having the structure:



.

[0081] Embodiment 3 provides the vinyl hydroxyl ether resin (VHER) of embodiment 1 having the structure:



.

[0082] Embodiment 4 provides the vinyl hydroxyl ether resin (VHER) of embodiment 1, wherein m is 1, 2, 3, 4, or 5.

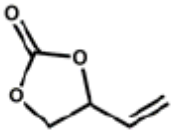
[0083] Embodiment 5 provides a polymerization product of a starting material composition, the starting material composition including the VHER according to any one of or combination of embodiments 1-4.

[0084] Embodiment 6 provides a method of making the VHER of embodiment 2, including:

combining Bisphenol A:

,

with vinyl ethylene carbonate:



,

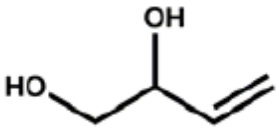
under conditions sufficient to give the VHER of embodiment 2.

[0085] Embodiment 7 provides a method of making the VHER of embodiment 2, including:

combining Bisphenol A:

,

with 3-butene-(1,2-diol):



,

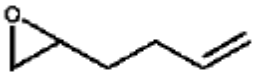
under conditions sufficient to give the VHER of embodiment 2.

[0086] Embodiment 8, provides a method of making the VHER of embodiment 3, including:

combining Bisphenol A:

,

with 1,2-epoxy-5-hexene:



,

under conditions sufficient to give the VHER of embodiment 3.

[0087] Embodiment 9 provides a method of making the VHER of embodiment 1, including:

combining Bisphenol A:

,

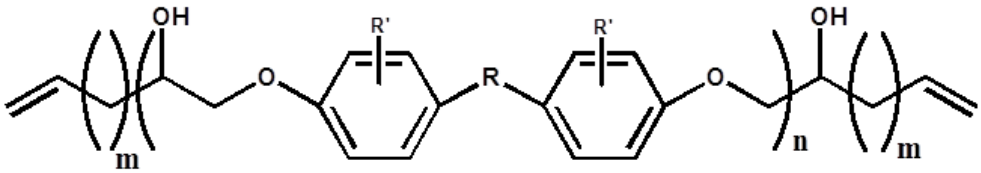
with 1,2-epoxy-6-heptene, 1,2-epoxy-7-octene, 1,2-epoxy-8-nonene, 1,2-epoxy-9-decene, or combinations thereof.

[0088] Embodiment 10 provides a polymerization product of a starting material composition, the starting material composition including the VHER according to embodiment 3.

CLAIMS

What is claimed is:

1. A vinyl hydroxyl ether resin (VHER) having the structure:



,

wherein

m is an integer ranging from 0 to 100,

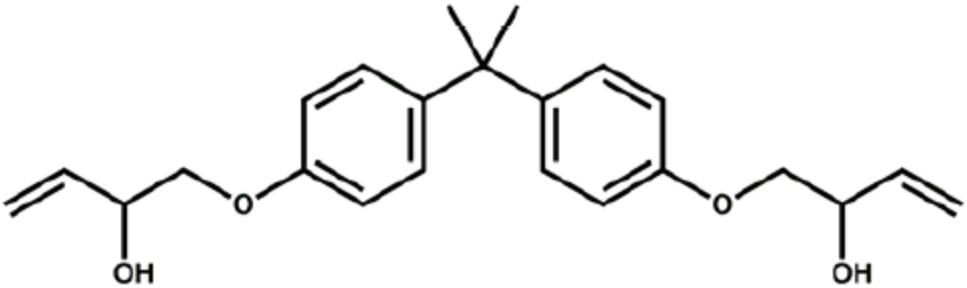
n is an integer ranging from 1 to 100,

at each occurrence R' is independently a substituted or unsubstituted (C_1-C_{10})hydrocarbyl,

R is O, SO_2, or $C(R^1)_2$, and

R^1 is independently hydrogen, phenyl, or substituted or unsubstituted (C_1-C_{10})hydrocarbyl.

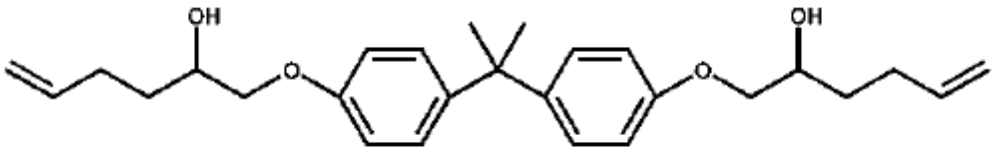
2. The vinyl hydroxyl ether resin (VHER) of claim 1 having the structure:



.

3. A polymerization product of a starting material composition, the starting material composition comprising the VHER of claim 1.

4. The vinyl hydroxyl ether resin (VHER) of claim 1 having the structure:



.

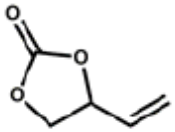
5. A polymerization product of a starting material composition, the starting material composition comprising the VHER of claim 4.

6. A method of making the VHER of claim 2, comprising:

combining Bisphenol A:

,

with vinyl ethylene carbonate:



,

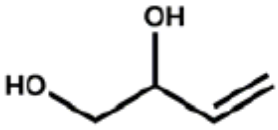
under conditions sufficient to give the VHER of claim 2.

7. A method of making the VHER of claim 2, comprising:

combining Bisphenol A:

,

with 3-butene-(1,2-diol):



,

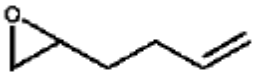
under conditions sufficient to give the VHER of claim 2.

8. A method of making the VHER of claim 3, comprising:

combining Bisphenol A:

,

with 1,2-epoxy-5-hexene:



,

under conditions sufficient to give the VHER of claim 3.

9. A method of making the VHER of claim 1, including:

combining Bisphenol A:

,

with 1,2-epoxy-6-heptene, 1,2-epoxy-7-octene, 1,2-epoxy-8-nonene, 1,2-epoxy-9-decene, or combinations thereof.

10. A polymerization product of a starting material composition, the starting material composition including the VHER according to claim 3.

ABSTRACT

Various embodiments disclosed relate to vinyl hydroxyl ether resins, polymerization products thereof, and methods of making either one of the same.

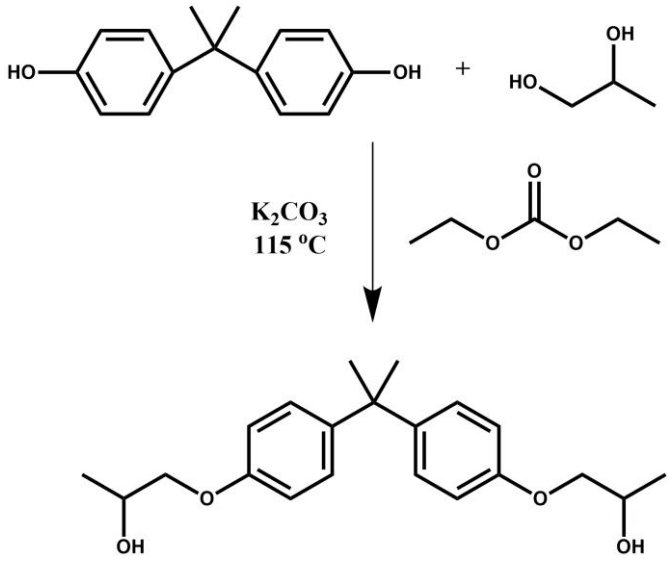


Figure 1

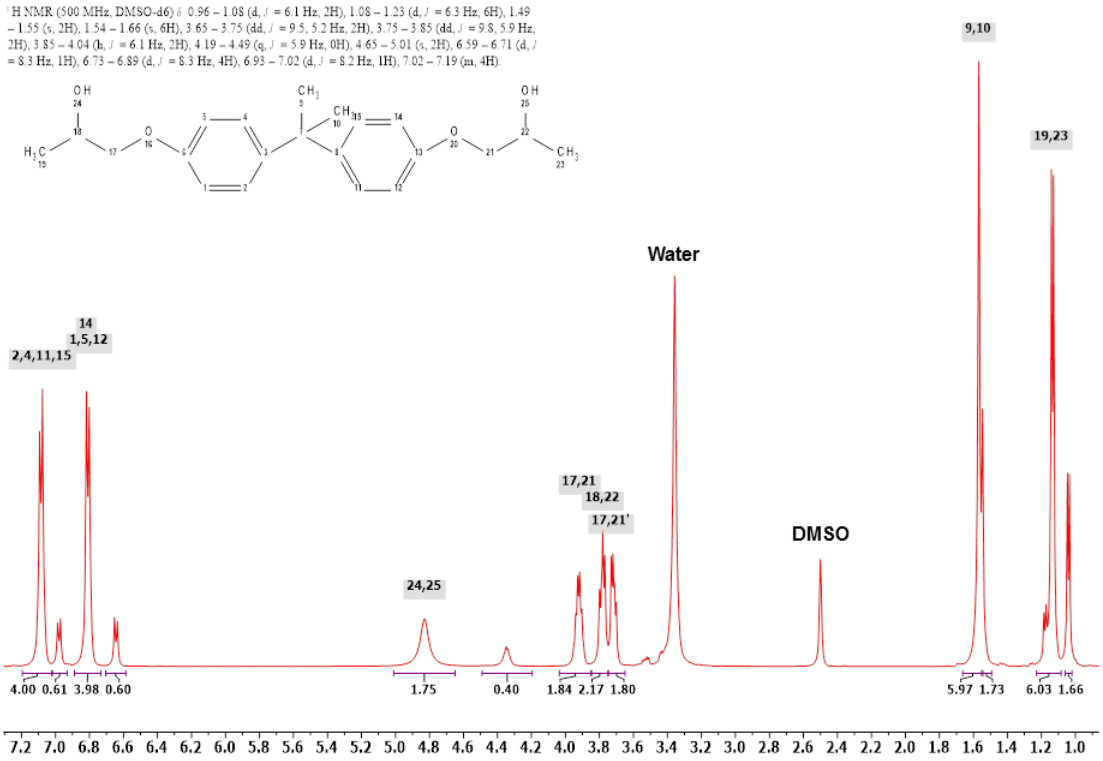

1 H NMR (500 MHz, DMSO-d6) δ 0.96 – 1.08 (d, J = 6.1 Hz, 2H), 1.08 – 1.23 (d, J = 6.3 Hz, 6H), 1.49 – 1.55 (s, 2H), 1.54 – 1.66 (s, 6H), 3.65 – 3.75 (dd, J = 9.5, 5.2 Hz, 2H), 3.75 – 3.85 (dd, J = 9.8, 5.9 Hz, 2H), 3.85 – 4.04 (h, J = 6.1 Hz, 2H), 4.19 – 4.49 (q, J = 5.9 Hz, 0H), 4.65 – 5.01 (s, 2H), 6.59 – 6.71 (d, J = 8.3 Hz, 1H), 6.73 – 6.89 (d, J = 8.3 Hz, 4H), 6.93 – 7.02 (d, J = 8.2 Hz, 1H), 7.02 – 7.19 (m, 4H).
9,10
19,23
Water
14
1,5,12
2,4,11,15
17,21
18,22
17,21'
DMSO
24,25
4.00 0.61 3.98 0.60
1.75
0.40
1.84 2.17 1.80
5.97 1.73
6.03 1.66
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0

Figure 2

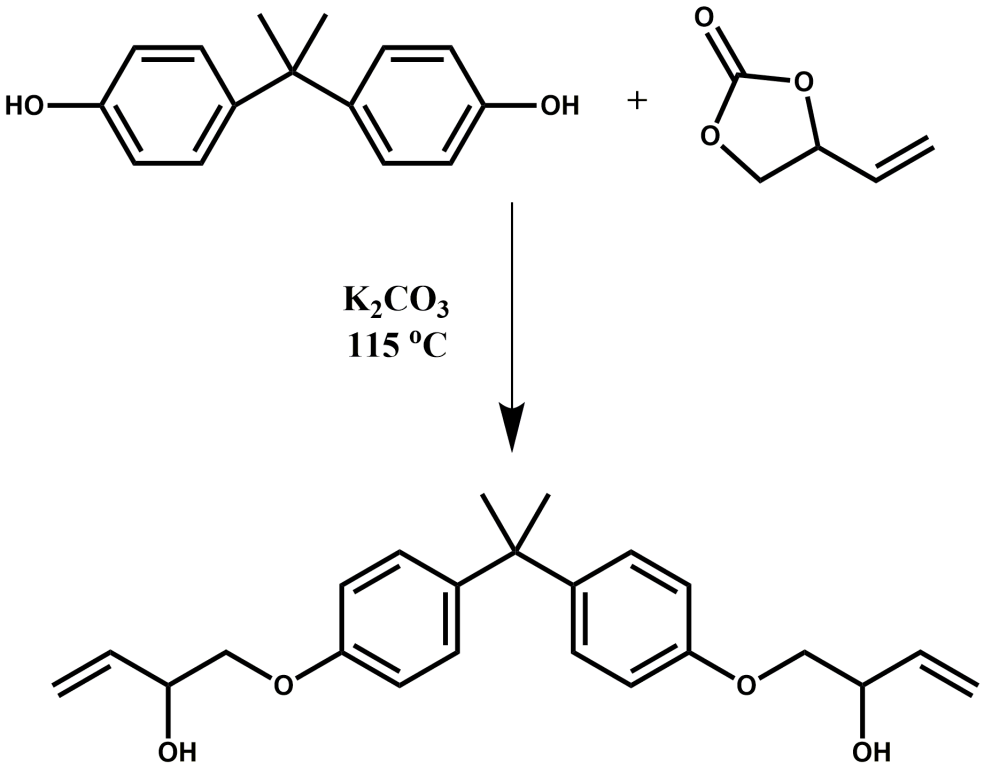


Figure 3

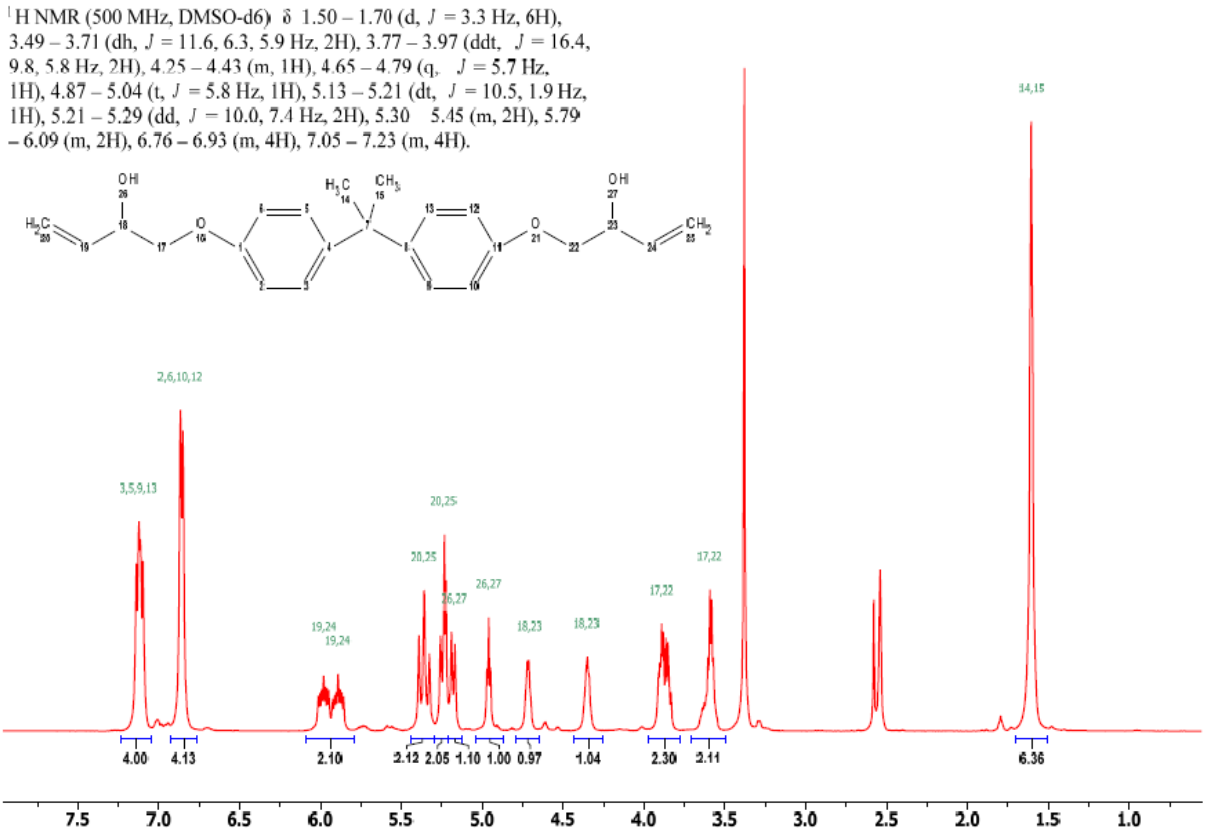

1 H NMR (500 MHz, DMSO-d6) δ 1.50 – 1.70 (d, J = 3.3 Hz, 6H), 3.49 – 3.71 (dh, J = 11.6, 6.3, 5.9 Hz, 2H), 3.77 – 3.97 (ddt, J = 16.4, 9.8, 5.8 Hz, 2H), 4.25 – 4.43 (m, 1H), 4.65 – 4.79 (q, J = 5.7 Hz, 1H), 4.87 – 5.04 (t, J = 5.8 Hz, 1H), 5.13 – 5.21 (dt, J = 10.5, 1.9 Hz, 1H), 5.21 – 5.29 (dd, J = 10.0, 7.4 Hz, 2H), 5.30 5.45 (m, 2H), 5.79 – 6.09 (m, 2H), 6.76 – 6.93 (m, 4H), 7.05 – 7.23 (m, 4H).
OH
26
H3C
20
19
18
17
O
16
1
2
3
4
5
6
H3C
14
CH3
15
7
8
9
10
13
12
11
O
21
22
23
24
OH
27
CH2
25
2,6,10,12
3,5,9,13
20,25
20,25
26,27
26,27
19,24
19,24
18,23
18,23
17,22
17,22
14,15
4.00
4.13
2.10
2.12
2.05
1.10
1.00
0.97
1.04
2.30
2.11
6.36
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

Figure 4

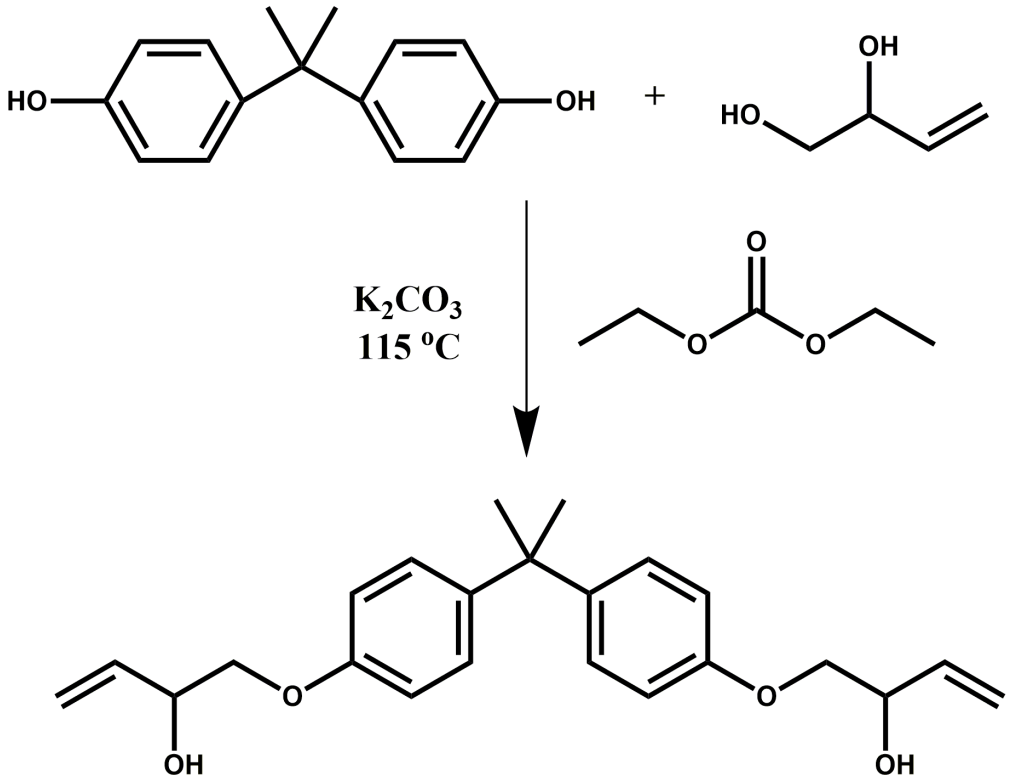


Figure 5

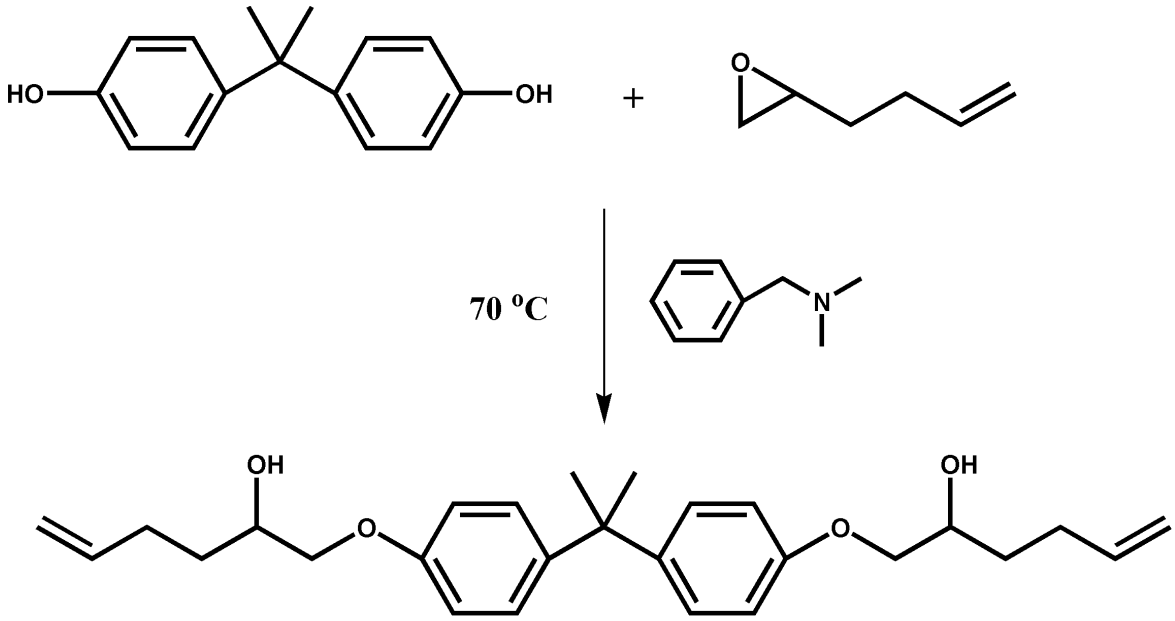


Figure 6

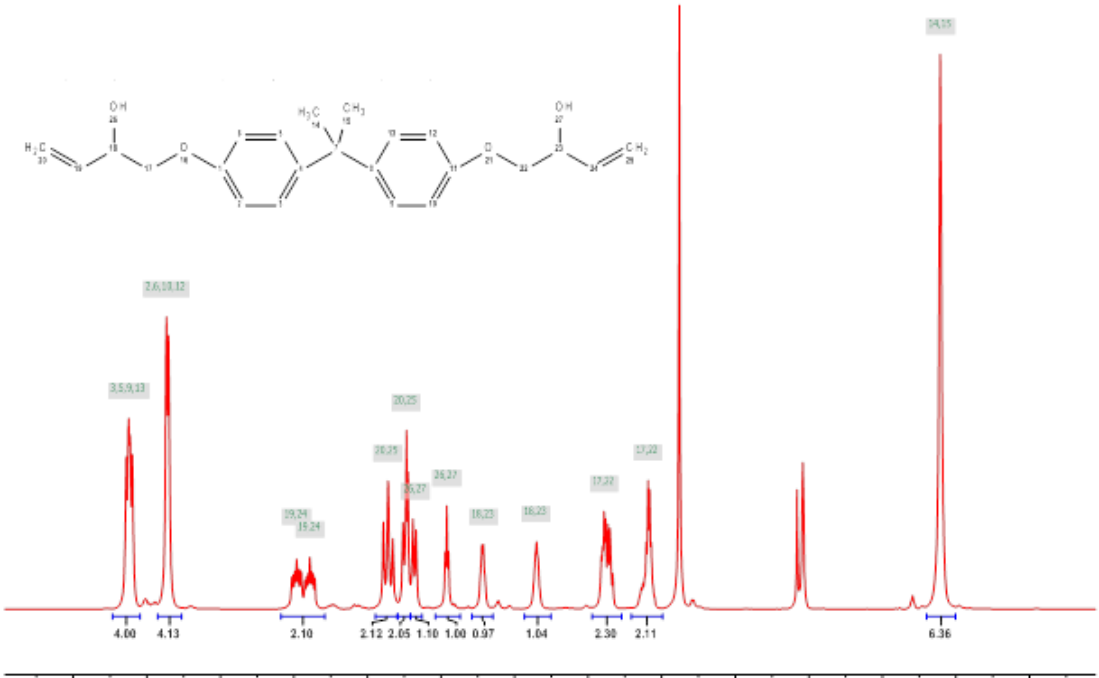
Derakane

VHER

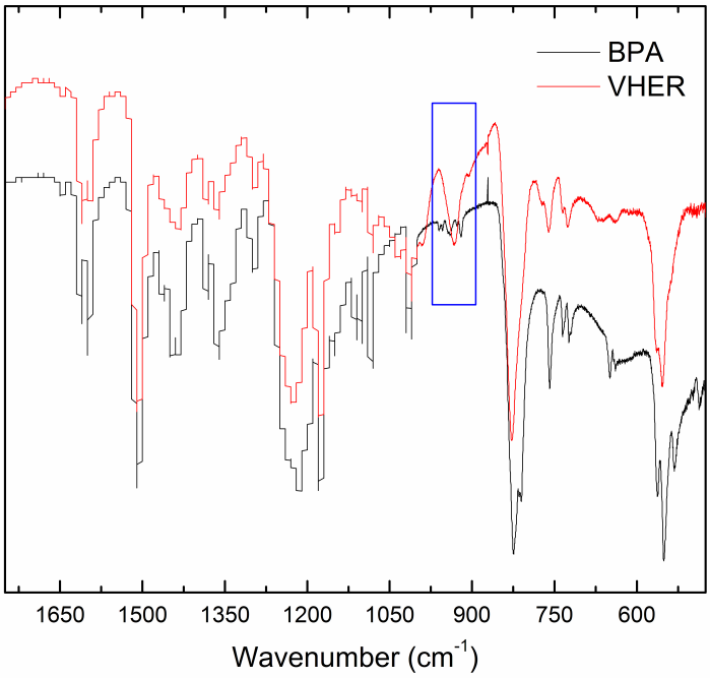
Cured Derakane

Cured VHER

Figure 7



8A)



8B)

Figure 8

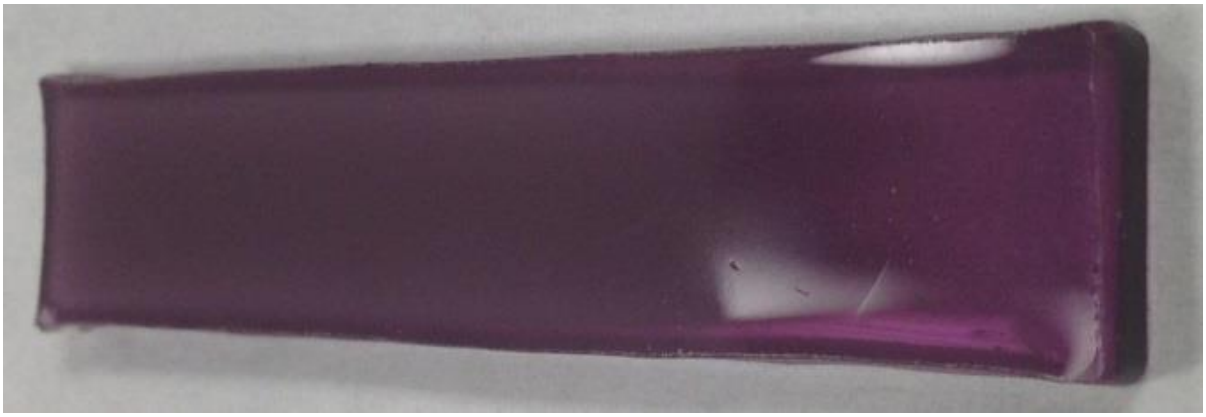


Figure 9

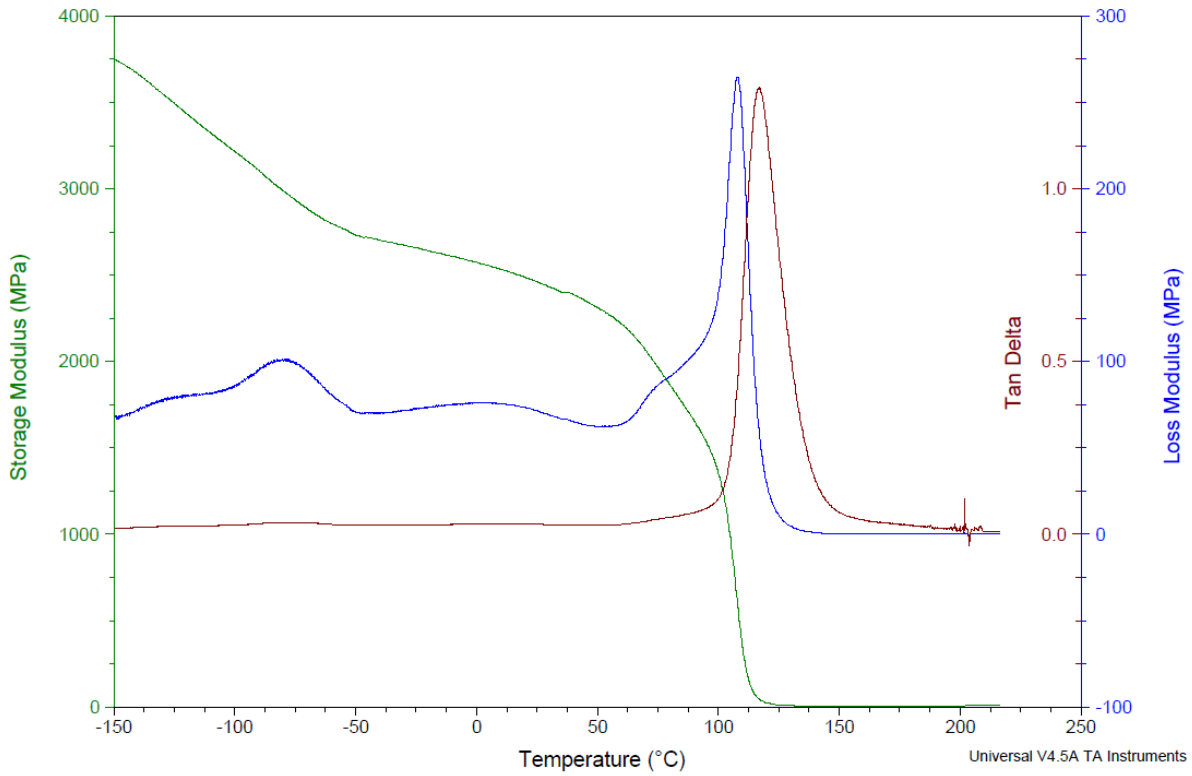
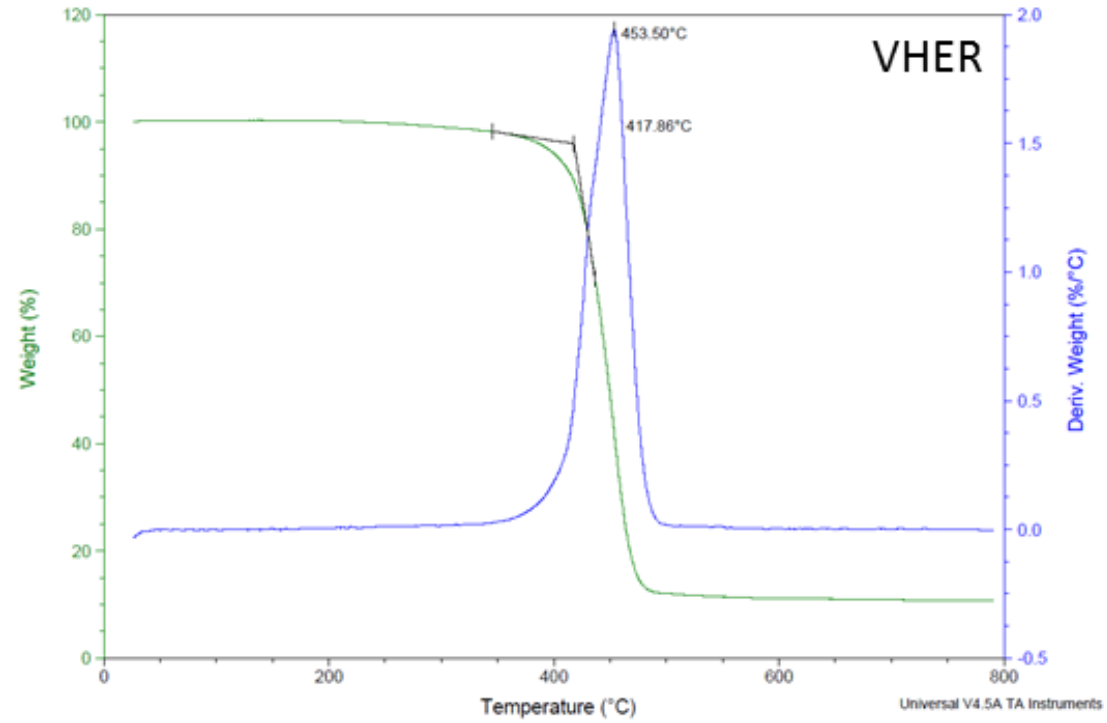

Storage Modulus (MPa)
4000
3000
2000
1000
0
Tan Delta
1.0
0.5
0.0
Loss Modulus (MPa)
300
200
100
0
-100
-150
-100
-50
0
50
100
150
200
250
Temperature (°C)
Universal V4.5A TA Instruments

Figure 10


VHER
453.50°C
417.86°C
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V4.5A TA Instruments

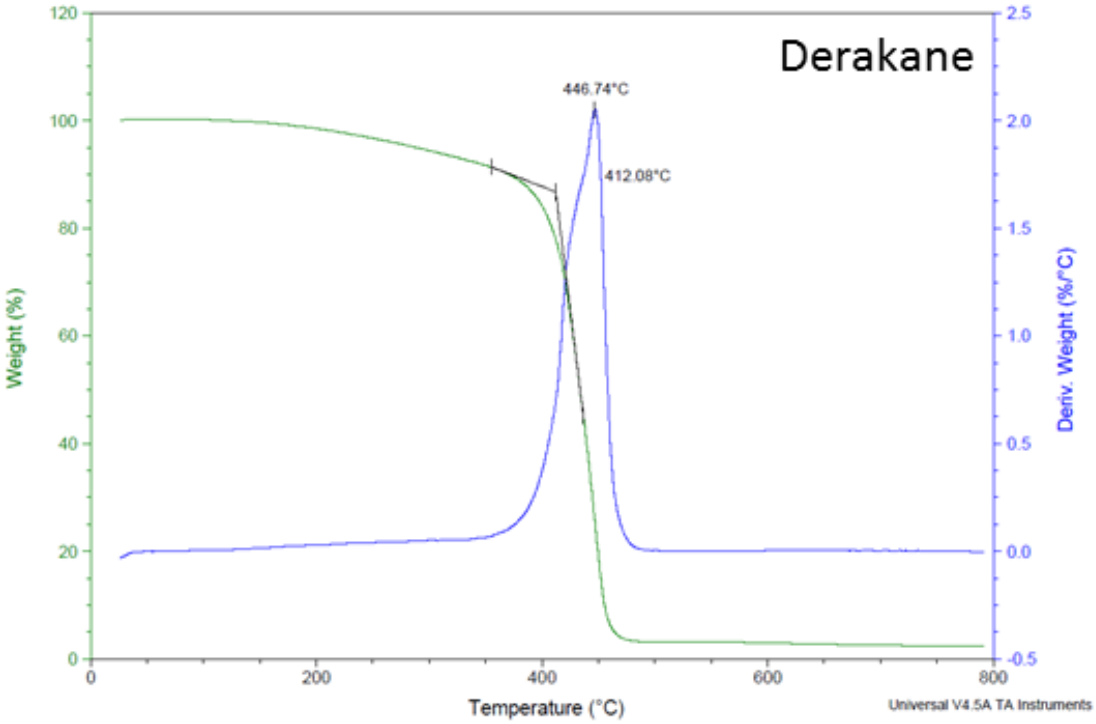

Derakane
446.74°C
412.08°C
Weight (%)
Deriv. Weight (%/°C)
Temperature (°C)
Universal V4.5A TA Instruments

Figure 11

Figure 12

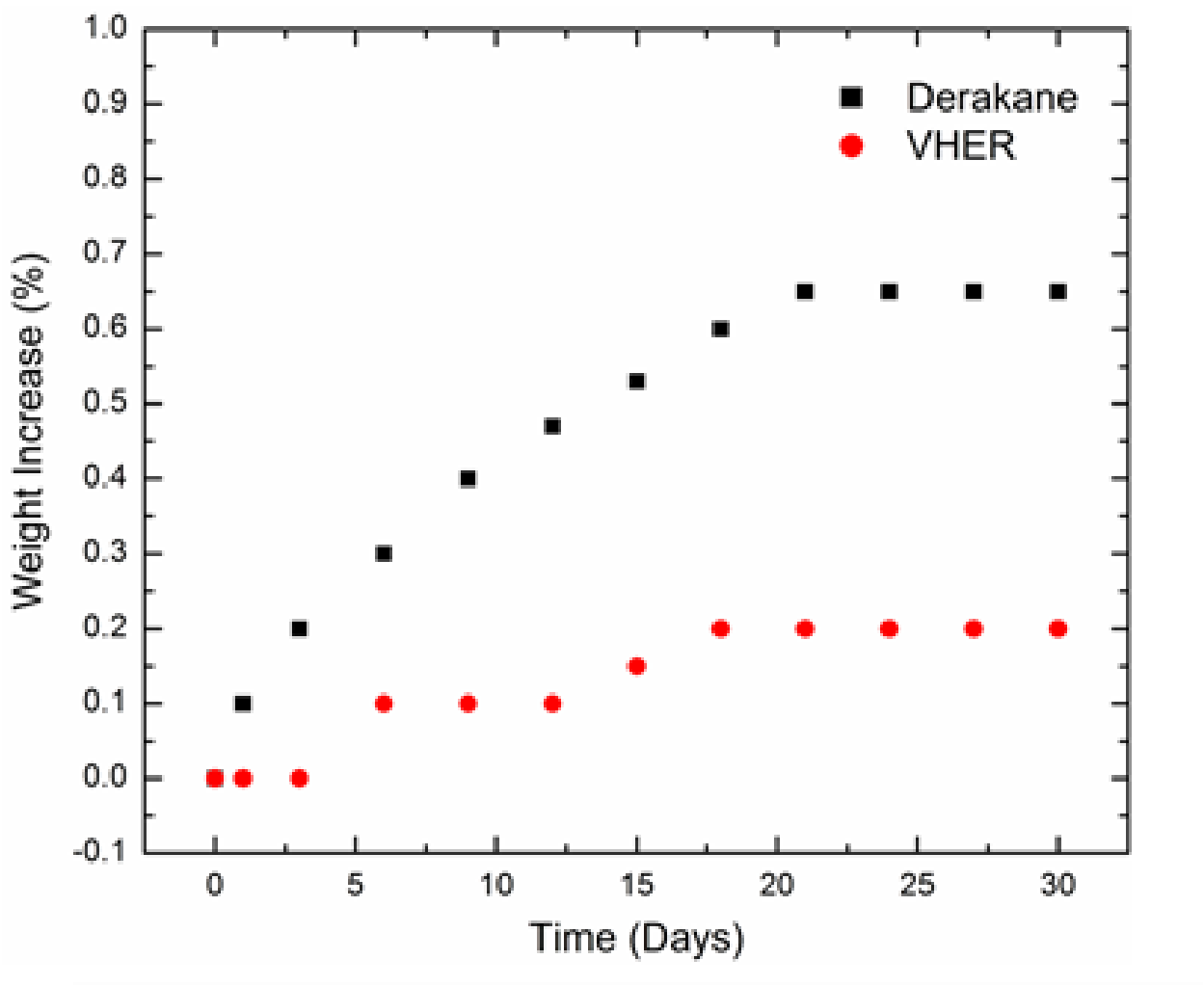

Derakane
VHER
Weight Increase (%)
Time (Days)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0
5
10
15
20
25
30

Figure 13

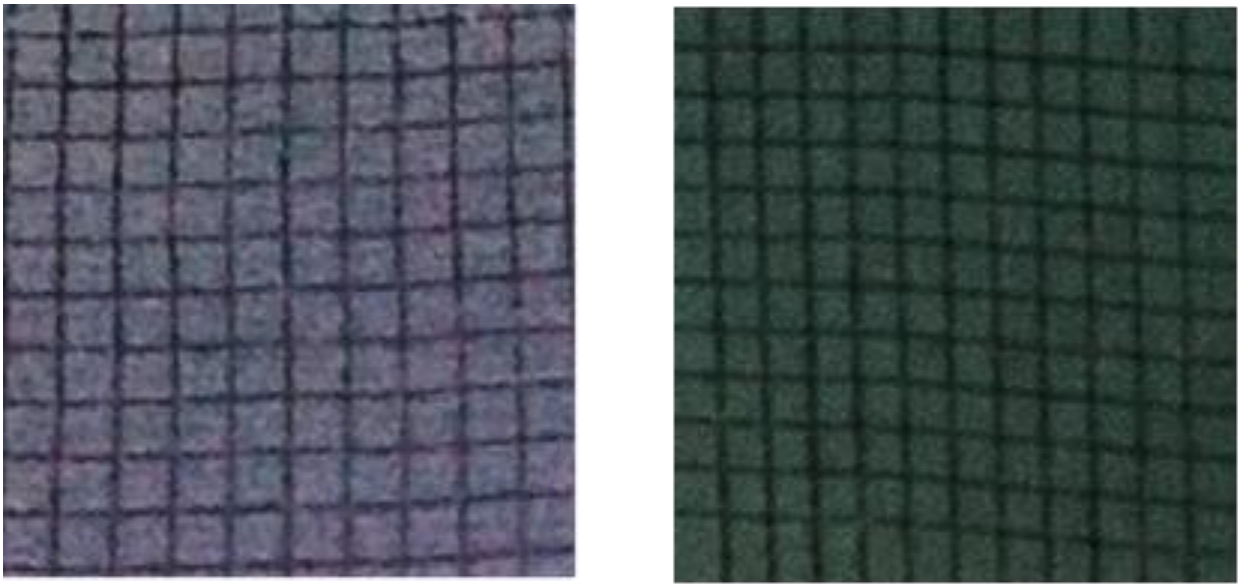


Figure 14

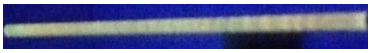
Test	VHER	Derakane 441-400 VER
0T		
1T		
2T		

Figure 15

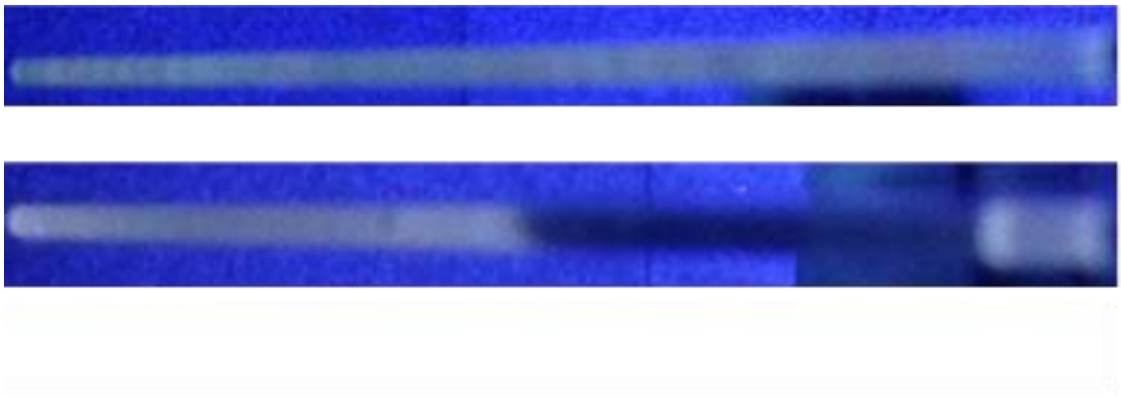


Figure 16

Appendix C

UNIVERSITY OF MASSACHUSETTS

AMHERST • BOSTON • DARTMOUTH • LOWELL • WORCESTER

CVIP Use Only

Commercial Ventures and Intellectual Property

Invention Disclosure

Lowell Campus Office:
600 Suffolk Street, 2nd Floor, Attn: Director, CVIP
Lowell, MA 01854
Tel: 978-934-3235

Central Office:
President's Office, Attn: Executive Director, CVIP
225 Franklin Street, 12th floor
Boston, MA 02110
Tel: 617-287-4088

UML#: 2015-038

Received: 21May15

Accepted: 19Jun15

Case Manager: R. Kaushik

University of Massachusetts
Uniform Invention Disclosure Form
(version 12/17/2012)

Title of Invention: Environmentally Benign Synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE) and Vinyl Ester Resin (VER)

	Investigator's Name & Title *(Please list Principal Investigator first and include all possible inventors)*	**Department**	**Institution** *(at time invention was made)*
1.	Name: Akshay Kokil Title: Post-doctoral Researcher	Dept: Chemistry	Institution: University of Massachusetts Lowell
2.	Name: Yongwoo Lee Title: Research Professor	Dept: Chemistry	Institution: University of Massachusetts Lowell
3.	Name: Priyank N. Shah Title: Post-doctoral Researcher	Dept: Chemistry	Institution: University of Massachusetts Lowell

Please check campus of lead Principal Investigator: Amherst Boston Dartmouth Lowell √ UMMC

To the Investigator(s):

The business of a university is the gathering and dissemination of knowledge. Making an invention and putting it to use in the service of the public is a thoroughly valid mode of accomplishing this objective.

Accordingly, the University encourages the inventive process; and within the limits of financial practicality, can often provide advice and assistance in bringing inventions to the point of public use.

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1. Background

Vinyl ester resins (VER) are high performance unsaturated resins with exceptional mechanical strength and corrosion resistance. In addition to their superior performance, these resins display lower viscosities than conventional epoxy resins resulting in significantly improved processability. Due to their superior properties and excellent processability, VER find use, either in pure form or as a matrix in fiber reinforced composites, in diverse industries, such as, ship building, automotive part construction, infrastructure polymer concrete reinforcements, corrosion resistance coatings (on chemical storage tanks, pipes and ducting, fume extraction systems, gas cleaning units), top-coat materials (with excellent adhesion to plastics, steel and concrete), optical fiber coating, UV curing inks and printed circuit board manufacture (*Jaswal, S.; Gaur, B. 'New trends in vinyl ester resisns' Rev. Chem. Eng. 2014, DOI 10.1515/revce-2014-0012*). The versatility of these resins for diverse applications has resulted in a huge global market and ever increasing potential.

VER are currently synthesized by addition reaction of epoxide resins with unsaturated carboxylic acids. A variety of chemical compounds containing the epoxy groups have been used for synthesis of VER. Particularly bisphenol-A (BPA) based VER resins are widely utilized due to their exceptional mechanical strength and chemical resistance. Currently for BPA based VER synthesis, the epoxy containing bisphenol-A

diglycidyl ether (BADGE) is reacted with either methacrylic acid or methyl methacylate. These resins were first commercialized as Epocryl resins by Shell Chemical Company and later as Derakane resins by Dow Chemical Company. Currently these resins are produced predominantly by Ashland, DSM and Reichold.

BADGE is currently synthesized using BPA and epichlorohydrin as starting materials. Patents issued for the synthesis of BADGE using BPA and epichlorohydrin, include U.S. Pat. No. 3121727 A to Baliker et al. assigned to Shell Oil Co. and U.S. Pat. No. 4877857 A to Shirtum et al. assigned to The Dow Chemical Company.

BPA based VER is synthesized from BADGE by the addition reaction of its epoxy groups with acrylic acid based monomers. Patents issued for the synthesis of VER using this synthetic protocol include U.S. Pat. No. 3256226 to Fekete et al., and No. 3317465 to Doyle et al., both assigned to H. H. Robertson Co.; No. 3345401 to May; No. 3373221 to May; No. 3377406 to Newey; and No. 3432478 to May, all assigned to Shell Oil Co.; No. 3548030 to Jernigan; and No. 3564074 to Swisher et al., both assigned to Dow Chemical Co.; No. 3634542 to Dowd et al.; and No. 3637618 to May, both assigned to Shell Oil Co.

The production of VER is still performed using the synthetic protocols reported more than 3 decades ago. Even though the synthetic protocol used is efficient, it requires the use of epichlorohydrin, which performs the dual role of a solvent and reactant. Epichlorohydrin however, has been identified by the U.S. Environmental Protection Agency (EPA) as a hazardous air pollutant and it also features on the list of controlled chemicals by the EPA. Hence, to ensure continued environmental sustainability and improved work place safety an alternative route for the synthesis of VER is required.

Most of the chemicals used for the synthesis of VER are derived from petroleum based feedstocks, which introduces price volatility. In 2014 all the major manufacturers of VER, namely Ashland, DSM and Reichold, announced an increase in the VER price due to the increased cost of raw materials derived from petroleum feedstocks. Hence, an alternate route for improved sustainability and reduced cost volatility of this commercially important resin is required.

We have reported in a recent publication (*RSC Advance, 2015, 5, 38673*) a multi-step protocol for the environmentally benign synthesis of VER from bio-waste glycerin. The publication reported a 4 step reaction protocol.

Here we report for the first time a new and different two step or single pot reaction protocol for the synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE) and VER.

2. Description of the Invention

We report here for the first time:

I) an environmentally benign “green” methodology for the synthesis of BABDHPE and VER

II) a novel two-step and single step synthetic protocol.

III) elimination of currently used toxic chemicals in VER synthesis, such as epichlorohydrin

IV) utilization of starting materials derived from bio-waste streams, which improves the environmental and cost sustainability of the procedure.

Following is the detailed two step protocol used for synthesis of BABDHPE and VER. The following procedure also outlines the concept for the synthesis of VER in a single step. Investigations are currently underway for demonstrating the synthesis of VER in a single step and will be included in this invention disclosure.

1) **One pot synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE)**

Materials: Bisphenol A, diethylene carbonate and potassium carbonate were procured from Sigma Aldrich and utilized without further purification. Crude glycerol as a bio-waste was procured from Maine Standard Biofuels. Glycerol in pure from was obtained using vacuum distillation.

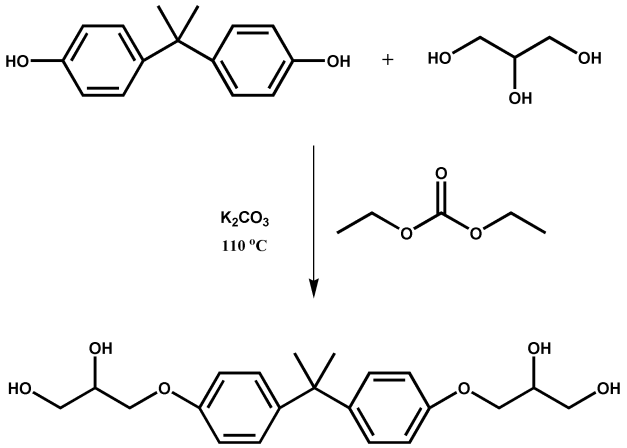

Figure 1. Reaction scheme for synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE).

Procedure:

In a single necked round bottom flask Bisphenol A (10 g, 43.80 mmol), Glycerol (24.20 g, 262.82 mmol), Diethyl carbonate (15.52 g, 131.4 mmol) and Potassium Carbonate (3 g, 21.70 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 110 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethylether and the ethanol byproduct. The hot reaction mixture was then added to a beaker containing 500 mL deionized water. A viscous reaction product was allowed to settle over time and the supernatant water removed. The crude reaction product was washed twice with 500 mL water to remove any unreacted glycerol. The 99% pure Bisphenol A bis(2,3-dihydroxypropyl)ether was isolated in quantitative yields. The purity of the reaction product was determined using proton NMR shown below (Figure 2). This solvent free reaction occurs through *in-situ* formation of glycerol carbonate as described in literature (Truscello A. M. et al. Green Chemistry 2013, 15, 625). The reaction can also be performed using commercially available glycerol carbonate instead of glycerol and diethyl carbonate.

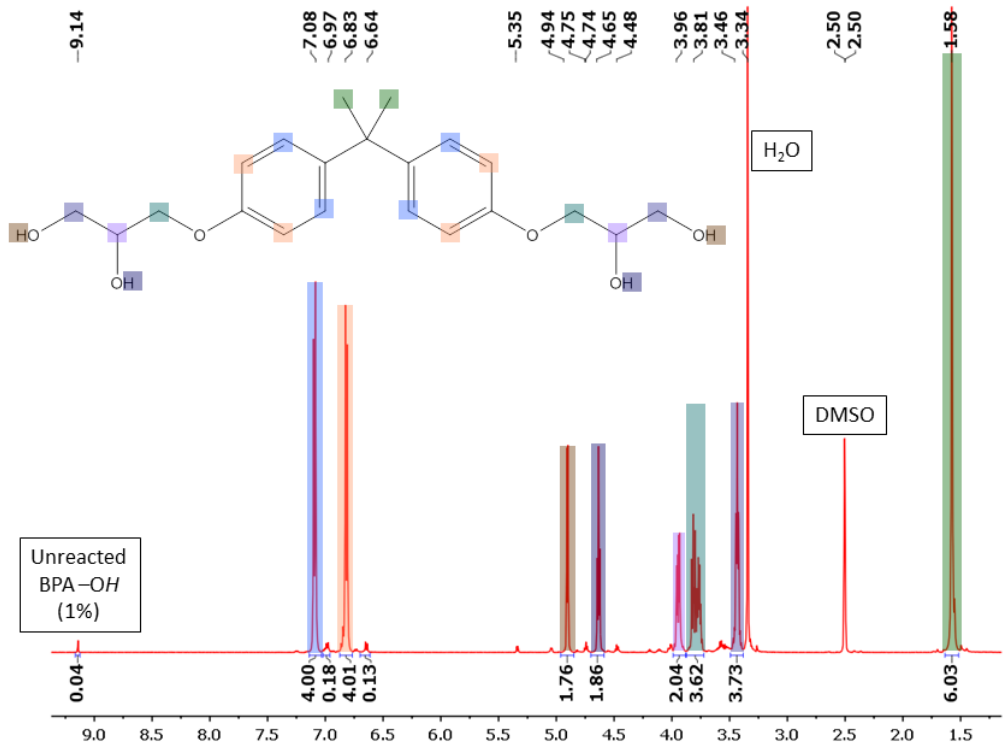

Figure 2. Proton NMR of isolated BABDHPE in DMSO-d6.

2) **Synthesis of VER**

Materials: Methyl methacrylate and Potassium Carbonate were procured from Sigma Aldrich and utilized without further purification. The isolated BABDHPE was utilized for the reaction.

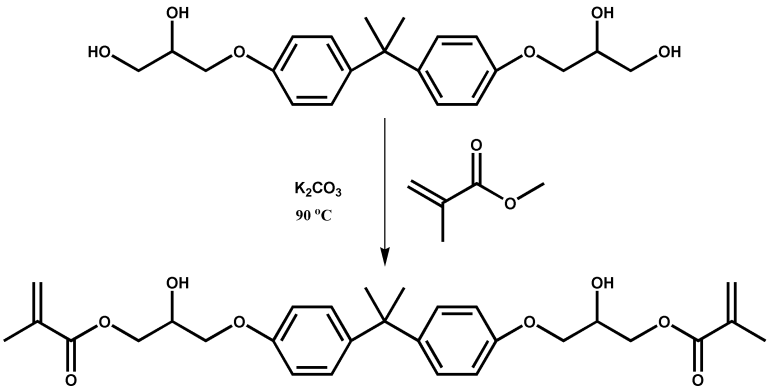

Figure 3. Reaction scheme for synthesis of VER by transesterification of BABDHPE.

Procedure:

In a single necked round bottom flask Bisphenol A bis(2,3-dihydroxypropyl)ether (1 g, 2.65 mmol), as received Methyl methacrylate (1.32 g, 13.28 mmol) and Potassium Carbonate (300 mg, 2.17 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously

stirred at 90 °C. After 18 h the reaction was stopped by applying vacuum to remove any unreacted methyl methacrylate and the methanol byproduct. The resulting product was analyzed by proton NMR shown below (Figure 4).

Transesterification is a well know reaction which can be performed using a variety of catalysts. Potassium carbonate was selected as an example here to demonstrate the feasibility of the reaction protocol. Further investigations are underway to improve the conversion of the reaction and will be included here. A 25% conversion was obtained in the current reaction protocol as evidenced by the presence of vinyl protons around 6.04 and 5.61 ppm.

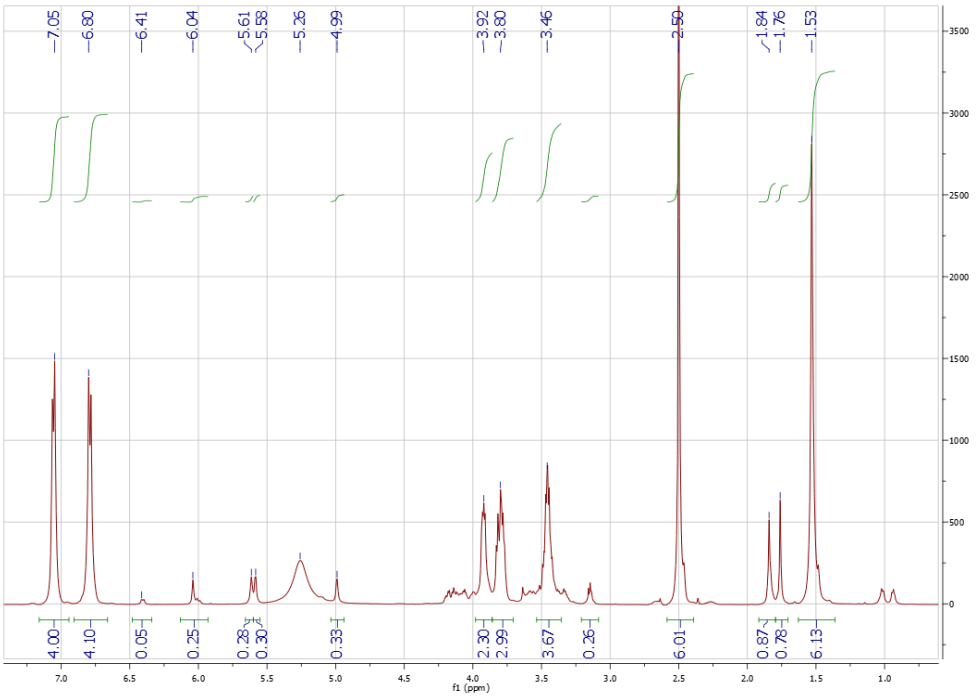

Figure 4. Proton NMR of the reaction product in DMSO-d6.

3) **Single pot synthesis of VER**

The catalyst (potassium carbonate) utilized for the two reactions reported above is the same and it is used in same concentrations. Hence, the above two reactions can be combined to obtain VER.

Materials: Bisphenol A, diethylene carbonate, potassium carbonate, and methyl methacrylate were procured from Sigma Aldrich and utilized without further purification. Crude glycerol as a bio-waste was procured from Maine Standard Biofuels. Glycerol in pure from was obtained using vacuum distillation.

Procedure: In a single necked round bottom flask Bisphenol A (1 g, 4.38 mmol), Glycerol (2.42 g, 26.28 mmol), Diethyl carbonate (1.552 g, 1.314 mmol) and Potassium Carbonate (300 mg, 2.17 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 110 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethyl carbonate, glycerol, and ethanol byproduct. To the crude reaction mixture 5 mL of dimethyl sulfoxide was added to reduce the viscosity of the reaction mixture and 3 mL of methyl methacrylate was added. The

transesterification reaction was performed at 110 °C with the application of mild vacuum to remove the azeotrope formed by methanol and methyl methacrylate. After 12 hours the vacuum was increased to remove any unreacted methyl methacrylate and methanol byproduct. The crude reaction mixture in dimethyl sulfoxide was then introduced into 1:8 mixture of methanol:deionized water to precipitate the product and centrifuged to obtain a viscous precipitate. The precipitate was washed 3 times with 1:8 mixture of methanol:deionized water to remove any trapped methyl methacrylate and glycerol derivative. The resulting crude product was analyzed by proton NMR and a 99% conversion was observed. The purification of the product was done by column chromatography on silica gel with a mixture of 3:7 hexanes:ethyl acetate as the eluent. The first fraction contained the VER product and was analyzed by proton NMR in DMSO d6 (Figure 5).

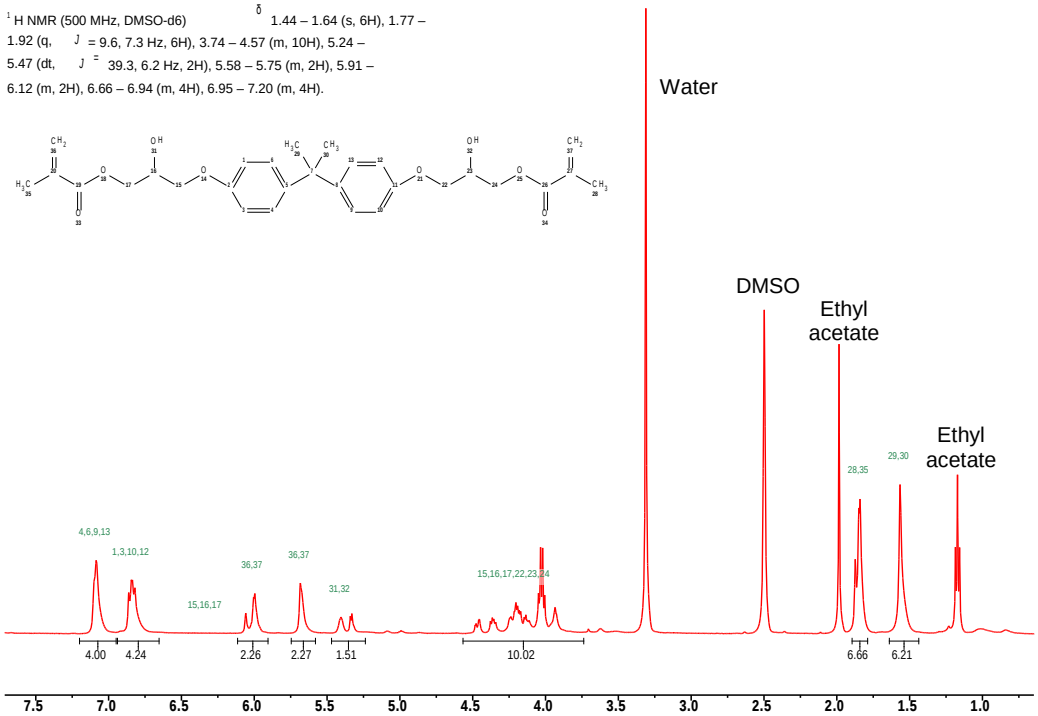

Figure 5. Proton NMR of the purified single pot VER in DMSO-d6.

3. What are the novel aspects of your invention and how does it improve upon prior art? Does your invention overcome any deficiencies or limitations in the prior art?

Following are the novel aspects of the invention:

1) The reaction schemes demonstrated and conceptualized have not been reported before and present a new "green" route for synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether, BADGE, VER and VER formulations.

2) The reaction schemes demonstrated and conceptualized eliminate the use of hazardous chemicals such as epichlorohydrin and styrene. Thus these reactions are environmentally benign in contrast to the methodology currently utilized in production of Bisphenol A bis(2,3-dihydroxypropyl)ether, BADGE, VER and VER formulations.

3) Improved cost assurance is provided by these reactions since they eliminate price volatility of currently used chemicals from petroleum feedstock.

4) A waste product form bio-diesel manufacturing, glycerol, is converted to a value added product using these synthetic protocols. It is expected enlarge and have a significant impact on the biofuel economy.

4. Does there exist an earlier, dated record of the invention's conception--a sketch, report, laboratory notebook entry, or the like-which:

We have laboratory notebook pages, computer generated chemical structures and emails.

5. a. Is this disclosure related to any earlier invention disclosure? If yes, identify and list showing docket number and title.

No

5. b. Is this disclosure related to any earlier invention disclosure at another institution?

No

6. What do you see as <u>commercial</u> uses of your invention?

The products obtained in the demonstrated and conceptualized/currently investigated reaction schemes are widely utilized resins used in diverse industries, such as, ship building, automotive part construction, infrastructure polymer concrete reinforcements, corrosion resistance coatings (on chemical storage tanks, pipes and ducting, fume extraction systems, gas cleaning units), top-coat materials (with excellent adhesion to plastics, steel and concrete), optical fiber coating, UV curing inks and printed circuit board manufacture

7. What firms do you think may be, or are, commercially interested in this technology; and why?

a) VER producing companies as they are looking for alternative, greener and cost effective newer approaches.

b) Fiber reinforced composite manufacturing firms, as they would be interested in cost-effective VER resin.

c) Coatings industry, as they would be interested in cost-effective VER resin.

8. Do you have a relationship, formal or informal, with any of these companies? What is the nature of the relationship?

No

9. What do you see as the greatest impediment to the commercial adoption of your invention?

None

10. Is further development of your invention now in progress? Scheduled? Dependent on commercial or federal sponsorship?

Yes, investigations are underway on the conceptualized schemes as described above and will be reported here.

11. Has any aspect of this invention been published, been presented at a scientific meeting, been discussed with non-UMass individuals, part of a student dissertation or otherwise disseminated?

q YES √ NO

If yes, please identify, list dates and circumstances. (Dates are important. If published, list the date recorded on microfilm or in a library.)

12. Are there any plans to publish or otherwise publicly disseminate any aspect of this invention in the future?

√ YES q NO

After a patent application, the reaction schemes will be reported in publications and presented at conferences.

13. Are you aware of related developments by other institutions or companies?

q YES √ NO

14. Has the research that led to the invention been sponsored or funded by industry, or funded by a grant from a government agency or private foundation?

√ YES q NO

If yes, you must provide CVIP with information on all funding sources for research that resulted in this invention. Please note that failure to report a funding source may result in a significant delay in proceeding with this disclosure, or may result in not being able to license the invention.

INDUSTRY OR FOUNDATION SPONSOR	GRANT #	CONTRACT #
SERDP-Sustainable green vinyl ester resin from renewable resources.		

Fund	Dept. ID	P/G #	Speed Type
53106-L	L630300401-L	S51300000024869-L	114132-L

(Case Manager's Initials _____) Verified that the grant information shown above is complete as listed with the University's offices of Sponsored Programs and/or Offices of Grants and Contracts.

15. Did the research that led to the invention use any information or materials (e.g., cell lines, DNA, protein, antibodies) provided by another institution or a company?

    q YES √ NO

    If yes, was a transmittal letter or agreement (e.g., Confidential Disclosure Agreement [CDA] or Materials Transfer Agreement [MTA]), used in connection with receipt of the information or materials?

    q YES q NO

    If yes to either, attach a copy of the CDA or MTA, or provide the name of the Investigator and address of the company.

16. Our technology evaluators or patent attorneys may wish to contact the Investigators with questions or to seek clarification. Please identify the primary Investigator Contact:

NAME:	PHONE:
Akshay Kokil	540-998-9495

17. Mailing address(es) for each Investigator(s) in order listed on page 1:

    Please provide your LOCAL or your HOME ADDRESS--where you are living now, not your University (i.e., Departmental P.O. Box) address. If you are a citizen of another country, then please indicate which country.

Investigator #1	Investigator #2
Full name: Akshay Kokil	Full name: Yongwoo Lee
Local or Home street address, city, state, zip code, country: 100 Pemberton Street, # 9, Dracut MA 01826	Local or Home street address, city, state, zip code, country:
Citizen of which country: India	Citizen of which country: U.S.A.
Work phone(s): 504-998-9495	Work phone(s): 978-934-3792
Work FAX :	Work FAX:
E-mail address: akshay_kokil@uml.edu	E-mail address: yongwoo_lee@uml.edu
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Investigator #3	Investigator #4
Full name: Priyank N. Shah Local or Home street address, city, state, zip code, country: 18 East Meadow Lane, Unit 101, Lowell, MA-01854 Citizen of which country: India Work phone(s): 978-761-9645 Work FAX: E-mail address: priyank_shah@uml.edu Local or Home phone (where you can be reached when you are not at work):	Full name: Local or Home street address, city, state, zip code, country: Citizen of which country: Work phone(s): Work FAX: E-mail address: Local or Home phone (where you can be reached when you are not at work):

Signature(s) of Investigator(s)

The undersigned agree(s) to cooperate with CVIP in the assessment, protection and commercialization of the invention. Further, each Covered Individual (as defined in the University Intellectual Property Policy (BOT T96-040)) does hereby assign, transfer and convey to University the entire right, title and interest in the invention and agrees to execute and deliver all documents requested by CVIP (including a Participation Agreement if not already executed) to record the assignment of rights to the University.

Name Typed	Signature	Date
1. Akshay Kokil		06/19/15
2. Yongwoo Lee		06/19/15
3. Priyank N. Shah		06/19/15
4.		

18. Any other comments you believe are important for the evaluation of this technology.

Appendix D

UNIVERSITY OF MASSACHUSETTS

AMHERST • BOSTON • DARTMOUTH • LOWELL • WORCESTER

CVIP Use Only

Commercial Ventures and Intellectual Property

Invention Disclosure

Lowell Campus Office:
600 Suffolk Street, 2nd Floor, Attn: Director, CVIP
Lowell, MA 01854
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Boston, MA 02110
Tel: 617-287-4088

UML#: 2015-039

Received: 21May15

Accepted _____

Case Manager: R. Kaushik

University of Massachusetts
Uniform Invention Disclosure Form
(version 12/17/2012)

Title of Invention: Environmentally Benign Single Pot Vinyl Ester Resin (VER) formulations with "green" reactive diluent

	Investigator's Name & Title *(Please list Principal Investigator first and include all possible inventors)*	**Department**	**Institution** *(at time invention was made)*
1.	Name: Akshay Kokil Title: Post-doctoral Researcher	Dept: Chemistry	Institution: University of Massachusetts Lowell
2.	Name: Yongwoo Lee Title: Research Professor	Dept: Chemistry	Institution: University of Massachusetts Lowell
3.	Name: Priyank N. Shah Title: Post-doctoral Researcher	Dept: Chemistry	Institution: University of Massachusetts Lowell

Please check campus of lead Principal Investigator: Amherst Boston Dartmouth Lowell √ UMMC

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Most of the chemicals used for the synthesis of VER are derived from petroleum based feedstocks, which introduces price volatility. In 2014 all the major manufacturers of VER, namely Ashland, DSM and Reichold, announced an increase in the VER price due to the increased cost of raw materials derived from petroleum feedstocks. Hence, an alternate route for improved sustainability and reduced cost volatility of this commercially important resin is required.

A typical VER composition consists of styrene as a reactive diluent. However, styrene is a highly carcinogenic chemical and has been identified as a hazardous air pollutant by the EPA. Hence, alternatives for styrene as reactive diluent in VER compositions are required.

We have reported in a recent publication (*RSC Advance, 2015, 5, 38673*) a multi-step protocol for the environmentally benign synthesis of VER from bio-waste glycerin. The publication reported a 4 step reaction protocol.

Here we report for the first time a new and different two step or single pot reaction protocol for the synthesis of VER formulations with "green" reactive diluent.

2. Description of the Invention

We report here for the first time:

I) an environmentally benign methodology for obtaining VER formulations with “green” reactive diluent

II) a novel two-step or in single pot synthetic protocol.

III) elimination of currently used toxic chemicals in VER synthesis and VER formulations, such as epichlorohydrin and styrene

IV) utilization of starting materials derived from bio-waste streams, which improves the environmental and cost sustainability of the procedure.

Following is the detailed two step protocol used for synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether and VER. The following procedure also outlines the concept for the synthesis VER formulations with a “green” diluent in two step procedures and in single step procedures. Investigations are currently underway for demonstrating the other procedures and will be included in this invention disclosure.

1) **One pot synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether**

Materials: Bisphenol A, diethylene carbonate and potassium carbonate were procured from Sigma Aldrich and utilized without further purification. Crude glycerol as a bio-waste was procured from Maine Standard Biofuels. Glycerol in pure from was obtained using vacuum distillation.

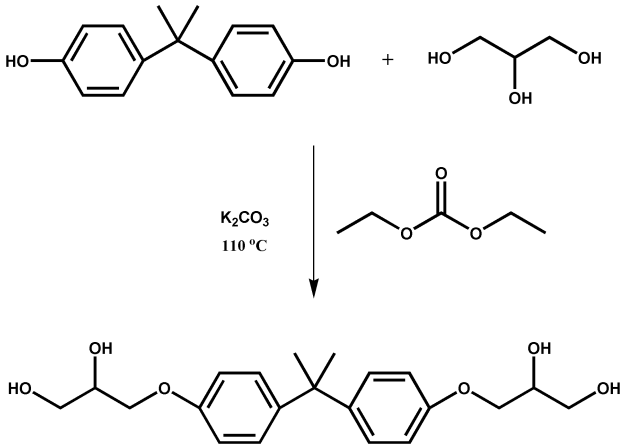

Figure 1. Reaction scheme for synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether.

Procedure:

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flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 110 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethylether and the ethanol byproduct. The hot reaction mixture was then added to a beaker containing 500 mL deionized water. A viscous reaction product was allowed to settle over time and the supernatant water removed. The crude reaction product was washed twice with 500 mL water to remove any unreacted glycerol. The 99% pure Bisphenol A bis(2,3-dihydroxypropyl)ether was isolated in quantitative yields. The purity of the reaction product was determined using proton NMR shown below (Figure 2). This solvent free reaction occurs through *in-situ* formation of glycerol carbonate as described in literature (Truscello A. M. et al. Green Chemistry 2013, 15, 625). The reaction can also be performed using commercially available glycerol carbonate instead of glycerol and diethyl carbonate. The presence of excess glycerol in the system affords the use of this reaction for obtaining one pot VER formulations as described below.

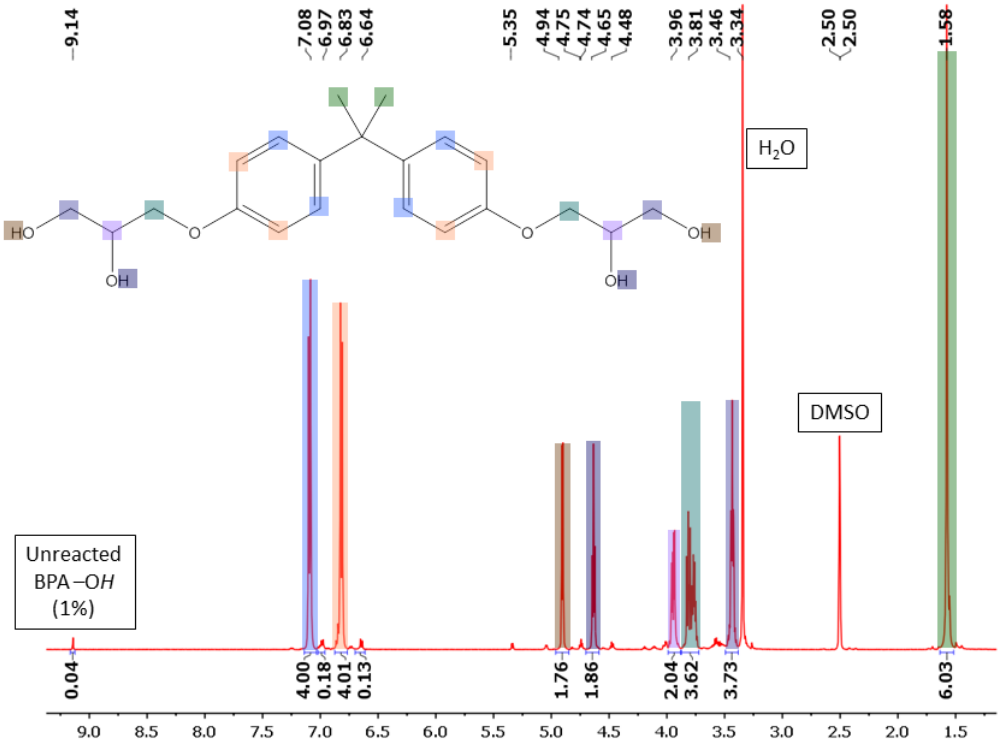

Figure 2. Proton NMR of isolated Bisphenol A bis(2,3-dihydroxypropyl)ether in DMSO-d6.

2) **Synthesis of VER**

Materials: Bisphenol A bis(2,3-dihydroxypropyl)ether, Methyl methacrylate, Potassium Carbonate

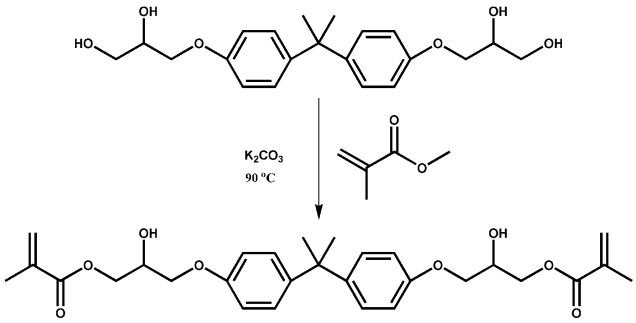

Figure 3. Reaction scheme for synthesis of VER by transesterification of Bisphenol A bis(2,3-dihydroxypropyl)ether.
Procedure:

In a single necked round bottom flask Bisphenol A bis(2,3-dihydroxypropyl)ether (1 g, 2.65 mmol), as received Methyl methacrylate (1.32 g, 13.28 mmol) and Potassium Carbonate (300 mg, 2.17 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 90 °C. After 18 h the reaction was stopped by applying vacuum to remove any unreacted methyl methacrylate and the methanol byproduct. The resulting product was analyzed by proton NMR shown below (Figure 4).

Transesterification is a well know reaction which can be performed using a variety of catalysts. Potassium carbonate was selected as an example here to demonstrate the feasibility of the reaction protocol. Further investigations are underway to improve the conversion of the reaction and will be included here. A 25% conversion was obtained in the current reaction protocol as evidenced by the presence of vinyl protons around 6.04 and 5.61 ppm.

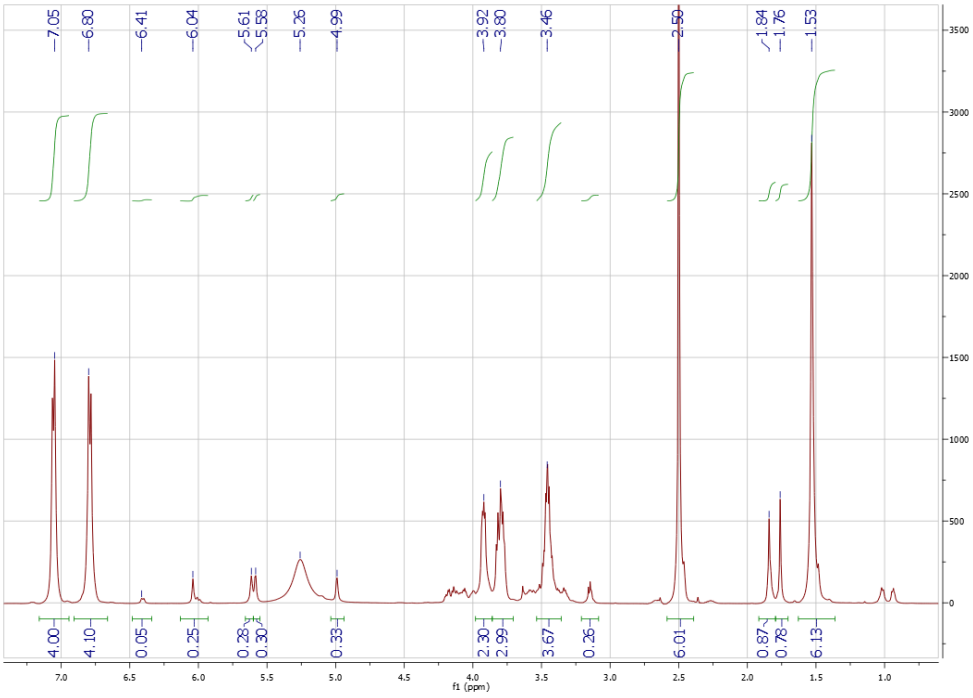

Figure 4. Proton NMR of the reaction product in DMSO-d6.

3) **Single pot synthesis of VER and VER formulations**

The catalyst (potassium carbonate) utilized for the two reactions reported above is the same and it is used in same concentrations. Hence, the above two reactions can be combined to obtain VER in a single step. The transesterification of excess glycerol with methyl methacrylate the reaction mixture will result in formation of a reactive diluent in the system. This will result in complete elimination or reduction in use of styrene as the reactive diluent. These investigations on this concept are underway and the results will be included here.

3. What are the novel aspects of your invention and how does it improve upon prior art? Does your invention overcome any deficiencies or limitations in the prior art?

Following are the novel aspects of the invention:

1) The reaction schemes demonstrated and conceptualized have not been reported before and present a new environmentally benign route for synthesis of VER formulations with a "green" reactive diluent.

2) The reaction schemes demonstrated and conceptualized eliminate the use of hazardous chemicals such as epichlorohydrin and styrene. Thus these reactions are environmentally benign in contrast to the methodology currently utilized in production of Bisphenol A bis(2,3-dihydroxypropyl)ether, VER and VER formulations.

3) Improved cost assurance is provided by these reactions since they eliminate price volatility of currently used chemicals from petroleum feedstock.

4) A waste product form bio-diesel manufacturing, glycerol, is converted to a value added product using these synthetic protocols. It is expected enlarge and have a significant impact on the biofuel economy.

4. Does there exist an earlier, dated record of the invention's conception--a sketch, report, laboratory notebook entry, or the like-which:

We have laboratory notebook pages, computer generated chemical structures and emails.

5. a. Is this disclosure related to any earlier invention disclosure? If yes, identify and list showing docket number and title.

No

5. b. Is this disclosure related to any earlier invention disclosure at another institution?

No

6. What do you see as <u>commercial</u> uses of your invention?

The products obtained in the demonstrated and conceptualized/currently investigated reaction schemes are widely utilized resins used in diverse industries, such as, ship building, automotive part construction, infrastructure polymer concrete reinforcements, corrosion resistance coatings (on chemical storage tanks, pipes and ducting, fume extraction systems, gas cleaning units), top-coat materials (with excellent adhesion to plastics, steel and concrete), optical fiber coating, UV curing inks and printed circuit board manufacture

7. What firms do you think may be, or are, commercially interested in this technology; and why?

a) VER producing companies as they are looking for alternative, greener and cost effective newer approaches.

b) Fiber reinforced composite manufacturing firms, as they would be interested in cost-effective and VER formulations.

c) Coatings industry, as they would be interested in cost-effective and green VER formulations with no or reduced hazardous air pollutants.

8. Do you have a relationship, formal or informal, with any of these companies?
   What is the nature of the relationship?

No

9. What do you see as the greatest impediment to the commercial adoption of your invention?

None

10. Is further development of your invention now in progress? Scheduled? Dependent on commercial or federal sponsorship?

Yes, investigations are underway on the conceptualized schemes as described above and will be reported here.

11. Has any aspect of this invention been published, been presented at a scientific meeting, been discussed with non-UMass individuals, part of a student dissertation or otherwise disseminated?

❑ YES √ NO

If yes, please identify, list dates and circumstances. (Dates are important. If published, list the date recorded on microfilm or in a library.)

12. Are there any plans to publish or otherwise publicly disseminate any aspect of this invention in the future?

√ YES ❑ NO

After a patent application, the reaction schemes will be reported in a publications and presented at conferences.

13. Are you aware of related developments by other institutions or companies?

❑ YES √ NO

14. Has the research that led to the invention been sponsored or funded by industry, or funded by a grant from a government agency or private foundation?

√ YES ❑ NO

If yes, you must provide CVIP with information on all funding sources for research that resulted in this invention. Please note that failure to report a funding source may result in a significant delay in proceeding with this disclosure, or may result in not being able to license the invention.

INDUSTRY OR FOUNDATION SPONSOR	GRANT #	CONTRACT #
SERDP-Sustainable green vinyl ester resin from renewable resources.		

Fund	Dept. ID	P/G #	Speed Type
53106-L	L630300401-L	S51300000024869-L	114132-L

(Case Manager's Initials _____) Verified that the grant information shown above is complete as listed with the University's offices of Sponsored Programs and/or Offices of Grants and Contracts.

15. Did the research that led to the invention use any information or materials (e.g., cell lines, DNA, protein, antibodies) provided by another institution or a company?

❑ YES √ NO

If yes, was a transmittal letter or agreement (e.g., Confidential Disclosure Agreement [CDA] or Materials Transfer Agreement [MTA]), used in connection with receipt of the information or materials?

❑ YES ❑ NO

If yes to either, attach a copy of the CDA or MTA, or provide the name of the Investigator and address of the company.

16. Our technology evaluators or patent attorneys may wish to contact the Investigators with questions or to seek clarification. Please identify the primary Investigator Contact:

NAME:	PHONE:
Akshay Kokil	540-998-9495

17. Mailing address(es) for each Investigator(s) in order listed on page 1:

Please provide your LOCAL or your HOME ADDRESS--where you are living now, not your University (i.e., Departmental P.O. Box) address. If you are a citizen of another country, then please indicate which country.

Investigator #1	Investigator #2
Full name: Akshay Kokil Local or Home street address, city, state, zip code, country: 100 Pemberton Street, # 9, Dracut MA 01826 Citizen of which country: India Work phone(s): 504-998-9495 Work FAX : E-mail address: akshay_kokil@uml.edu Local or Home phone (where you can be reached when you are not at work):	Full name: Yongwoo Lee Local or Home street address, city, state, zip code, country: Citizen of which country: U.S.A. Work phone(s): 978-934-3792 Work FAX: E-mail address: yongwoo_lee@uml.edu Local or Home phone (where you can be reached when you are not at work):
Investigator #3	**Investigator #4**
Full name: Priyank N. Shah Local or Home street address, city, state, zip code, country: 18 East Meadow Lane, Unit 101, Lowell, MA-01854 Citizen of which country: India Work phone(s): 978-761-9645 Work FAX: E-mail address: priyank_shah@uml.edu Local or Home phone (where you can be reached when you are not at work):	Full name: Local or Home street address, city, state, zip code, country: Citizen of which country: Work phone(s): Work FAX: E-mail address: Local or Home phone (where you can be reached when you are not at work):

Signature(s) of Investigator(s)

The undersigned agree(s) to cooperate with CVIP in the assessment, protection and commercialization of the invention. Further, each Covered Individual (as defined in the University Intellectual Property Policy (BOT T96-040)) does hereby assign, transfer and convey to University the entire right, title and interest in the invention and agrees to execute and deliver all documents requested by CVIP (including a Participation Agreement if not already executed) to record the assignment of rights to the University.

Name Typed	Signature	Date
1. Akshay Kokil		06/22/15
2. Yongwoo Lee		06/22/15
3. Priyank N. Shah		06/22/15
4.		

18. Any other comments you believe are important for the evaluation of this technology.

Appendix E

UNIVERSITY OF MASSACHUSETTS

AMHERST • BOSTON • DARTMOUTH • LOWELL • WORCESTER

CVIP Use Only

Commercial Ventures and Intellectual Property

Invention Disclosure

Lowell Campus Office:
600 Suffolk Street, 2nd Floor, Attn: Director, CVIP
Lowell, MA 01854
Tel: 978-934-3235

Central Office:
President's Office, Attn: Executive Director, CVIP
225 Franklin Street, 12th floor
Boston, MA 02110
Tel: 617-287-4088

UML #: 2015-040

Received: 21May15

Accepted: 19Jun15

Case Manager: R. Kaushik

University of Massachusetts
Uniform Invention Disclosure Form
(version 12/17/2012)

Title of Invention: Environmentally Benign Synthesis of Bisphenol A diglycidyl ether (BADGE)

	Investigator's Name & Title *(Please list Principal Investigator first and include all possible inventors)*	**Department**	**Institution** *(at time invention was made)*
1.	Name: Akshay Kokil Title: Post-doctoral Researcher	Dept: Chemistry	Institution: University of Massachusetts Lowell
2.	Name: Yongwoo Lee Title: Research Professor	Dept: Chemistry	Institution: University of Massachusetts Lowell
3.	Name: Priyank N. Shah Title: Post-doctoral Researcher	Dept: Chemistry	Institution: University of Massachusetts Lowell

Please check campus of lead Principal Investigator: Amherst Boston Dartmouth Lowell √ UMMC

To the Investigator(s):

The business of a university is the gathering and dissemination of knowledge. Making an invention and putting it to use in the service of the public is a thoroughly valid mode of accomplishing this objective.

Accordingly, the University encourages the inventive process; and within the limits of financial practicality, can often provide advice and assistance in bringing inventions to the point of public use.

In the sense used here, an "invention" has a presumed commercial use and value. The following indicates the preferred time to file a disclosure with CVIP.

- ☐ *Disclose to CVIP first, publish later:* Disclosing your invention to CVIP by no means proscribes publication; on the other hand, premature publication can have disastrous consequences, both legal and tactical, upon an effort to commercialize it by precluding the availability of patent protection in most countries.

- ☐ *Disclose as soon as the invention is clearly conceptualized*: It is not necessary to wait until the invention is reduced to practice, and filing early may be beneficial, particularly when other groups are filing related patent applications.

- ☐ *Consult with CVIP specialists:* CVIP specialists can assist you with such questions as determining inventorship, procedures when more than one institution is involved and protecting patentable inventions from improper public disclosure.

If you think you have made an invention, but you are not sure, then say so in your disclosure. Similarly, if you are uncertain as to whether your invention has commercial merit, say so. CVIP can assist you in making such determinations. This form should be considered as a guide to assist in the invention disclosure procedure as required by the University's Intellectual Property Policy.

1. Background

Bisphenol A diglycidyl ether (BADGE) resins are high performance epoxy resins with exceptional mechanical strength and corrosion resistance. Due to their superior properties, BADGE find use, either in pure form or as a matrix in fiber reinforced composites, in diverse industries, such as, adhesives, automotive part construction, infrastructure polymer concrete reinforcements, corrosion resistance coatings (on chemical storage tanks, pipes and ducting, fume extraction systems, gas cleaning units), top-coat materials (with excellent adhesion to plastics, steel and concrete) and printed circuit board manufacture (*Jaswal, S.; Gaur, B. 'New trends in vinyl ester resisns' Rev. Chem. Eng. 2014, DOI 10.1515/revce-2014-0012*). These epoxy resins are used in diverse applications and have a huge global market and ever increasing potential.

BADGE is currently synthesized using BPA and epichlorohydrin as starting materials. Patents issued for the synthesis of BADGE using BPA and epichlorohydrin, include U.S. Pat. No. 3121727 A to Baliker et al. assigned to Shell Oil Co. and U.S. Pat. No. 4877857 A to Shirtum et al. assigned to The Dow Chemical Company.

BADGE is also utilized for synthesis of unsaturated Vinyl Ester Resins, which is another highly valuable class of resins. VER are currently synthesized by addition reaction of epoxide resins with unsaturated carboxylic acids. Currently for BPA based VER synthesis, the epoxy containing BADGE is reacted with either methacrylic acid or methyl methacylate. These resins were first commercialized as Epocryl resins by Shell Chemical Company and later as Derakane resins by Dow Chemical Company. Currently these resins are produced predominantly by Ashland, DSM and Reichold.

BPA based VER is synthesized from BADGE by the addition reaction of its epoxy groups with acrylic acid based monomers. Patents issued for the synthesis of VER using this synthetic protocol include U.S. Pat. No. 3256226 to Fekete et al., and No. 3317465 to Doyle et al., both assigned to H. H. Robertson Co.; No. 3345401 to May; No. 3373221 to May; No. 3377406 to Newey; and No. 3432478 to May, all assigned to Shell Oil Co.; No. 3548030 to Jernigan; and No. 3564074 to Swisher et al., both assigned to Dow Chemical Co.; No. 3634542 to Dowd et al.; and No. 3637618 to May, both assigned to Shell Oil Co.

The production of BADGE is still performed using the synthetic protocols reported more than 3 decades ago. Even though the synthetic protocol used is efficient, it requires the use of epichlorohydrin, which performs the dual role of a solvent and reactant. Epichlorohydrin however, has been identified by the U.S. Environmental Protection Agency (EPA) as a hazardous air pollutant and it also features on the list of controlled chemicals by the EPA. Hence, to ensure continued environmental sustainability and improved work place safety an alternative route for the synthesis of BADGE is required.

The use of epichlorohydrin, which displaces significant price volatility, also introduces limited cost sustainability and profitablility of BADGE.

Here we report for the first time a new and different two step or single pot reaction protocol for the synthesis of BADGE.

2. Description of the Invention

We report here for the first time:

I) an environmentally benign “green” methodology for the synthesis of BADGE

II) a novel two-step and single step synthetic protocol.

III) elimination of currently used toxic chemicals in BADGE synthesis, such as epichlorohydrin

IV) utilization of starting materials derived from bio-waste streams, which improves the environmental and cost sustainability of the procedure.

Following is the detailed two step protocol used for synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE), a precursor to BADGE. The following procedure also outlines the concept for the synthesis of BADGE in two steps as well as in a single step. Investigations are currently underway for demonstrating the synthesis of BADGE and will be included in this invention disclosure.

1) **One pot synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE)**

Materials: Bisphenol A, diethylene carbonate and potassium carbonate were procured from Sigma Aldrich and utilized without further purification. Crude glycerol as a bio-waste was procured from Maine Standard Biofuels. Glycerol in pure from was obtained using vacuum distillation.

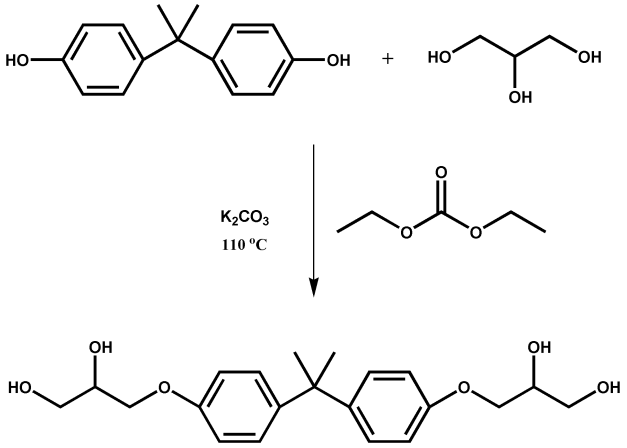

Figure 1. Reaction scheme for synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether (BABDHPE).

Procedure:

In a single necked round bottom flask Bisphenol A (10 g, 43.80 mmol), Glycerol (24.20 g, 262.82 mmol), Diethyl carbonate (15.52 g, 131.4 mmol) and Potassium Carbonate (3 g, 21.70 mmol) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 110 °C. After 18 h the reaction was stopped by first applying vacuum to remove any unreacted diethylether and the ethanol byproduct. The hot reaction mixture was then added to a beaker containing 500 mL deionized water. A viscous reaction product was allowed to settle over time and the supernatant water removed. The crude reaction product was washed twice with 500 mL water to remove any unreacted glycerol. The 99% pure Bisphenol A bis(2,3-dihydroxypropyl)ether was isolated in quantitative yields. The purity of the reaction product was determined using proton NMR shown below (Figure 2). This solvent free reaction occurs through *in-situ* formation of glycerol carbonate as described in literature (Truscello A. M. et al. Green Chemistry 2013, 15, 625). The reaction can also be performed using commercially available glycerol carbonate instead of glycerol and diethyl carbonate.

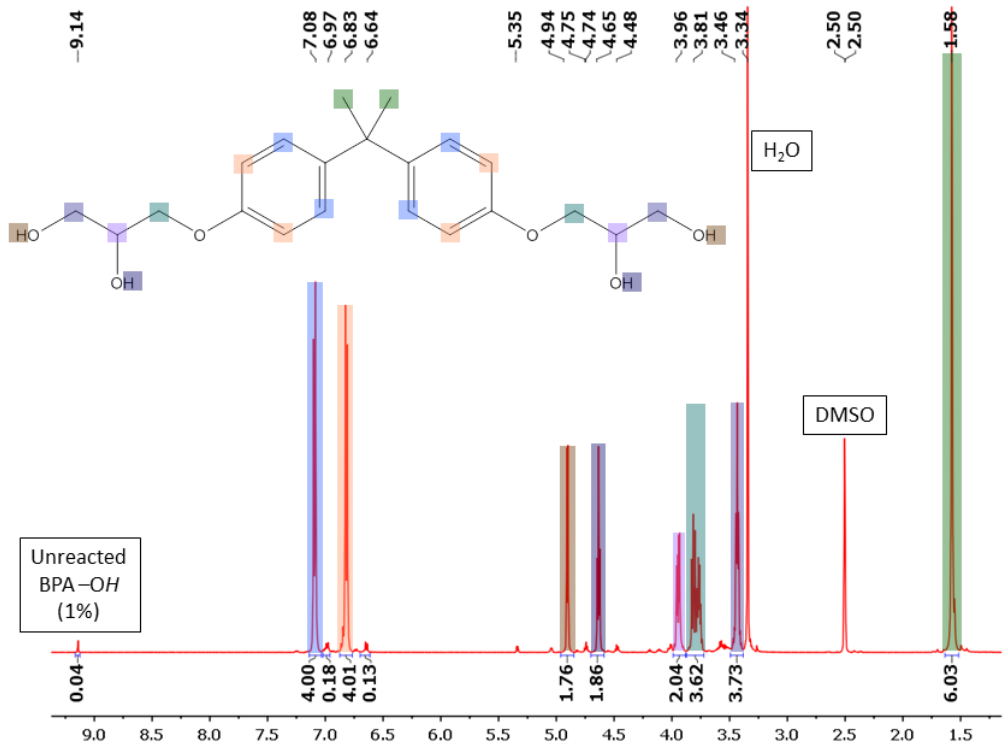

Figure 2. Proton NMR of isolated BABDHPE in DMSO-d6.

2) **Epichlorohydrin free synthesis of BADGE**

By employing the synthesized Bisphenol A bis(2,3-dihydroxypropyl)ether, BADGE can be synthesized by an environmentally benign procedure described below. The reaction can also be performed in a single pot.

As discussed below this synthetic strategy completely averts the use of toxic epichlorohydrin and also affords potentially useful BPA diglycidylether biscarbonate (BADGEBC).

2a) Synthesis of BADGEBC

Materials: Dimethyl carbonate and Potassium Carbonate were procured from Sigma Aldrich and utilized without further purification. The isolated BABDHPE was utilized for the reaction (Figure 3).

Procedure: In a single necked round bottom flask BABDHPE (1 g), as received dimethyl carbonate (10 mL) and Potassium Carbonate (300 mg) were introduced. The flask was connected to a Claisen distillation setup and the reaction mixture was vigorously stirred at 75 °C. After 18 h the reaction was stopped by applying vacuum to remove any unreacted dimethyl carbonate and the methanol byproduct. The obtained product was dissolved in 3 mL of dimethyl sulfoxide and added dropwise to 40 mL deionized water. The isolated precipitate, in quantitative yield, was analyzed using proton NMR (Figure 4). As seen in the NMR a quantitative conversion of BABDHPE to BADGEBC was obtained.

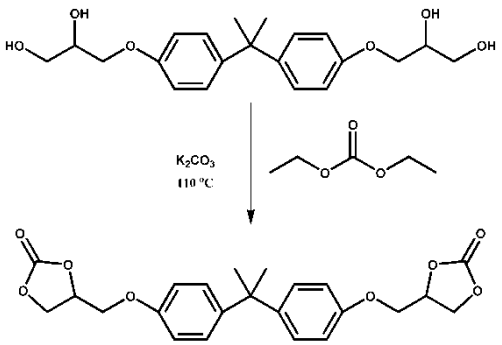

Figure 3. Reaction scheme for synthesis of BADGEBC.

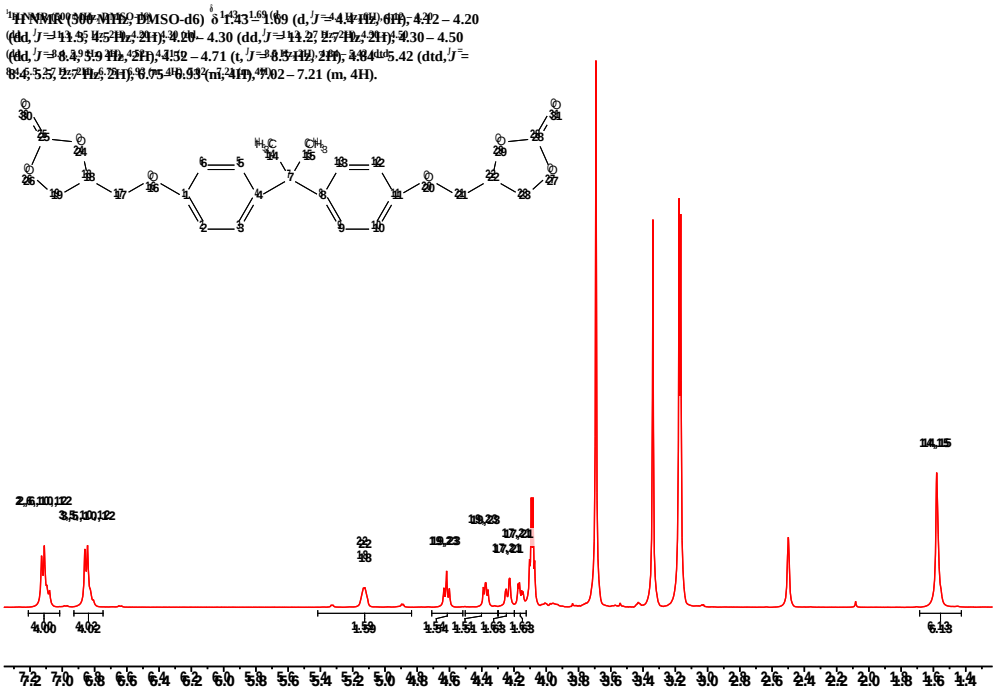

Figure 4. Proton NMR of the BADGEBC reaction product in DMSO-d6.

2b) Synthesis of BADGE

By employing the synthesized BADGEBC, BADGE can be synthesized using the reaction scheme presented below. The reaction can also be performed in a single pot. These investigations on this concept are underway.

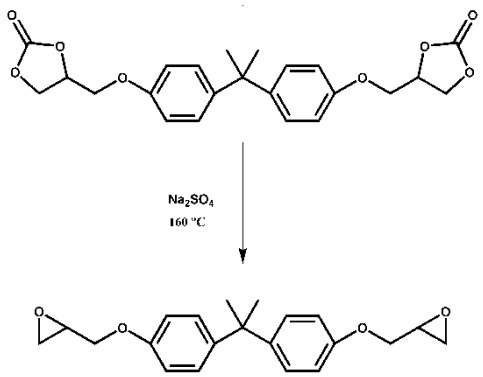

Figure 5. Reaction scheme for synthesis of BADGE from BADGEBC.

3. What are the novel aspects of your invention and how does it improve upon prior art? Does your invention overcome any deficiencies or limitations in the prior art?

Following are the novel aspects of the invention:

1) The reaction schemes demonstrated and conceptualized have not been reported before and present a new "green" route for synthesis of Bisphenol A bis(2,3-dihydroxypropyl)ether and BADGE.

2) The reaction schemes demonstrated and conceptualized eliminate the use of hazardous chemicals such as epichlorohydrin and styrene. Thus these reactions are environmentally benign in contrast to the methodology currently utilized in production of Bisphenol A bis(2,3-dihydroxypropyl)ether and BADGE.

3) Improved cost assurance is provided by these reactions since they eliminate price volatility of currently used chemicals from petroleum feedstock.

4) A waste product form bio-diesel manufacturing, glycerol, is converted to a value added product using these synthetic protocols. It is expected enlarge and have a significant impact on the biofuel economy.

4. Does there exist an earlier, dated record of the invention's conception--a sketch, report, laboratory notebook entry, or the like-which:

We have laboratory notebook pages, computer generated chemical structures and emails.

5. a. Is this disclosure related to any earlier invention disclosure? If yes, identify and list showing docket number and title.

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The products obtained in the demonstrated and conceptualized/currently investigated reaction schemes are widely utilized epoxy resins used in diverse industries, such as, adhesives, automotive part construction, infrastructure polymer concrete reinforcements, corrosion resistance coatings (on chemical storage tanks, pipes and ducting, fume extraction systems, gas cleaning units), top-coat materials (with excellent adhesion to plastics, steel and concrete), and printed circuit board manufacture.

7. What firms do you think may be, or are, commercially interested in this technology; and why?

a) BADGE producing companies as they are looking for alternative, greener and cost effective newer approaches.

b) Epoxy adhesives formulating companies

b) Fiber reinforced composite manufacturing firms, as they would be interested in cost-effective BADGE resin.

c) Coatings industry, as they would be interested in cost-effective BADGE resin.

8. Do you have a relationship, formal or informal, with any of these companies? What is the nature of the relationship?

No

9. What do you see as the greatest impediment to the commercial adoption of your invention?

None

10. Is further development of your invention now in progress? Scheduled? Dependent on commercial or federal sponsorship?

Yes, investigations are underway on the conceptualized schemes as described above and will be reported here.

11. Has any aspect of this invention been published, been presented at a scientific meeting, been discussed with non-UMass individuals, part of a student dissertation or otherwise disseminated?

q YES √ NO

If yes, please identify, list dates and circumstances. (Dates are important. If published, list the date recorded on microfilm or in a library.)

12. Are there any plans to publish or otherwise publicly disseminate any aspect of this invention in the future?

√ YES q NO

After a patent application, the reaction schemes will be reported in publications and presented at conferences.

13. Are you aware of related developments by other institutions or companies?

q YES √ NO

14. Has the research that led to the invention been sponsored or funded by industry, or funded by a grant from a government agency or private foundation?

√ YES q NO

If yes, you must provide CVIP with information on all funding sources for research that resulted in this invention. Please note that failure to report a funding source may result in a significant delay in proceeding with this disclosure, or may result in not being able to license the invention.

INDUSTRY OR FOUNDATION SPONSOR	GRANT #	CONTRACT #
SERDP-Sustainable green vinyl ester resin from renewable resources.		

Fund	Dept. ID	P/G #	Speed Type
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(Case Manager's Initials _____) Verified that the grant information shown above is complete as listed with the University's offices of Sponsored Programs and/or Offices of Grants and Contracts.

15. Did the research that led to the invention use any information or materials (e.g., cell lines, DNA, protein, antibodies) provided by another institution or a company?

q YES √ NO

If yes, was a transmittal letter or agreement (e.g., Confidential Disclosure Agreement [CDA] or Materials Transfer Agreement [MTA]), used in connection with receipt of the information or materials?

q YES q NO

If yes to either, attach a copy of the CDA or MTA, or provide the name of the Investigator and address of the company.

16. Our technology evaluators or patent attorneys may wish to contact the Investigators with questions or to seek clarification. Please identify the primary Investigator Contact:

NAME:	PHONE:
Akshay Kokil	540-998-9495

17. Mailing address(es) for each Investigator(s) in order listed on page 1:

Please provide your LOCAL or your HOME ADDRESS--where you are living now, not your University (i.e., Departmental P.O. Box) address. If you are a citizen of another country, then please indicate which country.

Investigator #1	Investigator #2
Full name: Akshay Kokil	Full name: Yongwoo Lee
Local or Home street address, city, state, zip code, country: 100 Pemberton Street, # 9, Dracut MA 01826	Local or Home street address, city, state, zip code, country:
Citizen of which country: India	Citizen of which country: U.S.A.
Work phone(s): 504-998-9495	Work phone(s): 978-934-3792
Work FAX :	Work FAX:
E-mail address: akshay_kokil@uml.edu	E-mail address: yongwoo_lee@uml.edu
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Investigator #3	Investigator #4
Full name: Priyank N. Shah Local or Home street address, city, state, zip code, country: 18 East Meadow Lane, Unit 101, Lowell, MA-01854 Citizen of which country: India Work phone(s): 978-761-9645 Work FAX: E-mail address: priyank_shah@uml.edu Local or Home phone (where you can be reached when you are not at work):	Full name: Local or Home street address, city, state, zip code, country: Citizen of which country: Work phone(s): Work FAX: E-mail address: Local or Home phone (where you can be reached when you are not at work):

Signature(s) of Investigator(s)

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Name Typed	Signature	Date
1. Akshay Kokil		06/19/15
2. Yongwoo Lee		06/19/5
3. Priyank N. Shah		06/19/15
4.		

18. Any other comments you believe are important for the evaluation of this technology.

Appendix F

UNIVERSITY OF MASSACHUSETTS

AMHERST • BOSTON • DARTMOUTH • LOWELL • WORCESTER

Commercial Ventures and Intellectual Property

Lowell Campus Office:
600 Suffolk Street, 2nd Floor, Attn: Director, CVIP
Lowell, MA 01854
Tel: 978-934-3235

Central Office:
President's Office, Attn: Executive Director, CVIP
225 Franklin Street, 12th floor
Boston, MA 02110
Tel: 617-287-4088

CVIP Use Only

Invention Disclosure

 # UML 2016-020

Received 12 Jan 16

Accepted 13 Jan 16

Case Manager R. Kaushik

University of Massachusetts
Uniform Invention Disclosure Form
(Version 12/17/2012)

Title of Invention: "Green" Vinyl Ester Resin (VER) from Glycerol Carbonate Methacrylate and Bisphenol A

	Investigator's Name & Title *(Please list Principal Investigator first and include all possible inventors)*	**Department**	**Institution** *(at time invention was made)*
1.	Name: Yongwoo Lee Title: Research Professor	Dept: Chemistry	Institution: UML
2.	Name: Priyank N. Shah Title: Post-Doc	Dept: Chemistry	Institution: UML

"Green" Vinyl Ester Resin (VER) from Glycerol Carbonate Methacrylate and Bisphenol A

Please check campus of lead Principal Investigator: Amherst☐ Boston☐ Dartmouth☐ Lowell☑

To the Investigator(s):

The business of a university is the gathering and dissemination of knowledge. Making an invention and putting it to use in the service of the public is a thoroughly valid mode of accomplishing this objective.

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If you <u>think</u> you have made an invention, but you are not sure, then say so in your disclosure. Similarly, if you are uncertain as to whether your invention has commercial merit, say so. CVIP can assist you in making such determinations. This form should be considered as a guide to assist in the invention disclosure procedure as required by the University's Intellectual Property Policy.

1. Background

In order for patent counsel to determine the patentability of this invention, it will be necessary to compare it to existing technology (referred to as "<u>prior art</u>"). This section should provide information to aid in that evaluation. Please identify and provide references to the prior art by patent number or journal article identification. Useful websites for patent searches include: (1)www.uspto.gov/patft/index.html, and (2) www.wipo.int/pctdb/en/ .

This invention disclosure is about the synthesis and characterization of green vinyl ester resin (GVER) from biowaste generated by biodiesel industries. We have synthesized vinyl ester resin using bisphenol A (BPA) or tetrabromobisphenol A (TBBPA) as one of the precursor and glycerol carbonate methacrylate (GCMA) as another precursor. We have used crude glycerin obtained during manufacturing of the biodiesel in preparation of GCMA. Conversion of glycerin to GCMA required a twostep synthesis. Firstly, glycerol carbonate (GC) was synthesized from glycerin and dimethyl carbonate under basic conditions. GCMA was

synthesized by reaction of GC with methyl methacrylate in presence of zirconium acetylacetonate.[1] Paper industries produce lignin as one of the waste, which has very limited applications.

Vinyl ester resin (VER), introduced in the late 1960s, is a low-cost material that can be processed to form a matrix of fiber-reinforced composites that are excellent materials for hulls, transportation vehicles, and many other military and commercial systems.[2] Fiber-reinforced composites produced from VER have become the material of choice for marine applications, especially next-generation Navy ships. VER is therefore finding increasing application in the transportation, construction, marine, and wind energy industries.[3,4,5] In the year 2000 alone, over 60 million pounds of VER were sold in North America and the Navy's need for VER has been significantly increasing. The 500-ton deckhouse structure for the ship PCU Zumwalt (DDG 1000) is fabricated from carbon/VER composites.

VER is a polymer matrix that can be processed at ambient temperature using vacuum-assisted resin transfer molding (VARTM) into massive carbon-fiber-reinforced composites.[6] The currently manufactured resin has three main disadvantages. First and foremost, VER is currently synthesized from petroleum feedstock, so it is subject to price volatility, supply unreliability and raw material unavailability in times of oil shortages. Second, VER is synthesized from epichlorohydrin which is a known environmental hazard that produces acute toxicity in case of inhalation, oral, and dermal exposure. Third, the styrene monomer, a major reactive diluent (RD) component of VER, is environmentally hazardous, being volatile, flammable, and toxic, in addition to being an irritant.

To ensure the continued viability of this strategic VER material, it is essential to develop VER synthesis routes that are not dependent on petroleum. Moreover, investigations of the VER synthesis routes that lead to elimination of the use of epichlorohydrin and the development of resin formulations that do not contain hazardous components such as styrene are necessary. To assure sustainability of the new processing route, starting materials should be derived from readily available renewable resources. Finally, the resultant VER must retain the desirable economic and performance characteristics of the current products.

Recently, significant milestones have been achieved in developing biodiesel which is a renewable biofuel and a promising alternative to conventional fossil diesel. Biodiesel can be produced by processing of rapeseed oil;[7] soybean and wastes of cooked oil;[8] rice straw[9]; vegetable oil mixtures of cottonseed, soybean and castor oils;[10] jatropha oil;[11] and crude palm oil.[12] Biodiesel is environmentally beneficial because it is

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[12] Man, Z., Elsheikh, Y. A., Bustam, M. A., Yusup, S., Abdul Mutalib, M. I., Muhammad, N. (2013) "A Brønsted ammonium ionic liquid-KOH two-stage catalyst for biodiesel synthesis from crude palm oil", *Industrial Crops and Products*, 41, 144-149

biodegradable, nontoxic and has low emission.[13] During manufacturing of biodiesel, approximately a 10 % volume of glycerin is produced as a by-product or waste.[14] Therefore, the effective utilization of glycerin enlarges the economy of biodiesel production; moreover, the conversion of glycerin to value added chemicals can expand the scope of green chemistry. [15]

There has been a considerable dearth of literature pertaining to systemic studies on the use of functional vinyl monomer such as glycidyl methacrylate (GMA),[16] which is a versatile bidentate monomer capable of imparting oxirane functionality to VER containing styrene or other vinyl monomers. Significant literature has been reported in VER without showing concern for the manufacturing on the environment. We have also published an article on synthesis of VER using GMA and BPA.[17] In the present work, we focused on the synthesis of the green vinyl ester resins (GVER) from waste glycerin via synthesis of GCMA. Figure 1 provides an overview of the process from the wastes used as starting materials to the final VER product.

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[14] Nanda, M. R., Yuan, Z., Qin, W., Ghaziaskar, H. S., Poirier, M., Xu, C. C. (2014) "Thermodynamic and kinetic studies of a catalytic process to convert glycerol into solketal as an oxygenated fuel additive", *Fuel*, 117, 470-477.

[15] Reddy, P. S., Sudarsanam, P., Mallesham, B., Raju, G., Reddy, B. M. (2011) "Acetalisation of glycerol with acetone over zirconia and promoted zirconia catalysts under mild reaction conditions" *Journal of Industrial and Engineering Chemistry*, 17, 377-381

[16] Malik, M., Choudhary, V., I. K. Varma (2001) "Effect of oxirane groups on curing behaviour and thermal stability of vinyl ester resins", *Journal of Applied Polymer Science*, 82, 416-423

[17] P. N. Shah, N. Kim, Z. Huang, M. Jayamanna, A. Kokil, A. Pine, J. Kaltsas, E. Jahngen, D. K. Ryan, S. Yoon, R. F. Kovar, Y. Lee, Green Vinyl Ester Resin from Renewable Biowaste Glycerin. *RSC Advances*, 2015, 48, 38673-38679.

2. Description of the Invention

Please describe specifically and in detail what you consider to be the invention, as distinct from the prior art. If you need them, use additional pages, drawings, diagrams, etc. Descriptions may be by references to a separate document (copy of a report, a preprint, excerpt from a grant application, or the like) attached hereto. If you do so, please identify each document positively. Important: where available include a continuation sheet or document showing scientific data in support of the invention claims.

We report of the first time the following:

1. A simple two step synthesis of glycerol carbonate methacrylate (GCMA) from glycerin has been proposed for the first time. In the synthesis, glycerin generated at biodiesel manufacturing plant was used.
2. The first intermediate on the synthetic route, glycerol carbonate was synthesized with ~98.5 % purity using waste glycerin for the first time. Secondly, the product was made catalyst free by simply passing over acidic resin. Glycerol carbonate possesses large number of applications in many diverse fields, which can potentially expand the market scope for proposed methodology.
3. The GCMA was synthesized with 81.0 % yield. The green GCMA will be very useful not only as a precursor in VER but also many other resins.
4. Green vinyl ester resins was successfully synthesized from BPA or TBBPA and GCMA at 90 °C using potassium carbonate as a catalysts.
5. The synthetic method consists of four steps and use renewable biowaste as starting materials, whose disposal is a big problem as by 2020 the production of glycerin will be six times higher than its demand.
6. The materials used during synthetic procedure are free of epichlorohydrin and halide compound that is both toxic and carcinogenic. The current manufacturing process of VER is based upon petroleum feed stock and using epichlorohydrin as one of the intermediate. We have proposed an entirely new alternative method for synthesis of VER in which we are using biowaste as a starting material and eliminated usage of epichlorohydrin.
7. Moreover, in previous literatures of green vinyl ester resin, we have used glycidol as one of the intermediate for the production of GVER. Glycidol is a potential carcinogen and its production is extremely energy intensive process as the decarboxylation from glycerol carbonate to glycidol is performed at 140 to 160 °C. In current proposed plan, we have eliminated step for formation of glycidol as one of the intermediate.
8. Elimination of steps in the extraction, isolation, and synthesis of resins from petroleum derived products. Offers the potential for *in situ* synthesis and process development, provided that sufficiently high yields and good separation can be accomplished during processing.
9. In previous synthetic route of vinyl ester resin from biowaste, we had used potassium cyanide as catalyst for the transesterification between glycidol and methyl methacrylate. In current work, we have used zirconium acetylacetonate as catalyst for transesterification between glycerol carbonate and methyl methacrylate. Using current synthetic route, we have eliminate use of toxic potassium cyanide.
10. The carbon fabric reinforced GVER panels will have great potential to be used in building hull and deck-house of the surface ship of Navy.

3. What are the novel aspects of your invention and how does it improve upon prior art? Does your invention overcome any deficiencies or limitations in the prior art?

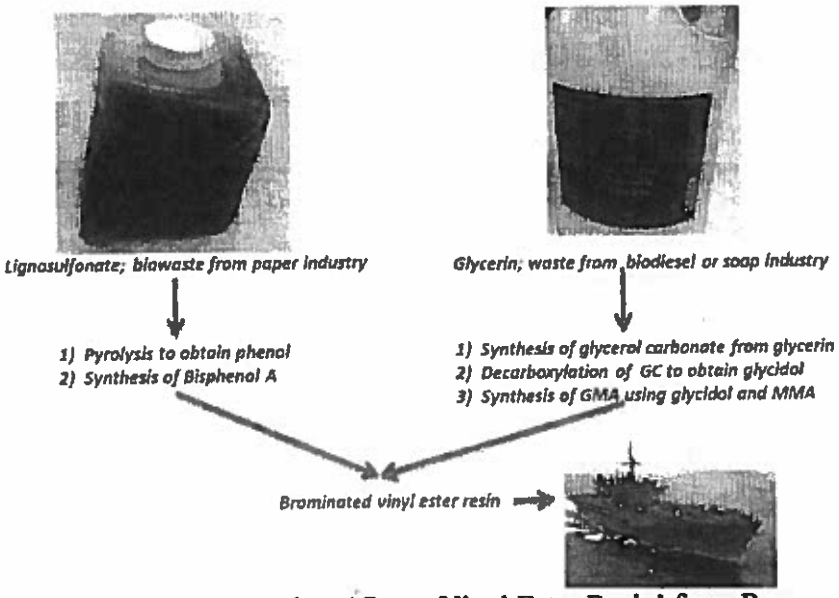

Figure 1. Illustration of the approach to 'Green Vinyl Ester Resin' from Renewable Resources.

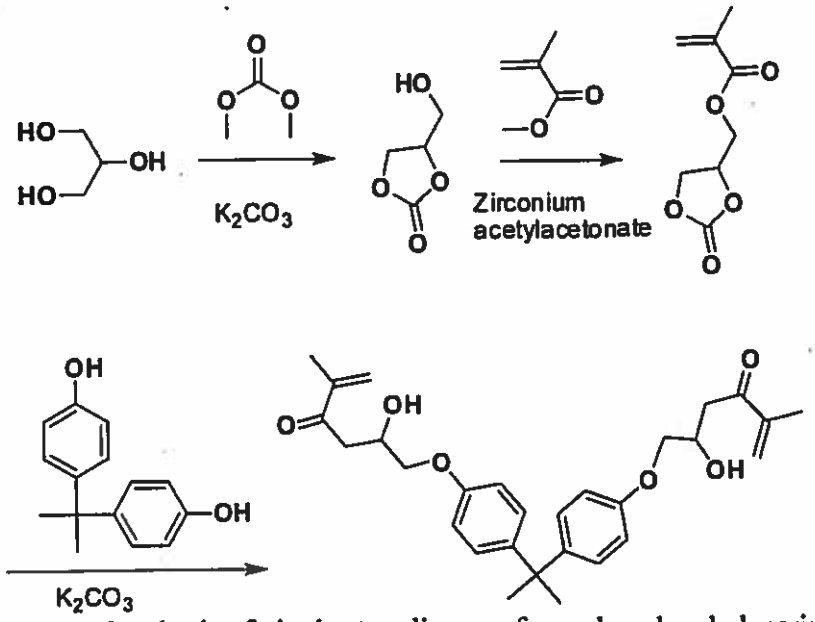

Figure 2. Synthesis of vinyl ester oligomer from phenol and glycerin.

EXPERIMENTAL SECTION

Materials.

Glycerin (Maine Standard Biofuels), potassium carbonate (99 % Sigma-Aldrich), dimethyl carbonate (99 % Alfa-Aesar), sodium sulfate (99.9 % Alfa-Aesar), methyl methacrylate (99.9 % Alfa-Aesar), potassium cyanide (Sigma-Aldrich), 2,4,-dimethyl,6-tert-butyl phenol (Alfa-Aesar), and N,N-dimethylbenzylamine, lignin (Flambeau River Paper and Sigma Aldrich).

Characterization.

NMR Spectroscopy. ^{1}H NMR spectra of the synthesized materials were recorded at 25 °C on a Bruker 500 MHz spectrometer using DMSO (Cambridge Isotope Lab., Inc.) as the solvent and tetramethylsilane (TMS) as the internal reference (δ H 0.00).

Refine Glycerol Carbonate Methacrylate (GCMA) from Glycerin.

The GCMA was synthesized by a two-step organic synthesis. The first intermediate, glycerol carbonate, was synthesized from glycerin and dimethyl carbonate under basic condition. GCMA was synthesized by reaction of glycerol carbonate and methyl methacrylate using zirconium acetylacetonate as described in Figure 2. Here, we will discuss the synthetic procedure of each intermediate.

Glycerol carbonate. In a typical setup, a 250 mL flask equipped with a magnetic stirrer, condenser and thermometer was charged with glycerin (40.05 g, 0.435 mol), dimethyl carbonate (117.45 g, 1.305 mol) and K_2CO_3 (1.8 g, 13.05 mmol). The reaction mixture was refluxed (73–75 °C) for 3 h. After completion of the reaction, methanol and the excess of dimethyl carbonate were distilled off at 40 °C under reduced pressure. The remaining glycerol carbonate was analyzed by ^{1}H NMR and FT-IR spectroscopy.

Glycerol Carbonate Methacrylate. A RB flaks was placed in an oil bath with magnetic stirring with a distillation apparatus over it. A flask was charged with 11.8 g (0.1 mole) of glycerol carbonate and 60.0 g (0.6 mole) of methyl methacrylate and 1.8 g of zirconium acetylacetonate and the mixture heated to 90 °C for 48 h. The reaction was terminated by removing the catalyst by addition of dilute phosphoric acid and removed by centrifugation. The organic layer was then washed with water to remove unreacted glycerol carbonate. The remaining methyl methacrylate was removed at rotovap, and the product was confirmed by ^{1}H NMR and ^{13}C NMR.

Synthesis of vinyl ester resins (VER). A 25 mL RB flask was charged with BPA (1.14 g, 5 mmol), GCMA (1.86 g, 10 mmol) and potassium carbonate (0.030 g). The flask had continuous flow of argon, and the temperature was raised to 90 °C, which was maintained for 18 h. After the reaction, the highly viscous liquid was transferred to a glass vial, and the product was analyzed by TLC, ^{1}H NMR, and FT-IR.

RESULTS AND DISCUSSION

Herein, we have demonstrated the feasibility of the sustainable, environmentally safe, 'green' vinyl ester resin (GVER) technology using renewable biowaste. The GVER structures will be made predominantly from biowaste, namely lignin, recovered from wood wastes, and glycerin, recovered from biodiesel wastes. These source materials are renewable, low-cost, and are becoming increasingly abundant and thus will eliminate dependence on imported oil. Figure 1 shows the sequence of reactions leading from lignin and/or wood wastes to GVER monomer.

Synthesis of glycerol carbonate methacrylate from glycerin.

GCMA was synthesized using glycerin as the main precursor. Glycerin is a side-product of the transesterification of triglyceride in manufacturing of biodiesel or the hydrolysis of triglyceride during saponification. We obtained vegetable glycerin from a local vendor Bulkapothecary (Streetsboro, OH), and crude glycerin from biodiesel manufacturing unit from Maine Standard Biofuel (Portland, ME).

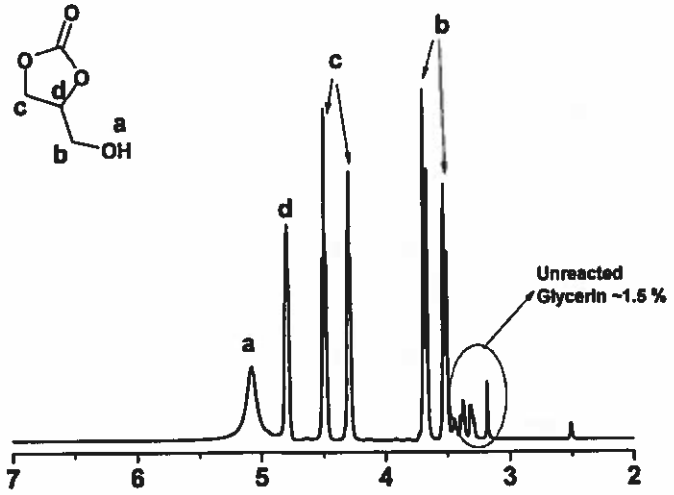

Figure 3. ^{1}H NMR of glycerol carbonate.

GC, a first intermediate in the synthetic route to GCMA from glycerin, is a very important material having a large number of applications in various fields. We have also developed tremendous interest in isolation of this material with 100 % purity. Various approaches had been adopted by different groups for the synthesis of the GC; such as, using (a) Novozyme 435 catalyst and dimethyl carbonate as a precursor[18], and (b) metal oxide as a catalyst and urea as a precursor[19]. In a new approach, GC was synthesized by reaction between glycerin and dimethyl carbonate at 73 °C for 3 h in the presence of potassium carbonate.[20] The method is promising, with several challenges for example the separation of potassium carbonate from the reaction mixture. Firstly, the reaction was performed at 73 °C and the GC was synthesized successfully. The product formation was confirmed by ^{1}H NMR as shown in Figure 3. The peak integration value suggested ~ 98.5 % conversion of glycerin to GC at 73 °C. In order to complete the reaction to 100.0 %, the reaction temperature was increased to 100 °C; however, as the temperature increased to 100 °C, formation of some side product was observed and unreacted glycerin was also found in the final mixture.

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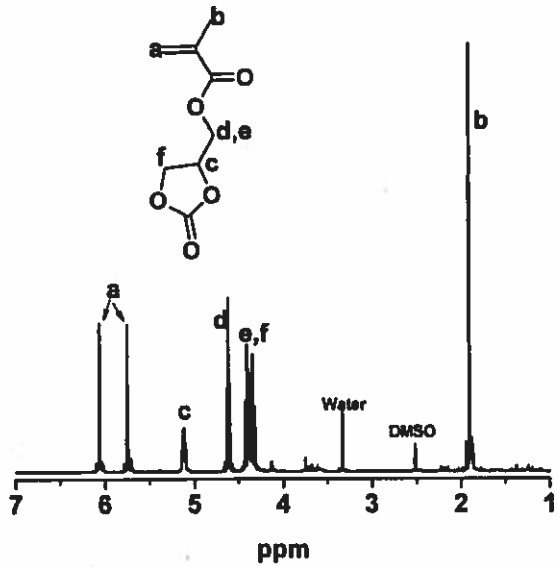

Figure 4. ^{1}H NMR of glycerol carbonate methacrylate.

Glycerol carbonate methacrylate (GCMA) is one of the precursors for the synthesis of vinyl ester resin monomer along with bisphenol A and tetrabromobisphenol A. The GCMA is synthesized by transesterification between methyl methacrylate and glycerol carbonate in the presence of zirconium acetylacetonate as a catalyst as mentioned previously.[1] Firstly, the temperature was maintained in the reaction flask to 70 °C and then it was raised to 100 °C over the period of 48 h. The catalyst was neutralized by hydrolysis with dilute phosphoric acid and removed by centrifugation. The remaining liquid was decanted in the flask and water was added to the reaction mixture. The organic layer was taken out and the excess of methyl methacrylate was removed at rotary evaporator. The structure of GCMA was confirmed by ^{1}H NMR as shown in Figure 4. The GCMA was isolated with 81.0 % yield.

Synthesis of vinyl ester resin (VER) monomer.

VER are formulated from VER monomer using a solvent/reactive diluent, typically styrene, as well as additives to meet specific needs. In general, VER has several advantages over other polymers. For example, toughened and brominated VER produces resins with higher strengths than polyesters and lower viscosity than epoxies. This low viscosity is critical for fabricating large ship structures by vacuum infusion. Fiberglass-reinforced VER composites are preferred for many topside applications where low detectability and radar transmission are important. Recent advances in compatible sizing have enabled stiffer reinforcement of VERs using carbon fiber.

The VER monomer was synthesized by a one pot reaction between BPA and GCMA in the presence of potassium carbonate as a catalyst. The reaction was performed at 90 °C using a magnetic stirrer. The ^{1}H NMR did not exhibit the –OH peak of the BPA, so it was presumed that the reaction was 100 % complete as shown in Figure 6. The product was purified by initially dissolving in acetone and later precipitation in water. VER settled down in acetone-water mixture and later isolated and dried under vacuum at room temperature.

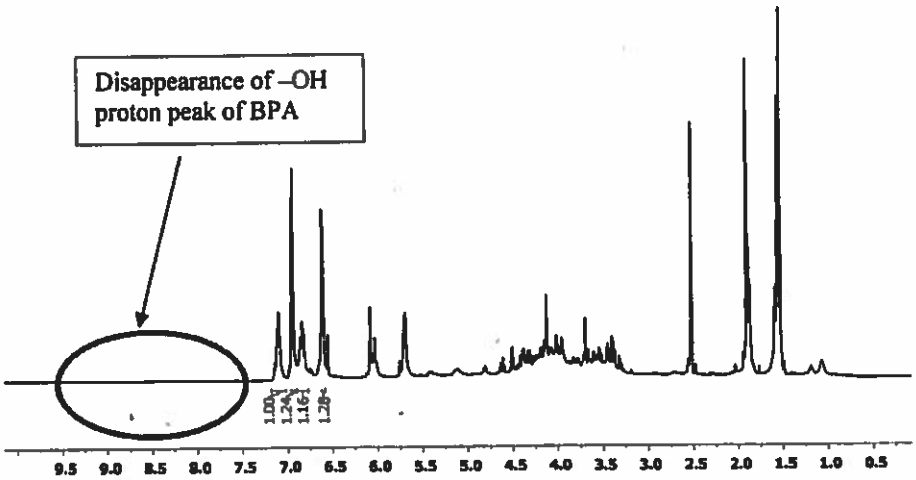

Figure 5. ^{1}H NMR of the Vinyl Ester Resin synthesized by reaction of glycerol carbonate methacrylate and bisphenol A.

4. Does there exist an earlier, dated record of the invention's conception--a sketch, report, laboratory notebook entry, or the like-which:

a.) describes your invention, and b.) can be independently corroborated?
(Note: This can be important in asserting and defending the claim to patent.)
If so, what is it, and where is it?

We have proposed entirely new synthetic route for synthesis of different kinds of VER starting from biowaste. We have laboratory notebook pages, internal monthly progress reports, and quarterly progress reports to SERDP as documented works.

5. a. Is this disclosure related to any earlier invention disclosure? If yes, identify and list showing docket number and title.

No.

5. b. Is this disclosure related to any earlier invention disclosure at another institution?

No

6. What do you see as commercial uses of your invention?

Different kinds of VER have large number of applications in various fields. We are preparing brominated VER, which will be used by US Navy in building hull of ships.

7. What firms do you think may be, or are, commercially interested in this technology; and why?

(a) VER producing companies as they are looking for alternative, greener and cost effective newer approaches. (b) Paper industries looking for applications of lignin

8. Do you have a relationship, formal or informal, with any of these companies? What is the nature of the relationship?

Ashland Inc.: They are our industrial teaming partner on the current program. They are currently producing VER and looking for less toxic approach

9. What do you see as the greatest impediment to the commercial adoption of your invention?

Purification of the biodiesel based glycerin is currently an energy consuming process.

10. Is further development of your invention now in progress? Scheduled? Dependent on commercial or federal sponsorship?

YES- We have two more years funding coming on the project so we will continue our research. We may have possibility to get bigger funding through ESTCP.

11. Has any aspect of this invention been published, been presented at a scientific meeting, been discussed with non-UMass individuals, part of a student dissertation or otherwise disseminated?

☐ YES √ NO

If yes, please identify, list dates and circumstances. (Dates are important. If published, list the date recorded on microfilm or in a library.)

12. Are there any plans to publish or otherwise publicly disseminate any aspect of this invention in the future?

√ YES ☐ NO

If yes, please identify and list dates.

13. Are you aware of related developments by other institutions or companies?

☐ YES √ NO

If yes, please identify.

14. Has the research that led to the invention been sponsored or funded by industry, or funded by a grant from a government agency or private foundation?

√ YES ☐ NO

If yes, you must provide CVIP with information on all funding sources for research that resulted in this invention. Please note that failure to report a funding source may result in a significant delay in proceeding with this disclosure, or may result in not being able to license the invention.

INDUSTRY OR FOUNDATION SPONSOR	GRANT #	CONTRACT #
SERDP-Sustainable green vinyl ester resin from renewable resources.		

Fund	Dept. ID	P/G #	Speed Type
53106-L	L630300401-L	S51300000024869-L	114132-L

(Case Manager's Initials _____) Verified that the grant information shown above is complete as listed with the University's offices of Sponsored Programs and/or Offices of Grants and Contracts.

15. Did the research that led to the invention use any information or materials (e.g., cell lines, DNA, protein, antibodies) provided by another institution or a company?

☐ YES √ NO

If yes, was a transmittal letter or agreement (e.g., Confidential Disclosure Agreement [CDA] or Materials Transfer Agreement [MTA]), used in connection with receipt of the information or materials?

☐ YES ☐ NO

If yes to either, attach a copy of the CDA or MTA, or provide the name of the Investigator and address of the company.

16. Our technology evaluators or patent attorneys may wish to contact the Investigators with questions or to seek clarification. Please identify the primary Investigator Contact:

NAME:	PHONE:
Yongwoo Lee	978-934-3792

17. Mailing address(es) for each Investigator(s) in order listed on page 1:

Please provide your LOCAL or your HOME ADDRESS--where you are living now, not your University (i.e., Departmental P.O. Box) address. If you are a citizen of another country, then please indicate which country.

Investigator #1	Investigator #2
Full name: Yongwoo Lee	Full name: Priyank N. Shah
Local or Home street address, city, state, zip code, country:	Local or Home street address, city, state, zip code, country: 297 Pawtucket Blvd, Unit 9, Lowell, MA-01854
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Local or Home phone (where you can be reached when you are not at work):	Local or Home phone (where you can be reached when you are not at work): 978-761-9645

Signature(s) of Investigator(s)

The undersigned agree(s) to cooperate with CVIP in the assessment, protection and commercialization of the invention. Further, each Covered Individual (as defined in the University Intellectual Property Policy (BOT T96-040)) does hereby assign, transfer and convey to University the entire right, title and interest in the invention and agrees to execute and deliver all documents requested by CVIP (including a Participation Agreement if not already executed) to record the assignment of rights to the University.

Name Typed	Signature	Date
1. Yongwoo Lee		12/28/2015
2. Priyank Shah		12/28/2015

18. Any other comments you believe are important for the evaluation of this technology.

We are planning to open dialogue with Ashland Inc. and Paper Company for filing patent on the current IP.

Appendix G

UNIVERSITY OF MASSACHUSETTS

AMHERST • BOSTON • DARTMOUTH • LOWELL • WORCESTER

CVIP Use Only

Commercial Ventures and Intellectual Property

Invention Disclosure

Lowell Campus Office:
600 Suffolk Street, 2nd Floor, Attn: Director, CVIP
Lowell, MA 01854
Tel: 978-934-3235

Central Office:
President's Office, Attn: Executive Director, CVIP
225 Franklin Street, 12th floor
Boston, MA 02110
Tel: 617-287-4088

 # UML _____

Received _____

Accepted _____

Case Manager_____

University of Massachusetts
Uniform Invention Disclosure Form
(version 12/17/2012)

Title of Invention: **High Value Phenol Enriched Phenolics by Cost-Effective Pyrolysis of Biowaste Lignin**

	Investigator's Name & Title *(Please list Principal Investigator first and include all possible inventors)*	**Department**	**Institution** *(at time invention was made)*
1.	Name: Yongwoo Lee Title: Research Professor	Dept: Chemistry	Institution: UML
2.	Name: Robert F. Kovar Title: Consultant	Dept:	Institution: R.F. Kovar & Associates
3.	Name: Namjoon Kim Title: Post-Doc	Dept: Chemistry	Institution: UML
4.	Name: Priyank N. Shah Title: Post-Doc	Dept: Chemistry	Institution: UML
5.	Name: AkshayKokil Title: Post-Doc	Dept: Chemistry	Institution: UML
6.	Name: Edwin Jahngen Title: Professor	Dept: Chemistry	Institution: UML
7.	Name: David K. Ryan Title: Professor	Dept: Chemistry	Institution: UML
8.	Name: Seongkyu Yoon Title: Professor	Dept: Chemical Engineering	Institution: UML

High Value Phenol Enriched Phenolics by Cost-Effective Pyrolysis of Biowaste Lignin

Please check campus of lead Principal Investigator: Amherst☐ Boston☐ Dartmouth☐ Lowell☑

To the Investigator(s):

The business of a university is the gathering and dissemination of knowledge. Making an invention and putting it to use in the service of the public is a thoroughly valid mode of accomplishing this objective.

Accordingly, the University encourages the inventive process; and within the limits of financial practicality, can often provide advice and assistance in bringing inventions to the point of public use.

In the sense used here, an "invention" has a presumed commercial use and value. The following indicates the preferred time to file a disclosure with CVIP.

> *Disclose to CVIP first, publish later:* Disclosing your invention to CVIP by no means proscribes publication; on the other hand, premature publication can have disastrous consequences, both legal and tactical, upon an effort to commercialize it by precluding the availability of patent protection in most countries.
>
> *Disclose as soon as the invention is clearly conceptualized*: It is not necessary to wait until the invention is reduced to practice, and filing early may be beneficial, particularly when other groups are filing related patent applications.
>
> *Consult with CVIP specialists:* CVIP specialists can assist you with such questions as determining inventorship, procedures when more than one institution is involved and protecting patentable inventions from improper public disclosure.

If you <u>think</u> you have made an invention, but you are not sure, then say so in your disclosure. Similarly, if you are uncertain as to whether your invention has commercial merit, say so. CVIP can assist you in making such determinations. This form should be considered as a guide to assist in the invention disclosure procedure as required by the University's Intellectual Property Policy.

1. Background

In order for patent counsel to determine the patentability of this invention, it will be necessary to compare it to existing technology (referred to as "<u>prior art</u>"). This section should provide information to aid in that evaluation. Please identify and provide references to the prior art by patent number or journal article identification. Useful websites for patent searches include: (1) www.uspto.gov/patft/index.html, and (2) www.wipo.int/pctdb/en/ .

Lignin is a major side-product in paper/pulp and agro based industries. Lignin cannot be digested by cattle and cannot be used in animal husbandry as a feed source. Also, as a material it possesses limited applications; as a result, disposal of a lignin is a big problem for paper and agro based industries. We report here for the first time pyrolysis of lignin under inert condition as shown in Figure 1, which affords condensable organic volatiles containing a wide variety of commercially attractive phenolic compounds. The pyrolysis of lignin was performed using flash vacuum pyrolysis method and phenol was extracted out of pyrolysate (i.e. the condensed organic volatile fraction). Bisphenol A (BPA) was synthesized from phenol and acetone in the presence of Amberlyst 15 catalyst. The bromination of BPA was performed in acetonitrile

using potassium bromide and bromine as reactants. The chemical structure of each intermediate was confirmed by ^{1}H NMR, HPLC and FT-IR spectroscopy.

Lignin biomass is easily available worldwide and considered to be renewable. Although it has very complex structure, the use of lignin is rapidly expanding for the development of technologies for the production of the useful chemicals from pyrolysis. Lignin is a highly branched, substituted, mononuclear aromatic polymer, which is often bound to cellulose and hemicelluloses fibers.[1] Thermal decomposition of lignin results in the production of char and condensable organic vapors during Flash Vacuum Pyrolysis (FVP). FVP process is carried out in the absence of oxygen at temperatures around 500˚C followed by a rapid cooling of the produced vapors.[2]

As one of the approach, we pyrolyzed lignin using super critical water condition; however, a very small amount of the lignin can be pyrolyzed using this protocol.[3] Therefore, the scale up of lignin pyrolysis using super critical water pyrolysis setup is a challenge. FVP was designed to increase the batch size and obtain high amount of phenol from lignin pyrolysis. Along with phenol, many other commercially attractive aromatic chemicals with one or two hydroxyl groups are obtained in the pyrolysate; such as, guaiacol (2-methoxyphenol), vanillin, butylated hydroxyl toluene and catechol (1,2-dihydroxybenzene).[4]

Temperature is one of the critical parameter to optimize the pyrolysis of lignin under mild vacuum. Slow pyrolysis at low temperatures and long residence times produces charcoal as a major pyrolysis biomass from lignin. Fast or flash pyrolysis produces high yield of liquid products (60 wt. % moisture free organic liquids on dry feed).[5] Temperatures above 700˚C maximizes gas yields (up to 80 wt. %). Product selectivity during the pyrolysis is poorly understood. Most of studies were conducted at low temperature (<450˚C) with long residence times (>5min) or slow heating rates. We are working towards increasing the yield of various phenolic compounds as well as phenol itself using FVP technique.

In the FVP, the residence time of samples in the hot zone is estimated to be ca. 10 ms and the steady-state concentration of substrate is $10^{-8}-10^{-9}$ mol/L.[6] Fast bimolecular reaction such as radical-radical couplings can occur at such a low concentrations.

The phenol was separated from related phenolic compounds by flash chromatography or distillation and used directly for VER synthesis. Extracted phenol was characterized using ^{1}H NMR. FVP is a promising method toward higher yields of phenol during limited-scope program experiments, which can be conducted in scaled-up multigram quantities in standard chemical equipment.

GC-MS data of pyrolyzed crude mixture showed the existence of phenol in our char (crude) samples . Phenol can be used for the synthesis of many other high value products such as BPA, TBBPA. It is also worth mentioning that bisphenol A (BPA) is an important chemical used in the manufacture of polycarbonates, epoxy resin, flame retardants, and other specialty products,[7] and is manufactured by acid catalyzed condensation of acetone and phenol.[8]

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[1]"Phenols from Lignin"; M. Kleinert, T. Barth, Chem. Eng. Technol. 2008, 31, 5, 736-745.

[2]"Pyrolysis of Lignin in the presence of tetramethylammonium hydroxide: a convenient method for S/G ratio determination"; K.I. Kuroda, N. Nishimura, A. Izumi, and D. R., J. of Agricultural and Food Chemistry, 50(5), 1022-1027 (2002).

[3]"Useful products from lignocellulosics by supercritical water technologies"; S. Saka, K. Ehara, S. Sakaguchi and K. Yoshida, 2nd Join International Conference on "Sustainable Energy and Environment (SEE 2006)", 1-23 November 2006, Bangkok, Thailand.

[4]"A Comparison of Monomeric Phenols Produced from Lignin by Fast Pyrolysis and Hydrothermal Conversions." L. Du, Z. Wang, S. Li, W. Song and W. Lin. International Journal of Chemical Reactor Engineering 11(1): 1-11. (2013).

[5]"Flash vacuum pyrolysis of methoxy-substituted lignin model compounds." P. F. Britt, A. C. Buchanan, M. J. Cooney, and D. R. Martineau,. J Org Chem 65(5): 1376-1389, (2000).

[6]"Flash vacuum pyrolysis of lignin model compounds" M. Cooney, P., Britt (1997), 89–95.

[7]Xu, R., Chi, C., Li, F., Zhang, B.(2013) "Immobilization of horseradish peroxidase on electrospun microfibrous membranes for biodegradation and adsorption of bisphenol A",*Bioresource Technology*, 149, 111-116

[8]Prokop, Z.,Hanková, L.,Jeřábek, K.(2004)"Bisphenol A synthesis–modeling of industrial reactor and catalyst deactivation", Reactive and Functional Polymers, 60, 77-83

2. Description of the Invention

Please describe specifically and in detail what you consider to be the invention, as distinct from the prior art. If you need them, use additional pages, drawings, diagrams, etc. Descriptions may be by references to a separate document (copy of a report, a preprint, excerpt from a grant application, or the like) attached hereto. If you do so, please identify each document positively. Important: where available include a continuation sheet or document showing scientific data in support of the invention claims.

We report of the first time the following:

1. Pyrolysis of different kinds of lignin under vacuum and helium conditions was performed. The resulting pyrolysate were analyzed using GC-MS. The difference between vacuum and helium conditions was investigated. Different kinds of lignin raw material obtained from various suppliers were tested to compare the yield of phenolic compounds. Flambeau river papers LLC supplied lignosulfonate and de-sugared lignosulfonate in both liquid and powder form. We also procured commercially available bulk size of lignin from TCI America and Sigma-Aldrich in alkaline and de-alkaline form.
2. Pyrolysis was performed in same apparatus at two different temperatures. A well-organized pyrolysis under two different temperature reduced chances of greater decomposition and increased the amount of phenolics. Secondly, it decreased the consumption of electricity and made pyrolysis more cost-effective.
3. Phenol was detected for the first time by flash vacuum pyrolysis of lignin, and along with phenols many other valuables phenolics were detected such as: Guaiacol; butylated hydroxytoluene; 2-methoxy-4-methylphenol; 4-ethyl-2-methoxyphenol; 2-methoxy-4-vinylphenol; 2,6-dimethoxyphenol; vanillin; 4-hydroxy-3-methoxyacetaphenone; catechol; homovanillic acid and many other.
4. Higher amount of phenolics were obtained when the mantle temperature was high, but at the same time the amount of butylated hydroxyl toluene increased significantly.
5. As the pyrolyzed material results in an aerosol of the volatile organics, efficient condensation of the evolved fractions is challenging. We have developed a glass wool and frit based passage for breaking the aerosol followed by scrubbers containing aqueous sodium hydroxide solution to efficiently trap all pyrolysate.
6. Currently lignin exhibit limited applications and as a result most of them are used as a low grade fuel. Our method defines a novel way for disposal of lignin to obtain commercially attractive chemical compounds, which can subsequently be utilized for synthesis of value added commercially attractive materials/products.
7. The char (residue) and gases generated after the pyrolysis can be used as a fuel for heating-up the pyrolysis apparatus.
8. Purification procedure of phenol enriched phenolics from pyrolysate by treating with 0.1 N NaOH solutions was also developed.
9. Pyrolysate was purified using flash column chromatography, Amberlyst-A21 resin, and fractional distillation and optimum purification conditions were established.
10. The obtained phenol and phenolics can be further used for the synthesis of higher value products such as bisphenol A (BPA) and tetrabromobisphenol A (TBBPA), which are the starting materials for the synthesis of commercially attractive Vinyl Ester Resin (VER).
11. Lab-scale FVP (flash vacuum pyrolysis) equipment was developed for lignin pyrolysis. Quartz glassware for pre-heating unit was changed from a round bottom flask to a large vessel (1000 ml ca.) to use more lignin powder in a single run. This new system allowed us to run at least 100-200 g of batch size at a time. Only vaporized lignin could move through quartz reactor in the furnace at 500 ˚C and being collected by liquid nitrogen cold trap unit after pyrolysis.

12. Temperature condition in the mantle was carefully examined and analyzed with GC-MS semi-quantitatively to examine the pre-heating effect on phenol production and efficiency.
13. Refined samples were followed by flash chromatography, passing over Amberlyst A-21 or fractional distillation to separate phenol out of phenolic mixture. We will continue this until obtaining decent amount of phenol to support scale-up process of resin. The semi-quantitative analysis was performed on GC-MS data to get more precise data analysis. We procured 11 monomeric forms of phenolic compounds as standards.
14. Each isolated phenolics can be used as precursor for many high value chemical products.

Detailed experimental procedure for obtaining phenolic starting materials from pyrolysis of lignin is as follows.

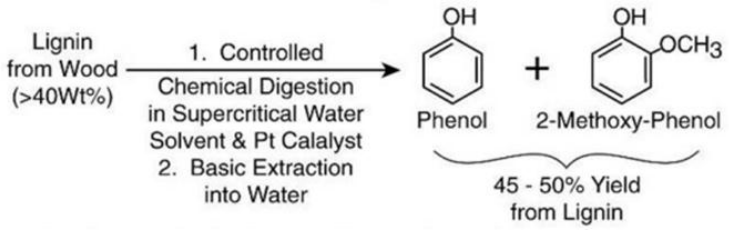


Figure 1. Isolation of phenol from lignin by pyrolysis of lignin.

Experimental Details.

Materials. Thermolyne 21100 high-temperature tube furnace reactor with thermocouple embedded, ground-glass joint grease, high temperature resistant grease, heating mantle (500ml and 250ml ca.) with on/off temperature controller, water-cooled condenser, 500 mL round-bottom quartz flasks, Sand (50-70 mesh particle size), vertical lift, clear fused quartz tube (25 mm ID x 28.8 mm OD, 24" length) with a 24/40 female taper joint on each end, two-ring stand and clamps, two Dewar flasks for cold trap with glassware, liquid nitrogen for cold trap, red tubing for line connection, vacuum pump, lignin powders (lignosulfonate, de-sugared calcium lignosulfonate, alkaline lignin, dealkaline lignin), glass wool, glass adapters, weigh boats, spatulas, Teflon PTEF rods, 20-mL glass scintillation vials, filtering paper, THF solvent, methanol, diethyl ether, 0.1N NaOH, 0.1N HCl, funnel glassware's, separating funnels, polyethylene bottles, crucible holders, foil tape, rotary evaporator, pH paper and digital weighing scales were prepared for setting up the reaction in/out of the hood and extraction of products afterward.

Design of Flash vacuum pyrolysis equipment. Significant efforts were made in order to design an efficient pyrolysis apparatus as shown in Figure 2. The currently used pyrolysis setup is described in Figure 3 with all detailed parts information.

- As can be seen in Design 1 in Figure 2, we firstly used a Pyrex tube for the pyrolysis, which was directly placed in the furnace and pyrolysis was performed at only one temperature. The amount of pyrolyzed material in the tube was later extracted using organic solvents. Then we moved to Design 2, where we applied a trap and mild vacuum during the pyrolysis, which was performed at one temperature. Subsequently, we modified the pyrolysis setup to design 3, where the pyrolysis was performed at two different temperatures. The primary pyrolysis takes place at quartz's round bottom flask, where the temperature of the mantle was ~350 ˚C. Currently we are using design 4, where the primary pyrolysis takes place in the quartz reactor.
- In the detailed set-up, a 1000 mL quartz reactor was placed in a heating mantle, where primary pyrolysis takes place. The generated gases moves to the clear fused quartz reactor tube (25 mm ID x 28.8 mm OD with a 24/40 female taper joint on each end, 24 in. length), which was placed in a hot

furnace, where secondary pyrolysis takes place at high temperature. Thermal decomposition of vaporized samples was efficient with improved thermal conductivity using thin cylinder type quartz tubing. Heat distribution is important in FVP because the sample will be exposed to high temperatures in a very short time period.

- One end of quartz reactor tube was connected to the 3-way adapter for N_2 flow and sample vessel. The other end was connected to cold trap unit which is connected to the vacuum pump (three cold trap glassware were connected). The sample lignin (100-200 g) was placed in the quartz vessel

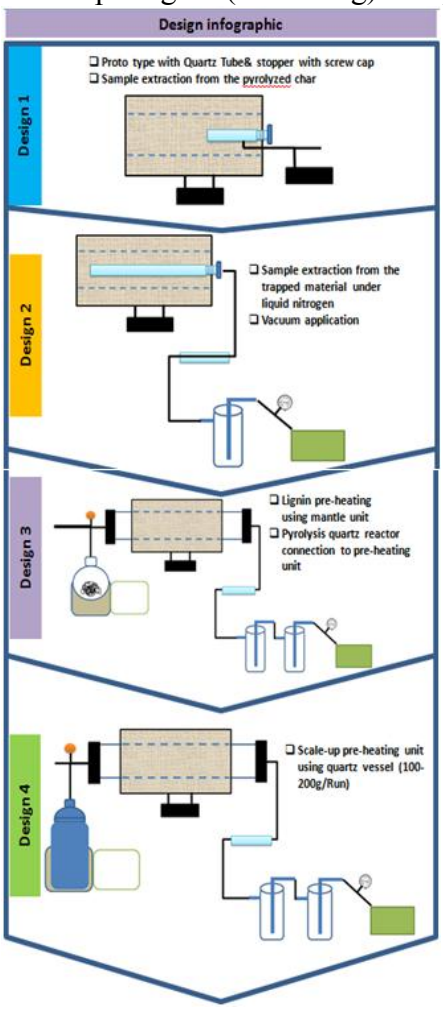


Figure 2. FVP design infographic.

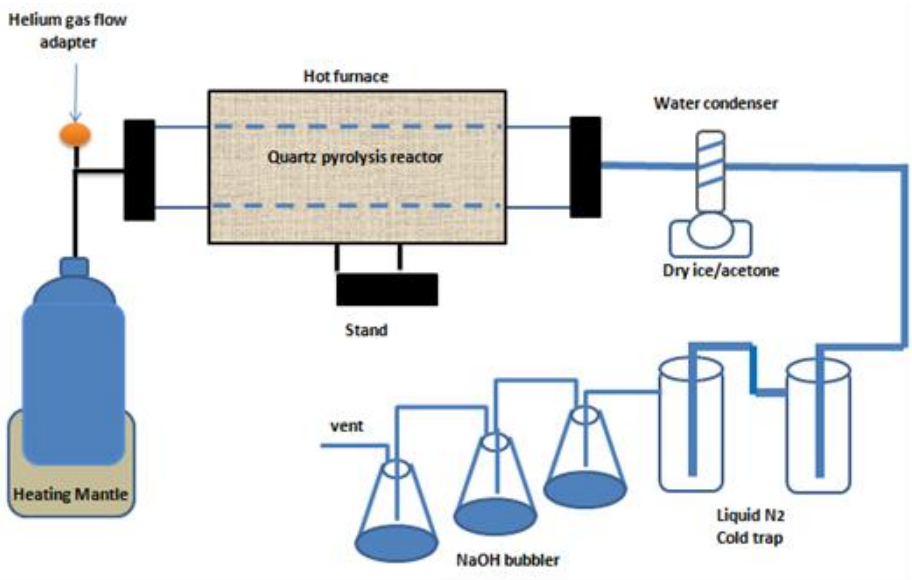


Figure 3. Schematic diagram of current FVP at UML.

Phenol refinement using purification technique from crude product of lignin pyrolysis. The pyrolysate contained small amount of moisture water. The organic fraction was first extracted using ether layer. The organic layer was further treated with 0.1 N NaOH solutions. Phenol is slight acidic in nature and it will form a sodium salt by reacting with NaOH solution and will stay in aqueous layer. The aqueous layer is further neutralized using 0.1 N HCl solutions and phenol is extracted using ether again. Refinement procedure is illustrated in the Figure 4.

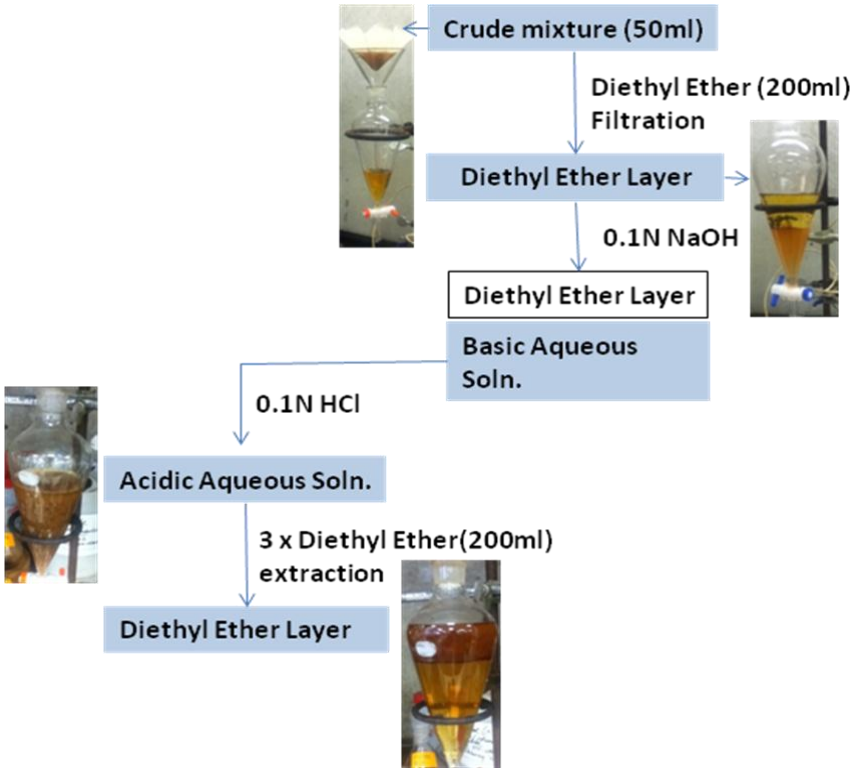


Figure 4.Phenol refinement by solvent extraction.

Phenol separation using Flash Chromatography. Despite of the purification by solvent extraction, the ether layer still had many other compounds along with phenol. Therefore, further purification of the organic layer was essential. The organic layer was purified again using flash chromatography. The silica-gel was used as a stationary phase and the hexane: ethyl acetate (8:2) was used as a mobile phase. By using the mentioned solvent composition and phenol as a reference peak, a very strong spot was observed as a first eluent, which was separated and analyzed using GC-MS. Subsequently, the second and third spots were also collected and analyzed using GC-MS and NMR analysis.

*Phenol refinement using Amberlyst A-21 resin from crude product of lignin pyrolysis***.** Recently it has been widely demonstrated that insoluble nitrogen-based polystyrene resins can be successfully used for the removal of excess electrophilic reagents, as well as acidic products generated during solution phase reactions. Among them, well-known polystyrene resins such as Amberlyst, Amberlite, Dowex are commercially available at very low cost, with a variety of functionalities, high loading capacities. We selected Amberlyst A-21 as the basic polymeric resin for the purification. The refinement was conducted in diethyl ether and dichloromethane. The contact time between the resin and the pyrolysate solution was varied between 0 min to 1 hour. The color of the resin changed from white to red upon addition to the pyrolysate solution. The red colored resin was filtered after desired contact time and washed with the pure solvent (diethyl ether or dichloromethane) to remove any un-reacted compounds. To extract the phenolic compounds, the resin was washed with THF. Upon washing with THF the resin color again changed to white, indicating the removal of the chemisorbed phenolic compounds.

*Phenol refinement using vacuum distillation from crude product of lignin pyrolysis***.** Fractional distillation is an industrially viable protocol for refinement and isolation of a multitude of organic chemicals. To determine the feasibility of the procedure we performed vacuum distillation, using a claisen distillation setup, on the crude pyrolysate. Two fractions were collected at 150 °C and 180 °C. The distilled fractions and the residual solid were analyzed semi-quantitatively using GC-MS spectrometry.

GC-MS analysis of Pyrolyzed Lignin. The filtered lignin pyrolysis samples were analyzed by the method of Du et al.,[9]with modifications. General conditions for all measurements are given below.

GC-MS:	Agilent 7890 GC with 5973 MS
Column:	RestekRtx Wax 30 m x 0.25 mm
SP1Temp Program:	40 C for 3 min then 4 C/min ramp to 100C and hold for 3 min then 6 C/min ramp to 240 C and hold for 10 min, total run time 54.3 min
Injection Mode:	Splitless
Injection Volume:	2.0 µL
Column Flow:	1.0 mL/min UHP He
MS Library:	NIST Mass Spectral Library 2008

Synthesis of bisphenol A from phenol. A 50mL flask was charged with phenol (10.0 g, 106.3 mmol), 100 mg Amberlyst-15, 187.75 mg of 2-diethylamino-ethanethiol hydrochloride and acetone (2.80 g, 48.31 mmol). The reaction mixture was heated to 65-90 ˚C for 24 h with constant stirring. After 24 hours, the reaction mixture was cooled to ambient temperature, and the product was analyzed by TLC and ^{1}H NMR. The BPA was purified by column chromatography using 3:7 ethyl acetate: hexane ratio.

Procedure for synthesis of tetrabromobisphenol A (TBBPA). Into a 1000 mL round-bottom flask were charged bisphenol A (2.2829g, 10 mmol) and acetonitrile (15 mL). Separately prepared was a solution of KBr (4.76 g, 40 mmol) in water (10 mL) to which was added bromine (8 g, 50 mmol), and the resulting

[9]"A Comparison of Monomeric Phenols Produced from Lignin by Fast Pyrolysis and Hydrothermal Conversions." L. Du, Z. Wang, S. Li, W. Song and W. Lin. International Journal of Chemical Reactor Engineering 11(1): 1-11. (2013).

mixture was stirred to form an aqueous solution of KBr_3 at 30 ℃. This solution was added rapidly to the bisphenol A solution by utilizing a pressure-equalizing funnel within 2-3 min. The bromine color disappeared immediately, and white crystals of TBBPA were obtained within 5 min of reaction time at 30 ℃. Hydrazine hydrate (80%) was added to destroy the residual bromine, and the mixture was poured into water to separate the precipitated TBBPA. The precipitated reaction mass was separated from the mother liquor by vacuum filtration, utilizing a Buchner funnel, and then was washed twice with deionized water and dried in oven at 100 ℃. The total isolated yield of TBBPA was 99%, and the purity of the crystals was found to be 99.38% with a bromine content of 58.74%.

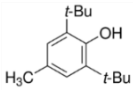
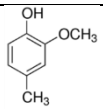
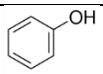
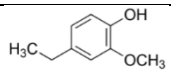
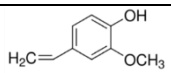
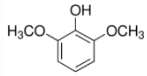
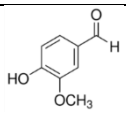
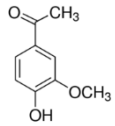
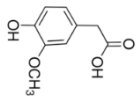
Result and Discussion.

We have performed pyrolysis at two different temperatures, which will reduce the consumption of electricity and increase the yield of pyrolysate. Initially pyrolysis was performed in a flask at 350 ˚C, and then the pyrolyzed products moves to pyrolysis reactor, where the temperature was 500 ˚C which attributed to homolysis of the weakest bond in the molecule (C−O bond). Although the decomposition of lignin begins at 160˚C, it appears to be a slow, steady process extending up to 800-900 ˚C.[10] Key features of FVP are a rapid heating and a rapid quenching of product vapor to obtain maximum quantity of liquid. We made pre-heating chamber for efficient generation of vapor to get more uniform and stable product. At low pressures heat transfer is accomplished by collision of the substrate with the quartz reactor tube walls. Overtime, carbonaceous residues can remain in the pyrolysis tubing and may affect the heat and mass transfer during the pyrolysis.

Semi-quantitative GC-MS analysis using standard monomeric phenolic compounds. We generally used percentage output yield (%) calculated from total peak area. In case of diluted samples which have more background effect, we applied semi-quantitative analysis. Among the monomeric phenolic compounds identified between 26-46 minutes retention time range, we selected eleven, the most abundant, species as standards including phenol, catechol and guaiacol to compare each standard distribution within total standard set as listed in Table 1.

[10]"Fast pyrolysis technology development." R. Venderbosch, and W. Prins, Biofuels, Bioproducts and Biorefining 4(2): 178-208, (2010).

Table 1: Standard monomeric phenolic compounds identified using GC-MS in FVP

R_t	Standards	Label	Compound formula
28.471	Guaiacol	S1	
29.846	Butylated hydroxytoluene	S2	
30.289	2-methoxy-4-methylphenol	S3	
31.314	Phenol	S4	
31.659	4-ethyl-2-methoxyphenol	S5	
34.376	2-methoxy-4-vinylphenol	S6	
35.477	2,6-dimethoxyphenol	S7	
39.559	Vanillin	S8	
40.569	4-hydroxy-3-methoxyacetaphenone	S9	
41.523	Catechol	S10	
44.853	Homovanillic acid	S11	

Lignin raw material effect on the yield of phenolic compounds (standards) by FVP. Six different kinds of lignin were obtained from various supplier and tested the distribution of phenolic compounds produced by FVP. The materials are listed below.

1. FlambeauL: Sugared lignosulfonate from Flambeau River Paper (Liquid)
   lignosulfonate containing 35% sugars and 55% lignin based on dry matter of 63%.
2. FlambeauP: De-sugared lignosulfonate from Flambeau River Paper (Power)
   desugared lignosulfonate with 4-12% sugars and 74-80% lignin based on dry matter of 55%.
3. Sigma1: Lignin alkali form from Sigma Aldrich (#471003)
   low sulfonate form (4% sulfur)
4. Sigma2: Lignin Alkali form from Sigma Aldrich (#370959)
   5% moisture impurities
5. TCI1: De-alkaline form from TCI America (#L0082)
6. TCI2: Alkaline form from TCI America (#L0045)

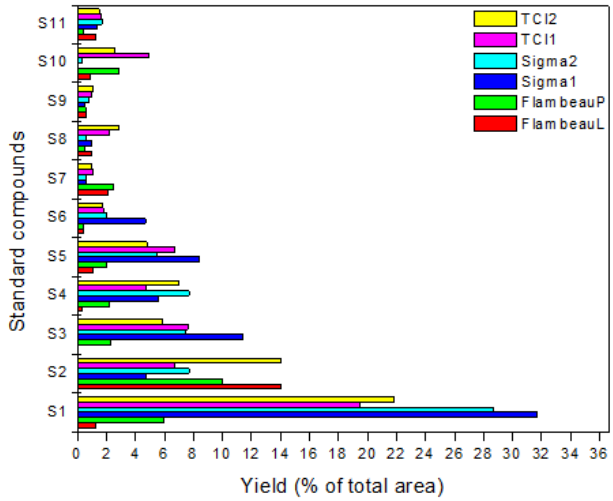


Figure 5. Raw lignin materials were tested using various supplier's material.

The intensive semi-quantitative GC-MS analysis was performed using various lignin source material obtained from various suppliers is shown in Figure 5. Depending on the wood process, commercial lignin is treated in different ways and result in different final composition.

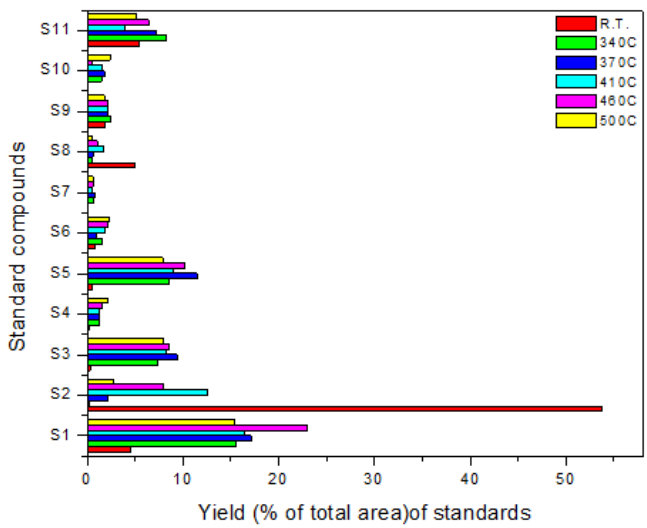


Figure 6. Recovery yield of standards at different reactor temperature.

Reactor temperature effect on phenol production by FVP. Temperature is one of the important variables to examine the yield of pyrolysis under low pressure vacuum. The Preliminary LC/MS data suggested that the amount of phenol recovery could be increased at high temperature compared with low temperature output. Based on the preliminary data obtained from LC-MS, we set the 6 different reactor temperature conditions as shown in Figure 6. Standard compounds were identified using GC-MS. We conducted multiple pyrolysis at various temperatures to make semi-quantitative data set. It suggested that higher amount of phenolics can be obtained at high temperature pyrolysis.

Pre-heating effect on phenol production by FVP. The higher temperature pyrolysis can decompose the amount of pyrolysate as a result the yield can decrease drastically. We have developed a pre-heating method, in which, lignin is treated at 350 ˚C in a quartz flask and the primary pyrolysis takes place there. The pyrolyzed product (mainly bimolecular structures) further pyrolyzed in hot furnace at high temperature.

Lignin pre-heating units for vapor production was attached at the entrance of pyrolysis reactor so that the vaporized lignin can enter hot zone in the furnace for pyrolysis. The lignin was weighted into a quartz

vessel before and after pyrolysis. Lignin vapor created at 300-500 ˚C in heating mantle was transfer directly to the quartz pyrolysis reactor placed inside of furnace at 500 ˚C. The amount of various phenolics at this condition can be observed in Figure 8. It was shown that the trapped materials contained more phenolic compounds (over 70 % out of total peaks identified within our GC retention time frame during 20-50 min) than that of char extract (49 %).

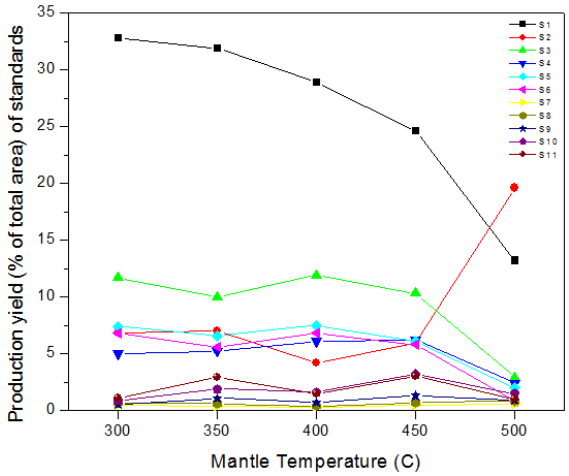


Figure 7. Lignin pre-heating effect on phenol production. Pyrolysis was performed at various mantle temperatures maintaining reaction temperature at 500 ˚C. Pyrolyzed samples were collected in the cold trap unit and analyzed using GC-MS.

GC-MS analysis of refined phenol by solvent extraction. Large amount of phenolic compound could be obtained by FVP of lignin. The phenol portion from the mixture of pyrolysate was relatively small to guaiacol. Aqueous basic extraction of pyrolysis oil into ether will be followed by separation, filtration and re-acidification. Basic aqueous layer that contains phenolic components should be rich in phenolic components and poor in other undesirable products. Refined samples were analyzed semi-quantitatively using GC-MS spectrometry. Three samples were prepared during the refinement process using either partitioning based on the original suggestion by Dr. Kovar. Detailed procedure was listed on refinement SOP in Appendix. Non-phenolic compounds are supposed to be separated from phenolic compounds after refinement. Comprehensive analysis on 11 standards phenolic compound was performed (Figure 8). Most of case refinement process was quite successful showing great improvement in K-3 than crude mixture, starting original mixture, except 2-methoxy-4-vinylphenol (S6). In case of phenol compound (S4), the last sample (K-3) showed similar recovery yield (1.9%) compared to the original crude mixture (2.1%).

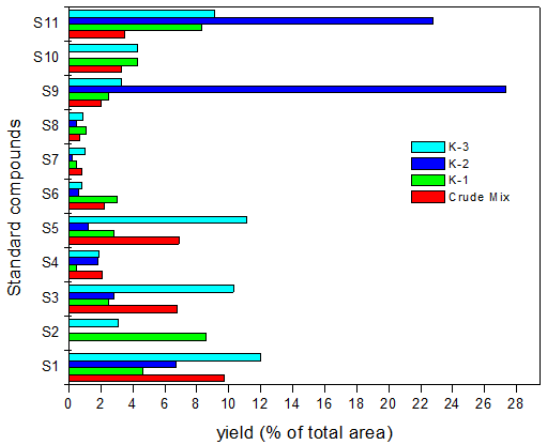


Figure 8.GC-MS analysis of refined samples.

GC-MS analysis of refined phenol by flash chromatography. The distribution of phenolic compounds was investigated on three column fractions (Table 2). First fraction (Fraction1) contained majority of phenol compound among three samples. Each fraction has different distribution pattern of phenolic compounds as in Figure 9. Using the flash chromatography technique, we could increase the purity of phenol produced by FVP followed by refinement.

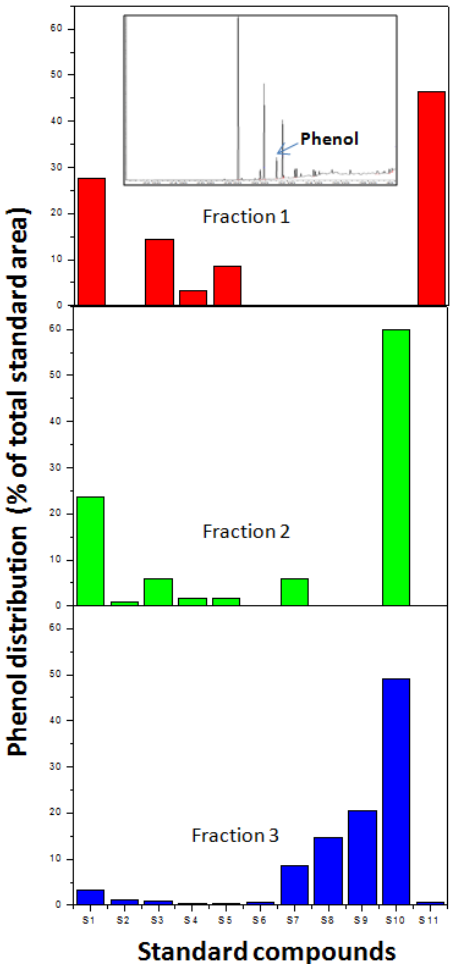


Figure 9: Refined phenol using flash chromatography

Table 2: GC-MS analysis of refined phenol by flash chromatography.

Standard compounds	Label	Fraction 1 (%)	Fraction 2 (%)	Fraction 3 (%)
Guaiacol	S1	27.7	23.7	3.4
Butylated hydroxytoluene	S2	0.0	0.9	1.3
2-methoxy-4-methylphenol	S3	14.3	6.0	0.9
Phenol	S4	3.2	1.8	0.3
4-ethyl-2-methoxyphenol	S5	8.5	1.6	0.3
2-methoxy-4-vinylphenol	S6	0.0	0.0	0.6
2,6-dimethoxyphenol	S7	0.0	6.0	8.6
vanillin	S8	0.0	0.0	14.6
4-hydroxy-3-methoxyacetaphenone	S9	0.0	0.0	20.5
catechol	S10	0.0	60.0	49.0

Homovanillic acid	S11	46.4	0.0	0.7
Total (%)		100	100	100

GC-MS analysis of refined phenol by Amberlyst-A21 resin. The basic Amberlyst A-21, polystyrene grafted with a tertiary amino group, was selected as it can react with the acidic phenols to form ammonium phenoxides on the polymer, thus removing phenols from the mixtures. The refinement was conducted in diethyl ether and dichloromethane. The contact time between the resin and the pyrolysate solution was varied between 0 min to 1 hour. The color of the resin changed from white to red upon addition to the pyrolysate solution. The red colored resin was filtered after desired contact time and washed with the pure solvent (diethyl ether or dichloromethane) to remove any un-reacted compounds. To extract the phenolic compounds, the resin was washed with THF. Upon washing with THF the resin color again changed to white, indicating the removal of the chemisorbed phenolic compounds. Refined samples were analyzed semi-quantitatively using GC-MS spectrometry. As seen in Figure 10 upon use of diethyl ether as the solvent standard S2 was enriched by and order of magnitude. Standards S9, S10 and S11 were also enriched as high as 300%.

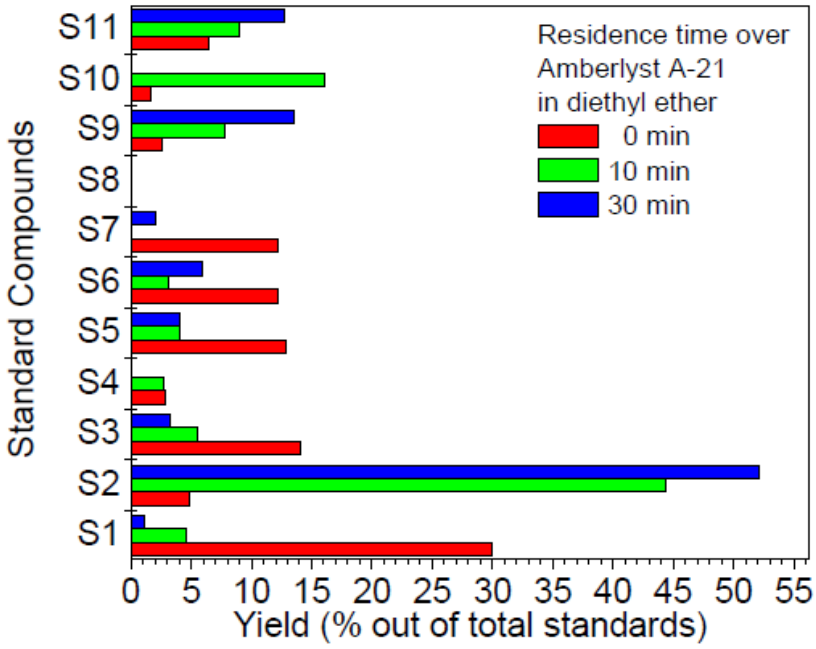


Figure 10. Relative percentage of standard compounds measured after refinement of the pyrosylate in diethyl ether with Amberlyst A-21 by GC-MS.

Upon using dichloromethane as the solvent the enrichment in phenolic components was more pronounced. As seen in Figure 11, the standard S2 was again enriched by an order of magnitude. Importantly, only two other standards, namely S4 and S10, were enriched by almost 300%.

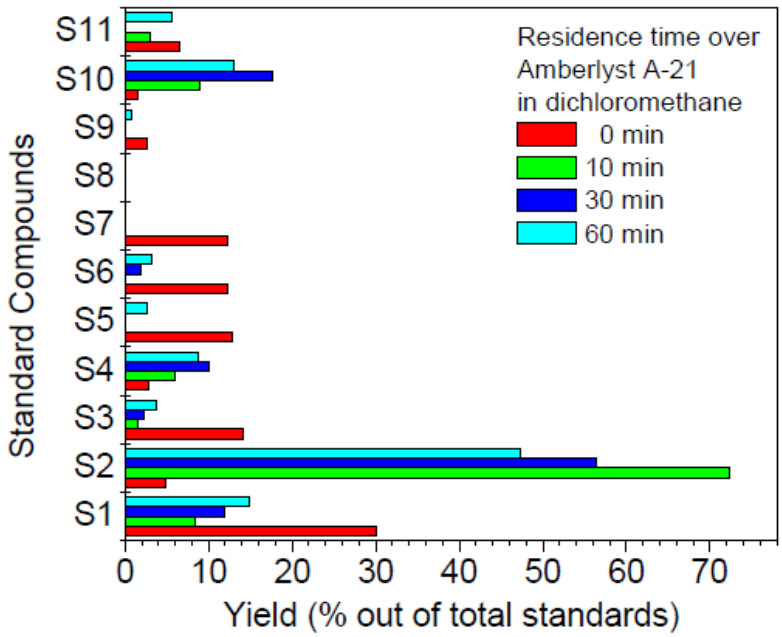


Figure 11. Relative percentage of standard compounds measured after refinement of the pyrolysate in dichloromethane with Amberlyst A-21.

GC-MS analysis of refined phenol by fractional distillation. Fractional distillation is an industrially viable protocol for refinement and isolation of a multitude of organic chemicals. To determine the feasibility of the procedure we performed vacuum distillation, using a claisen distillation setup, on the crude pyrolysate. Two fractions were collected at 150 °C and 180 °C. The distilled fractions and the residual solid were analyzed semi-quantitatively using GC-MS spectrometry. Figure 12 displays that separation of phenols can readily be performed using distillation protocols. It can be seen that at 150 °C a highly enriched phenolic fraction is obtained. On the other hand the residual solid mainly consists of standard S11.

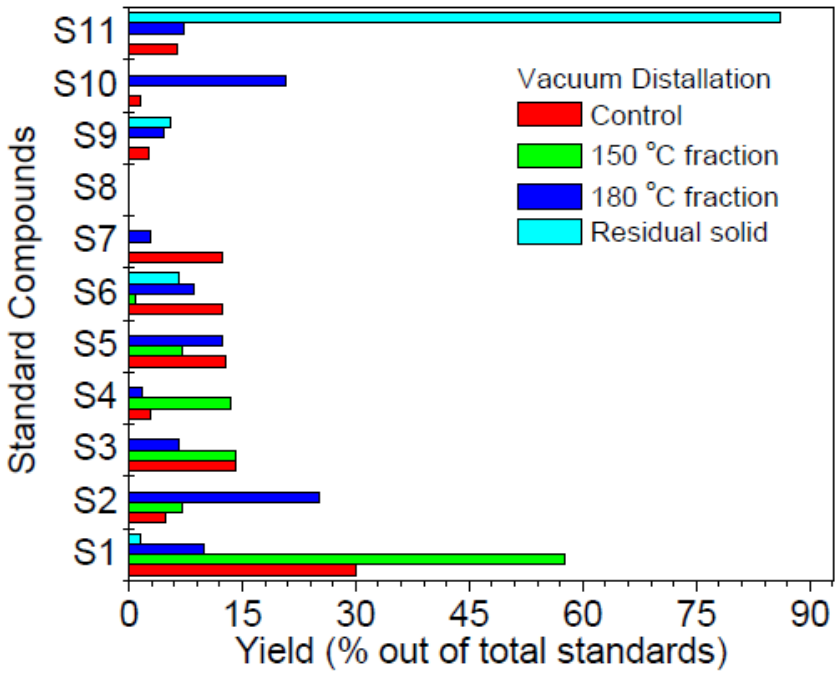


Figure 12. Relative percentage of standard compounds measured after refinement of the pyrosylate by vacuum distillation.

Synthesis of BPA using phenol. We have been working on the pyrolysis of lignin and extraction of phenol from the pyrolyzed product. Meanwhile, BPA was synthesized in a solvent-free manner, in which phenol (commercial) was first melted in an oil bath at 60 ˚C then combined with acetone in the presence of thio-glycolic acid as a promoter.[11] The reaction was performed in a sealed reactor. The mixture yielded a crude product subsequently identified as a mixture of BPA and unreacted phenol using TLC and ^{1}H NMR. The synthesized BPA was purified by column chromatography using hexane: ethyl acetate in a 7:3 ratio as a solvent mixture. The BPA was isolated with 7.0 % yield and product was confirmed by ^{1}H NMR as shown in Figure 13.

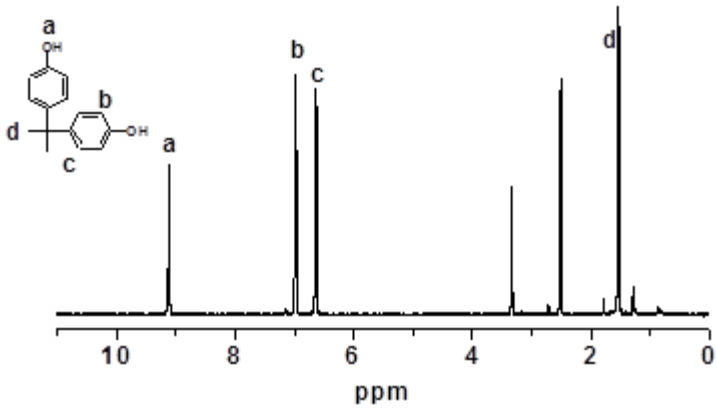


Figure 13.^{1}H NMR of bisphenol A.

Bromination of BPA was performed under mild conditions at room temperature with a short reaction time; moreover, the workup procedure for the isolation of the brominated BPA was also simple as it was isolated by simple precipitation in water.[12] The TBBPA was synthesized successfully as can be seen in ^{1}H NMR. (Figure 14) The usage of tetrabromobisphenol A (TBBPA) instead of BPA will yield highly efficient flame retardant material.

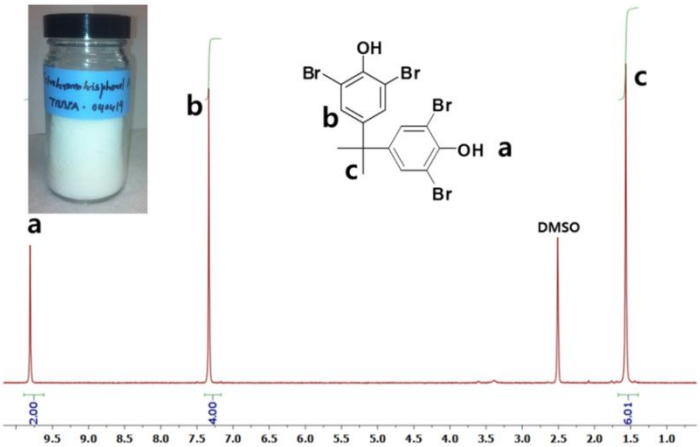


Figure 14: ^{1}H NMR and image of tetrabromobisphenol A synthesized under ambient condition.

[11] "A novel solid acid for synthesis of bisphenol A"; L. Hou, Q. Cai, B. Lu ; X. Li, X. Xiao, Y. Han, S. Cui; Catalysis Letters 111, 153-157 (2006).

[12]. "Instantaneous, Facile and Selective Synthesis of Tetrabromobisphenol A using Potassium Tribromide: An Efficient and Renewable Brominating Agent"Kumar, L., Sharma, V., Mahajan, T., and Agarwal, D. D., Organic Process Research &Development 14, 174–179, (2010).

3. What are the novel aspects of your invention and how does it improve upon prior art? Does your invention overcome any deficiencies or limitations in the prior art?

- Lignin is a major side-product in paper/pulp and agro based industries. Lignin cannot be digested by cattle and cannot be used in animal husbandry as a feed source. Also, as a material it possesses limited applications; as a result, disposal of a lignin is a big problem for paper and agro based industries.
- We report here for the first time pyrolysis of lignin under inert conditions, which affords condensable organic volatiles containing a wide variety of commercially attractive phenolic compounds.
- Currently lignin exhibit limited applications and as a result most of them are used as a low grade fuel. Our method defines a novel way for disposal of lignin to obtain commercially attractive chemical compounds, which can subsequently be utilized for synthesis of value added commercially attractive materials/products.
- Pyrolysis was performed in same apparatus at two different temperatures. A well-organized pyrolysis under two different temperature reduced chances of greater decomposition and increased the amount of phenolics. Secondly, it decreased the consumption of electricity and made pyrolysis more cost-effective.
- Phenol was detected for the first time by flash vacuum pyrolysis of lignin, and along with phenols many other valuables phenolics were detected such as: Guaiacol; butylated hydroxytoluene; 2-methoxy-4-methylphenol; 4-ethyl-2-methoxyphenol; 2-methoxy-4-vinylphenol; 2,6-dimethoxyphenol; vanillin; 4-hydroxy-3-methoxyacetaphenone; catechol; homovanillic acid and many other.
- The obtained phenol and phenolics can be further used for the synthesis of higher value products such as bisphenol A (BPA) and tetrabromobisphenol A (TBBPA), which are the starting materials for the synthesis of commercially attractive Vinyl Ester Resin (VER).
- Each isolated phenolics can be used as precursor for many high value chemical products.

4. Does there exist an earlier, dated record of the invention's conception--a sketch, report, laboratory notebook entry, or the like-which:

a.) describes your invention, and b.) can be independently corroborated?

(Note: This can be important in asserting and defending the claim to patent.)

If so, what is it, and where is it?

We have proposed a method to isolate phenol enriched pyrolysate during pyrolysis of a certain kind of lignin.

5. a. Is this disclosure related to any earlier invention disclosure? If yes, identify and list showing docket number and title.

No.

5. b. Is this disclosure related to any earlier invention disclosure at another institution?

No.

6. What do you see as commercial uses of your invention?

Lignin is a waste product in pulp and paper industry, as it has limited application its disposal is a big problem for industry. Here, we have proposed isolation of many high valued products from lignin pyrolysis.

7. What firms do you think may be, or are, commercially interested in this technology; and why?

Paper and agro based industries looking for applications of the lignin waste

8. Do you have a relationship, formal or informal, with any of these companies? What is the nature of the relationship?

Flamebeau River Paper LLC: They are our supplier for lignin and looking for production of phenolics by the pyrolysis of lignin.

9. What do you see as the greatest impediment to the commercial adoption of your invention?

The pyrolysis of lignin consumes significant energy.

10. Is further development of your invention now in progress? Scheduled? Dependent on commercial or federal sponsorship?

YES- We have two more years funding coming on the project so we will continue our research.
We have a possibility to secure a subsequent bigger funding through ESTCP.

11. Has any aspect of this invention been published, been presented at a scientific meeting, been discussed with non-UMass individuals, part of a student dissertation or otherwise disseminated?

❑YES √ NO

If yes, please identify, list dates and circumstances. (Dates are important. If published, list the date recorded on microfilm or in a library.)

12. Are there any plans to publish or otherwise publicly disseminate any aspect of this invention in the future?

√YES ❑ NO

If yes, please identify and list dates.

13. Are you aware of related developments by other institutions or companies?

❑YES √ NO

If yes, please identify.

14. Has the research that led to the invention been sponsored or funded by industry, or funded by a grant from a government agency or private foundation?

√YES ❑ NO

If yes, you must provide CVIP with information on <u>all</u> funding sources for research that resulted in this invention. Please note that failure to report a funding source may result in a significant delay in proceeding with this disclosure, or may result in not being able to license the invention.

INDUSTRY OR FOUNDATION SPONSOR	GRANT #	CONTRACT #
SERDP-Sustainable green vinyl ester resin from renewable resources.		

Fund	Dept. ID	P/G #	Speed Type
53106-L	L630300401-L	S51300000024869-L	114132-L

(Case Manager's Initials _____) Verified that the grant information shown above is complete as listed with the University's offices of Sponsored Programs and/or Offices of Grants and Contracts.

15. Did the research that led to the invention use any information or materials (e.g., cell lines, DNA, protein, antibodies) provided by another institution or a company?

❑YES √ NO

If yes, was a transmittal letter or agreement (e.g., Confidential Disclosure Agreement [CDA] or Materials Transfer Agreement [MTA]), used in connection with receipt of the information or materials?

❑YES ❑ NO

If yes to either, attach a copy of the CDA or MTA, or provide the name of the Investigator and address of the company.

16. Our technology evaluators or patent attorneys may wish to contact the Investigators with questions or to seek clarification. Please identify the primary Investigator Contact:

NAME:	PHONE:
Yongwoo Lee	978-934-3792

17. Mailing address(es) for each Investigator(s) in order listed on page 1:
Please provide your LOCAL or your HOME ADDRESS--where you are living now, not your University (i.e., Departmental P.O. Box) address. If you are a citizen of another country, then please indicate which country.

Investigator #1	Investigator #2
Full name:Yongwoo Lee Local or Home street address, city, state, zip code, country: Citizen of which country: USA Work phone(s): 978-934-3792 Work FAX : E-mail address: Yongwoo_Lee@uml.edu Local or Home phone (where you can be reached when you are not at work):	Full name: Robert F. Kovar Local or Home street address, city, state, zip code, country: Citizen of which country: USA Work phone(s): Work FAX: E-mail address: bobkovar@comcast.net Local or Home phone (where you can be reached when you are not at work):
Investigator #3	**Investigator #4**
Full name: Priyank N. Shah Local or Home street address, city, state, zip code,	Full name: Namjoon Kim Local or Home street address, city, state, zip code,

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Investigator #5	Investigator #6
Full name: Akshay Kokil Local or Home street address, city, state, zip code, country: 100 Pemberton St. #9, Dracut, MA 01826 Citizen of which country: India Work phone(s): 978-934-3738 Work FAX: E-mail address: Akshay_Kokil@uml.edu Local or Home phone (where you can be reached when you are not at work):	Full name: Edwin Jahngen Local or Home street address, city, state, zip code, country: Citizen of which country: USA Work phone(s): 978-934-3693 Work FAX: E-mail address: Edwin_Jahngen@uml.edu Local or Home phone (where you can be reached when you are not at work):
Investigator #7	Investigator #8
Full name: David K. Ryan Local or Home street address, city, state, zip code, country: Citizen of which country: USA Work phone(s): (978) 934-3698 Work FAX: E-mail address: David_Ryan @ uml.edu Local or Home phone (where you can be reached when you are not at work):	Full name: Seongkyu Yoon Local or Home street address, city, state, zip code, country: Citizen of which country: Work phone(s): 978-934-4741 Work FAX: E-mail address: Seongkyu_Yoon@uml.edu Local or Home phone (where you can be reached when you are not at work):

Signature(s) of Investigator(s)

The undersigned agree(s) to cooperate with CVIP in the assessment, protection and commercialization of the invention. Further, each Covered Individual (as defined in the University Intellectual Property Policy (BOT T96-040)) does hereby assign, transfer and convey to University the entire right, title and interest in the invention and agrees to execute and deliver all documents requested by CVIP (including a Participation Agreement if not already executed) to record the assignment of rights to the University.

Name Typed	Signature	Date
1. Yongwoo Lee		11-06-14
2. Robert F. Kovar		11-06-14
3. Namjoon Kim		11/06/2014
4. Priyank N. Shah		11/06/14
5. Akshay Kokil		11/06/14
6. Edwin Jahngen		07.Nov.14.
7. David K. Ryan		11/6/14
8. Seongkyu Yoon		11/6/14

18. Any other comments you believe are important for the evaluation of this technology.
We are planning to open dialogue with Ashland Inc. and Paper Company for filing patent on the current IP.

Appendix H

UNIVERSITY OF MASSACHUSETTS

AMHERST • BOSTON • DARTMOUTH • LOWELL • WORCESTER

CVIP Use Only

Commercial Ventures and Intellectual Property

Invention Disclosure

Lowell Campus Office:
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President's Office, Attn: Executive Director, CVIP
225 Franklin Street, 12th floor
Boston, MA 02110
Tel: 617-287-4088

 # UML _____

Received _____

Accepted _____

Case Manager_____

University of Massachusetts
Uniform Invention Disclosure Form
(version 12/17/2012)

Title of Invention: **Sustainable "Green" Vinyl Ester Resin (VER) from Renewable Resources**

	Investigator's Name & Title *(Please list Principal Investigator first and include all possible inventors)*	**Department**	**Institution** *(at time invention was made)*
1.	Name: Yongwoo Lee Title: Research Professor	Dept: Chemistry	Institution: UML
2.	Name: Robert F. Kovar Title: Consultant	Dept:	Institution: R.F. Kovar & Associates
3.	Name: Priyank N. Shah Title: Post-Doc	Dept: Chemistry	Institution: UML
4.	Name: Namjoon Kim Title: Post-Doc	Dept: Chemistry	Institution: UML
5.	Name: Akshay Kokil Title: Post-Doc	Dept: Chemistry	Institution: UML
6.	Name: Edwin Jahngen Title: Professor	Dept: Chemistry	Institution: UML

Sustainable "Green" Vinyl Ester Resin (VER) from Renewable Resources

Please check campus of lead Principal Investigator: Amherst☐ Boston☐ Dartmouth☐ Lowell☑

To the Investigator(s):

The business of a university is the gathering and dissemination of knowledge. Making an invention and putting it to use in the service of the public is a thoroughly valid mode of accomplishing this objective.

Accordingly, the University encourages the inventive process; and within the limits of financial practicality, can often provide advice and assistance in bringing inventions to the point of public use.

In the sense used here, an "invention" has a presumed commercial use and value. The following indicates the preferred time to file a disclosure with CVIP.

> *Disclose to CVIP first, publish later:* Disclosing your invention to CVIP by no means proscribes publication; on the other hand, premature publication can have disastrous consequences, both legal and tactical, upon an effort to commercialize it by precluding the availability of patent protection in most countries.
>
> *Disclose as soon as the invention is clearly conceptualized*: It is not necessary to wait until the invention is reduced to practice, and filing early may be beneficial, particularly when other groups are filing related patent applications.
>
> *Consult with CVIP specialists:* CVIP specialists can assist you with such questions as determining inventorship, procedures when more than one institution is involved and protecting patentable inventions from improper public disclosure.

If you think you have made an invention, but you are not sure, then say so in your disclosure. Similarly, if you are uncertain as to whether your invention has commercial merit, say so. CVIP can assist you in making such determinations. This form should be considered as a guide to assist in the invention disclosure procedure as required by the University's Intellectual Property Policy.

1. Background

In order for patent counsel to determine the patentability of this invention, it will be necessary to compare it to existing technology (referred to as "prior art"). This section should provide information to aid in that evaluation. Please identify and provide references to the prior art by patent number or journal article identification. Useful websites for patent searches include: (1) www.uspto.gov/patft/index.html, and (2) www.wipo.int/pctdb/en/ .

We present here for the first time a novel and commercially attractive synthetic protocol for obtaining green vinyl ester resin (GVER). Our synthetic strategy utilizes a commercial waste material, glycerin from biodiesel manufacturing, and converts it into a value added commercially attractive resin.

Vinyl ester resin (VER), introduced in the late 1960s, is a low-cost material utilized as the matrix in fiber-reinforced composites, which are extensively utilized in the manufacture of ship hulls, bodies of the

transportation vehicles, and many other military and commercial systems.[1] Due to their excellent mechanical and flame resistant properties, fiber-reinforced composites produced from VER have become the ideal building blocks for marine applications, especially next-generation Navy ships. As an example, the 500-ton deckhouse structure for the ship PCU Zumwalt (DDG 1000) is fabricated from carbon/VER composites. VER based fiber-reinforced building blocks are also finding increasing application in the transportation, construction, marine, and wind energy industries.[2,3,4] In the year 2000, over 60 million pounds of VER was sold in North America alone, and the Navy's need for VER has been significantly increasing.

VER, as a polymer matrix, can be processed at ambient temperature using vacuum-assisted resin transfer molding (VARTM) into massive carbon-fiber-reinforced composites.[5] The current synthetic protocol use in VER production has three main disadvantages. First and foremost, VER is currently synthesized using the starting materials obtained from petroleum feedstock. Hence, the production is directly related to the economics and supply of petroleum based products which can be rather volatile. Second, VER is synthesized from epichlorohydrin which is a known environmental hazard that produces acute toxicity in case of inhalation, oral, and dermal exposure. Third, the styrene monomer, a major reactive diluent (RD) component of VER, is environmentally hazardous, being volatile, flammable, and toxic, in addition to being an irritant.

To ensure the continued viability and cost effectiveness of this strategic VER material, it is essential to develop VER synthesis routes that are not dependent on starting materials from petroleum feedstock. Moreover, investigations of the VER synthesis routes that lead to elimination of the use of epichlorohydrin and the development of resin formulations that do not contain hazardous components such as styrene are necessary. Therefore, the use of starting materials derived from readily available renewable resources is relevant and attractive to assure sustainability and economic viability of VER production.. Importantly, the resultant VER must also retain the desirable economic and performance characteristics of the current commercially available resin.

Recently, significant advances have been made in the synthesis of biodiesel for renewable resources and it has become a promising alternative to diesel obtained from crude oil. Biodiesel can be produced by processing of rapeseed oil;[6] soybean and used cooking oil;[7] rice straw[8]; vegetable oil mixtures of cottonseed, soybean and castor oils;[9] jatropha oil;[10] and crude palm oil.[11] Biodiesel is environmentally beneficial because it is biodegradable, nontoxic and has low emission.[12] During manufacturing of biodiesel, approximately a 10 %

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[1] Martin, J.S., Laza, J.M., Morrás, M.L., Rodríguez, M. L., León, M. (2000) "Study of the curing process of a vinyl ester resin by means of TSR and DMTA" *Polymer*, 41, 4203–4211

[2] Nazareth da Silva, A.L., Teixeira, S.C.S., Widal, A.C.C., Coutinho, F.M.B. (2001) "Mechanical properties of polymer composites based on commercial epoxy vinyl ester resin and glass fiber" *Polymer Testing*, 20, 895-899

[3] Rosu D., Rosu L., Cascaval, C. N. (2008) "Effect of ultraviolet radiation on vinyl ester network based on bisphenol A" *Journal of Photochemistry and Photobiology A: Chemistry*, 194, 275-282

[4] Leitten, Jr., C.F., Griffith, W.L., Compere, A.L., and Shaffer, J.T. (2010) "High-Volume, Low-Cost Precursors for Carbon Fiber Production", *Society of Automotive Engineers* 02FCC-144.

[5] Griffith, W.L., Leitten, Jr. C.F., and Shaffer, J.T. (1999) "Low Cost Carbon Fiber from Renewable Resources"; Compere, A.L., *Oak Ridge National Laboratory Report*

[6] Hájek, M., Skopal, F., Čapek, L., Černoch, M., Kutálek, P. (2012) "Ethanolysis of rapeseed oil by KOH as homogeneous and as heterogeneous catalyst supported on alumina and CaO", *Energy*, 48, 392-397

[7] Koberg, M., Abu-Much, R., Gedanken, A. (2011) "Optimization of bio-diesel production from soybean and wastes of cooked oil: combining dielectric microwave irradiation and a SrO catalyst", *Bioresource Technology*, 102, 1073-1078

[8] Zheng, L., Hou, Y., L.,Wu , Yang, S., Li, Q., Yu, Z. (2012) "Biodiesel production from rice straw and restaurant waste employing black soldier fly assisted by microbes" *Energy*, 47, 225-229

[9] Meneghetti, S. M. P., Meneghetti, M. R., Serra, T. M., Barbosa, D. C., Wolf, C. R. (2007) "Biodiesel production from vegetable oil mixtures: cottonseed, soybean and castor oils" *Energy Fuels*, 21, 3746–3747

[10] Lee, H.V., Taufiq-Yap, Y.H., Hussein, M.Z., Yunus, R. (2013) "Transesterification of jatropha oil with methanol over Mg-Zn mixed metal oxide catalysts" *Energy*, 49, 12-18

[11] Man, Z., Elsheikh, Y. A., Bustam, M. A., Yusup, S., Abdul Mutalib, M. I., Muhammad, N. (2013) "A Brønsted ammonium ionic liquid-KOH two-stage catalyst for biodiesel synthesis from crude palm oil", *Industrial Crops and Products*, 41, 144-149

[12] Chen, G., Fang, B. (2011) "Preparation of solid acid catalyst from glucose–starch mixture for biodiesel production", *Bioresource Technology*, 102, 2635-2640

volume of glycerin is produced as a byproduct or waste.[13] Therefore, the effective utilization of glycerin enlarges the economy of biodiesel production; moreover, the conversion of glycerin to value added chemicals can expand the scope of green chemistry.[14]

There has been a considerable dearth of literature pertaining to systematic investigations on the use of functional vinyl monomer such as glycidyl methacrylate (GMA),[15] which is a versatile bidentate monomer capable of imparting oxirane functionality to VER containing styrene or other vinyl monomers. VER has received extensive attention in the fields of resin synthesis and composite manufacturing, however, to date no investigation has focused on minimizing or completely averting the environmental impacts and improving the economic viability of the resin.

We present here for the first time, synthesis of GVER using commercially available bisphenol A (BPA) or tetrabromobisphenol A (TBBPA) and glycidyl methacrylate (GMA). Crude glycerin, obtained from the waste stream of biodiesel industry, was converted to GMA, a valuable monomer by itself. Conversion of glycerin to GMA was performed using facile and cost effective synthetic protocols. In the first step, glycerol carbonate (GC) was synthesized from glycerin and dimethyl carbonate under basic conditions. Glycidol was synthesized from GC by decarboxylation with sodium sulphate at high temperature (180 ˚C) under reduced pressure. Further reaction of glycidol with methyl methacrylate in the presence of potassium cyanide and 2,4-dimethyl 6-tert butyl phenol yielded GMA. Figure 1 provides an overview of the process, starting from the glycerin obtained from waste streams to the final VER product.

[13] Nanda, M. R., Yuan, Z., Qin, W., Ghaziaskar, H. S., Poirier, M., Xu, C. C. (2014) "Thermodynamic and kinetic studies of a catalytic process to convert glycerol into solketal as an oxygenated fuel additive", *Fuel*, 117, 470-477.

[14] Reddy, P. S., Sudarsanam, P., Mallesham, B., Raju, G., Reddy, B. M. (2011) "Acetalisation of glycerol with acetone over zirconia and promoted zirconia catalysts under mild reaction conditions" *Journal of Industrial and Engineering Chemistry*, 17, 377-381

[15] Malik, M., Choudhary, V., I. K. Varma (2001) "Effect of oxirane groups on curing behaviour and thermal stability of vinyl ester resins", *Journal of Applied Polymer Science*, 82, 416-423

2. Description of the Invention

Please describe specifically and in detail what you consider to be the invention, as distinct from the prior art. If you need them, use additional pages, drawings, diagrams, etc. Descriptions may be by references to a separate document (copy of a report, a preprint, excerpt from a grant application, or the like) attached hereto. If you do so, please identify each document positively. Important: where available include a continuation sheet or document showing scientific data in support of the invention claims.

We report of the first time the following:

1. Synthesis of glycidyl methacrylate (GMA), a valuable commercially attractive monomer, using glycerin obtained from the waste streams of the biodiesel industry is presented.
2. The first intermediate for the synthesis of GMA, glycerol carbonate (GC), was synthesized with ~98.5 % purity using waste glycerin for the first time. The reaction was performed without the use of any solvents using an environmentally benign synthetic strategy. The GC was made catalyst free by simply passing over an acidic resin. Glycerol carbonate possesses large number of applications in many diverse fields, which can potentially expand the market scope for proposed methodology.
3. The second intermediate glycidol was synthesized using a solvent-less synthetic protocol and isolated with 55.0 % yield. The synthesis of glycidol from biowaste glycerin can be very viable approach as glycidol is an valuable intermediate for many synthetic processes.
4. Using the synthesized glycidol, GMA was synthesized with 41.8 % yield without the use of any solvents. The obtained green GMA will be very useful not only as a precursor in VER but also many other resins.
5. Green vinyl ester resins were successfully synthesized from BPA or TBBPA and GMA at 60-70 ˚C using amine based catalysts.
6. The synthetic method consists of four steps and use renewable biowaste as starting materials, whose disposal is a big problem as by 2020 the amount of glycerin, obtained in the waste stream of biodiesel production, will be six times higher than its demand.
7. The reported procedure for synthesis of GVER, is free of epichlorohydrin and halide compounds that are both toxic and carcinogenic.
8. This synthetic protocol eliminates the required steps of extraction, isolation, and synthesis of resins from petroleum derived products.
9. This procedure offers the potential for *in situ* synthesis and process development, provided that sufficiently high yields and good separation can be accomplished during processing.
10. The current manufacturing process of VER is based upon petroleum feed stock and using epichlorohydrin as one of the intermediate. We have proposed an entirely new alternative method for synthesis of VER in which we are using biowaste as a starting material and eliminated usage of epichlorohydrin.
11. The carbon fabric reinforced GVER panels will have great potential for applications in building hull and deck-house of the surface ships in the Navy as well as applications in various other construction industries.

The detailed description of the environmentally benign procedure for synthesis of GVER is as follows.

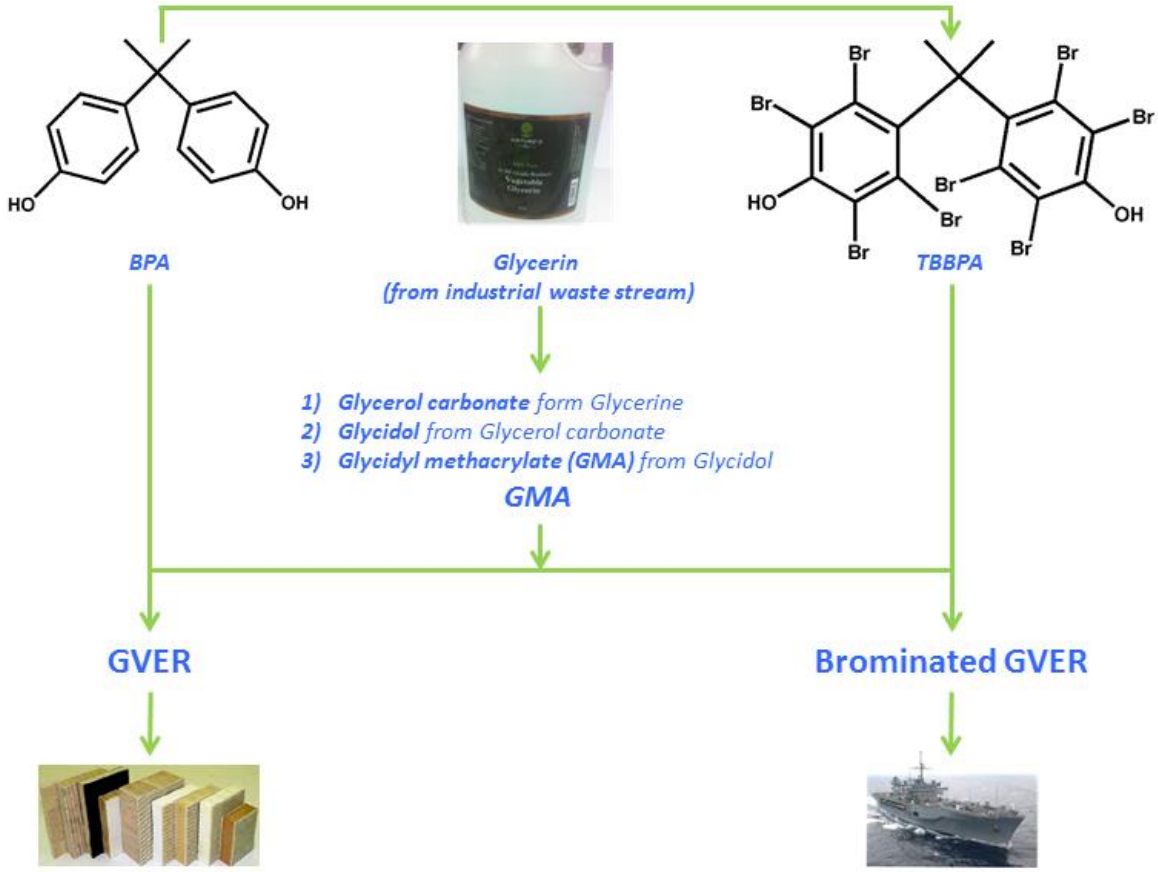

Figure 1. Illustration of the approach to 'Green Vinyl Ester Resin' from Renewable Resources.

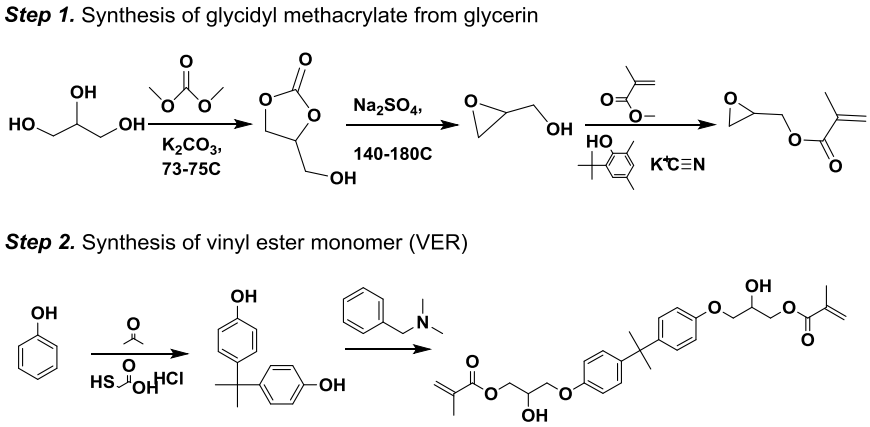

Figure 2. Synthesis of vinyl ester oligomer from phenol and glycerin.

EXPERIMENTAL DETAILS

Materials.

Glycerin from biodiesel waste stream (Maine Standard Biofuels), potassium carbonate (99 % Sigma-Aldrich), dimethyl carbonate (99 % Alfa-Aesar), sodium sulfate (99.9 % Alfa-Aesar), methyl methacrylate (99.9 % Alfa-Aesar), potassium cyanide (Sigma-Aldrich), 2,4,-dimethyl,6-tert-butyl phenol (Alfa-Aesar), and N,N-dimethylbenzylamine.

Characterization.

NMR Spectroscopy. ^{1}H NMR spectra of the synthesized materials were recorded at 25 ˚C on a Bruker 500 MHz spectrometer using DMSO (Cambridge Isotope Lab. Inc.) as the solvent and tetramethylsilane (TMS) as the internal reference (δ H 0.00).

Chromatographic system. The liquid chromatograph (Water's Alliance system model 2695 HPLC system) is equipped with a photodiode array (PDA) detector (Water's model 2996) monitored at 277 nm and a 4.6 mm × 15 cm column that contains 3-µm packing (Polar - Diol). The column temperature is maintained at 25 ˚C with a flow rate of 1.0 mL/min and an injection volume of 1 uL. The system was run isocratic with a 70:30 mixture of hexane and ethyl acetate. Samples were prepared in ethyl acetate.

Protocols for synthesis of glycidyl methacrylate (GMA) from Glycerin.

The GMA was synthesized by a multistep organic synthesis. The first intermediate, glycerol carbonate, was synthesized from glycerin and dimethyl carbonate under basic condition. The second intermediate, glycidol, was synthesized by decarboxylation of glycerol carbonate in the presence of sodium sulfate at high temperature. Finally, the GMA was synthesized by reaction of glycidol and methyl methacrylate as described in Figure 2. Here, we will discuss the synthesis procedure of each intermediate.

Glycerol carbonate. In a typical setup, a 250 mL flask equipped with a magnetic stirrer, condenser and thermometer was charged with glycerin (40.05 g, 0.435 mol), dimethyl carbonate (117.45 g, 1.305 mol) and K_2CO_3 (1.8 g, 13.05 mmol). The reaction mixture was refluxed (73–75 ˚C) for 3 h. After completion of the reaction, methanol and the excess of dimethyl carbonate were distilled off at 40 ˚C under reduced pressure. The remaining glycerol carbonate was analyzed by ^{1}H NMR and FT-IR spectroscopy.

Glycidol. A distillation apparatus with a 100 mL round bottom (RB) flask was placed in an oil bath with magnetic stirring. A RB flask was charged with 40.0 g of the glycerol carbonate and 4.0 g of anhydrous sodium sulphate. The reaction mixture was continuously stirred using magnetic stirrer under reduced pressure and the flask was heated to 160 ˚C. The glycidol was allowed to be distilled off for 3 h. The glycidol (as distillation product) was collected and stored under ambient conditions. The success of the reactions (i.e., purity of both glycerol carbonate and glycidol) were determined by ^{1}H NMR and FTIR.

Glycidyl methacrylate. To a flask containing 50.0 g (0.5 moles) of methyl methacrylate and 7.4 g (0.1 mol) of glycidol, was added 0.05 grams of 2,4-dimethyl-6-tert butyl phenol as polymerization inhibitor and 0.055 g (0.85 millimoles) of potassium cyanide. A claisen distillation apparatus was connected to the flask and the reaction mixture heated to 70-80 °C for 2 h. The reaction mixture was immediately vacuum distilled and two fractions were collected.

Synthesis of vinyl ester resins (VER). A 25 mL round bottom flask was charged with BPA (1.14 g, 5 mmol), GMA (1.42 g, 10 mmol) and N,N-dimethylbenzylamine (0.0065 g, 0.05 mmol). The flask had continuous flow of argon, and the temperature was raised to 70 ˚C, which was maintained for 6 h. After the reaction, the highly viscous liquid was transferred to a glass vial, and the product was analyzed by TLC, ^{1}H NMR, and FT-IR.

RESULTS AND DISCUSSION

Herein, we report of the first time conversion of biowaste glycerin to value added commercially attractive GVER, using sustainable, and environmentally benign 'green' synthetic protocols. These source materials are renewable, low-cost, and are becoming increasingly abundant and thus will eliminate the

dependence on imported oil and make the GVER production cost-effective. Figure 1 shows the sequence of reactions leading from glycerin, derived from biodiesel waste, to GVER monomer.

Synthesis of glycidyl methacrylate from glycerin.

GMA was synthesized using glycerin as the main precursor. Glycerin is a byproduct of the trans esterification of triglyceraldehyde in manufacture of biodiesel or the hydrolysis of triglyceraldehyde during saponification. We obtained crude glycerin byproduct from a biodiesel production company, Maine Standard Biofuels.

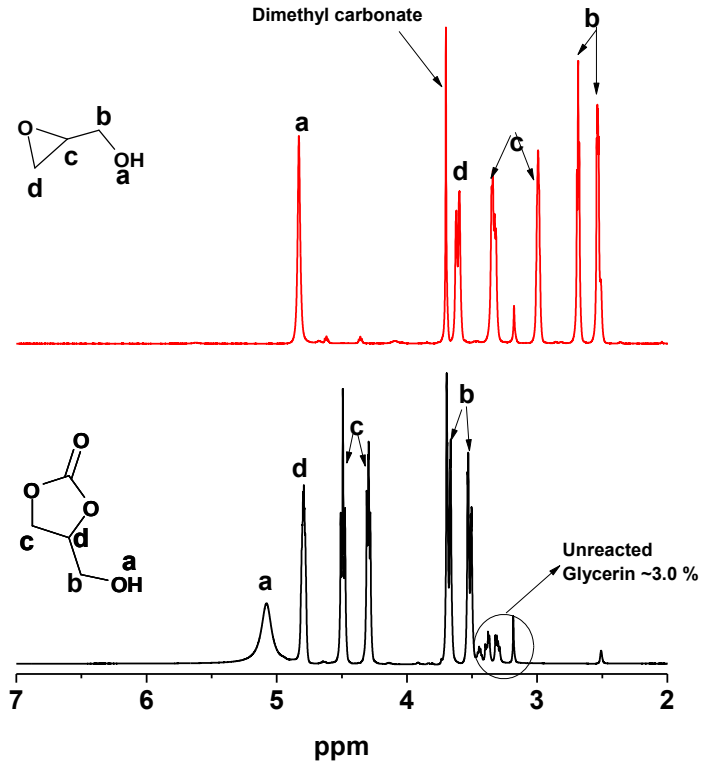

Figure 3. ^{1}H NMR of glycerol carbonate and glycidol.

GC, a first intermediate in the synthetic route to GMA from glycerin, is a very important material having a large number of applications in various fields. We have also developed procedures for isolation of this material with 100 % purity. Various approaches had been adopted by different groups for the synthesis of the GC; such as, using (a) Novozyme 435 catalyst and dimethyl carbonate as a precursor[16], and (b) metal oxide as a catalyst and urea as a precursor[17]. In a new approach, we synthesized GC by reaction between glycerin and dimethyl carbonate at 73 ˚C for 3 h in the presence of potassium carbonate.[18] The product formation was confirmed by ^{1}H NMR as shown in Figure 3. The peak integration value suggested ~ 97.0 % conversion of

[16] "Lipase-catalyzed synthesis of glycerol carbonate from renewable glycerol and dimethyl carbonate through transesterification" Kim S. C., Kim, Y. H., Lee, H., Yoon, D. Y., Song B. K. Journal of Molecular Catalysis B: Enzymatic, 49, 75–78, (2007).
[17] "Efficient synthesis of glycerol carbonate from glycerol and urea with lanthanum oxide as a solid catalyst"; L. Wang, Y. Ma, Y . Wang, S. Liu, and Y. Deng; Catalysis Communications 12 (2011)1458-1462.
[18] "Hyperbranched aliphatic polyethers obtained from environmentally benign monomer: glycerol carbonate", Rokicki, G., Rakoczy, P., Parzuchowski, P., and Sobiecki, M., Green Chem., 7, 529–539 (2005).

glycerin to GC at 73 ˚C. In order to complete the reaction to 100.0 %, the reaction temperature was increased to 100 ˚C; however, as the temperature increased to 100 ˚C, formation of some side product was observed and unreacted glycerin was also found in the final mixture. The FT-IR spectra of glycerol carbonate synthesized at 73 ˚C clearly showed peaks of –C=O at 1772.51 cm^{-1} and –OH at 3456.9 cm^{-1} as shown in Figure 4.

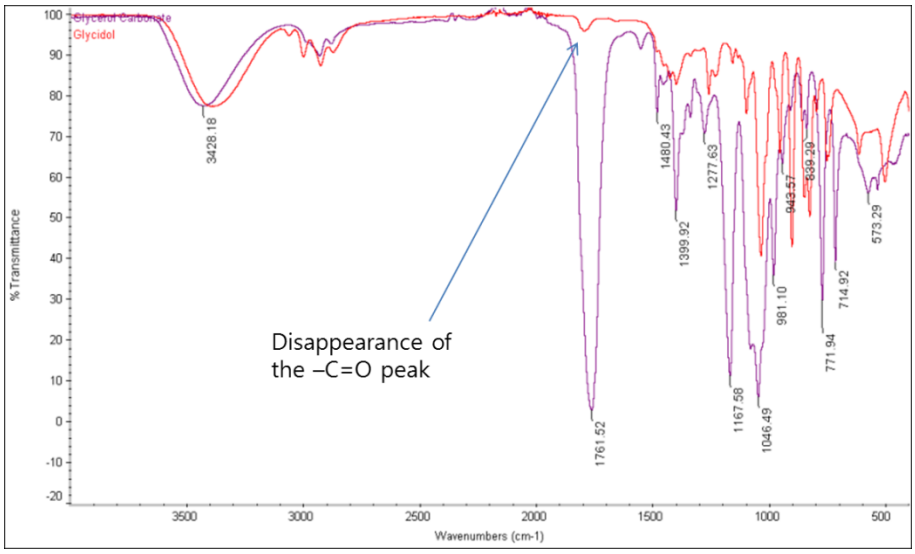

Figure 4. FT-IR of glycerol carbonate and glycidol.

Glycidol is the second intermediate during the synthesis of GMA from glycerin. Glycidol can be obtained by decarboxylation of GC as shown in Figure 2. Glycidol was synthesized by heating of GC in the presence of sodium sulfate.

In a typical setup for the synthesis of glycidol, a claisen distillation setup was placed on a round bottom flask and the end of the distillation apparatus was connected to a small vacuum pump. Three cold traps were used between the distillation apparatus and a high pressure vacuum pump. Glycidol was synthesized by heating the glycerol carbonate in the presence of sodium sulfate at 180 ˚C for 3 h.[19] The formation of glycidol is confirmed by ^{1}H NMR by matching the integration value of each proton as shown in Figure 4. Strong evidence is provided by the FT-IR exhibiting a clear disappearance of the –C=O peak at 1761 cm^{-1} as shown in Figure 4. The product was isolated with 55.0 % yield.

[19] "Method for preparing glycidol"; J.D. Malkemus, V.A. Currier, J.B. Bell Jr.; US patent 2,856,413,Oct. 14 1958

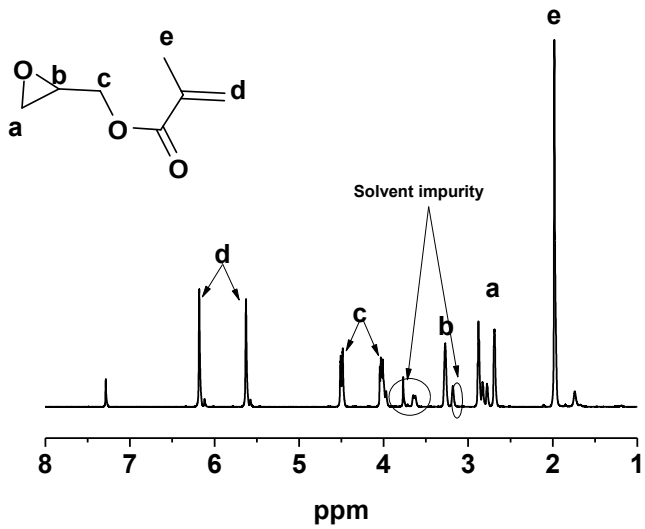

Figure 5. ^{1}H NMR of glycidyl methacrylate.

Glycidyl methacrylate (GMA) is one of the precursors for the synthesis of vinyl ester resin monomer along with bisphenol A and tetrabromobisphenol A. The GMA was synthesized by trans esterification between methyl methacrylate and glycidol in the presence of potassium cyanide as a catalyst and 2,4-dimethyl-6-tertbutylphenol.[20] Firstly, the pressure was reduced in the reaction flask, and the temperature was raised to 70 ˚C. The temperature of 70 ˚C was maintained for 2 h, and after that unreacted methyl methacrylate and methanol were distilled off. In a second fraction unreacted glycidol was collected and in last fraction GMA was obtained. The structure of GMA was confirmed by ^{1}H NMR as shown in Figure 5. The GMA was isolated with 41.0 % yield.

Synthesis of vinyl ester resin (VER) monomer.

VER are formulated from VER monomer using a solvent/reactive diluent, typically styrene, as well as additives to meet specific needs. In general, VER has several advantages over other polymers. For example, toughened and brominated VER produces resins with higher strengths than polyesters and lower viscosity than epoxies. This low viscosity is critical for fabricating large ship structures by vacuum infusion. Fiberglass-reinforced VER composites are preferred for many topside applications where low detectability and radar transmission are important. Recent advances in compatible sizing have enabled stiffer reinforcement of VERs using carbon fiber.

The VER monomer was synthesized by a one pot reaction between BPA and GMA in the presence of amine catalyst. The reaction was performed at 70 ˚C (Bowen, et. al. 1965). The ^{1}H NMR did not exhibit the –OH peak of the BPA, so it was presumed that the reaction was 100 % complete but, the integration value did not match precisely. The TLC showed three spots. The integration values in the ^{1}H NMR and the higher number of spots in TLC confirmed the presence of product in the reaction mixture as shown in Figure 6.

[20] "Process for the production of glycidyl methacrylate"; R. Ackerman, H. Kolb, G. Morlock, G. Schrey-er"; US patent 4,228,084, Oct. 14, 1980

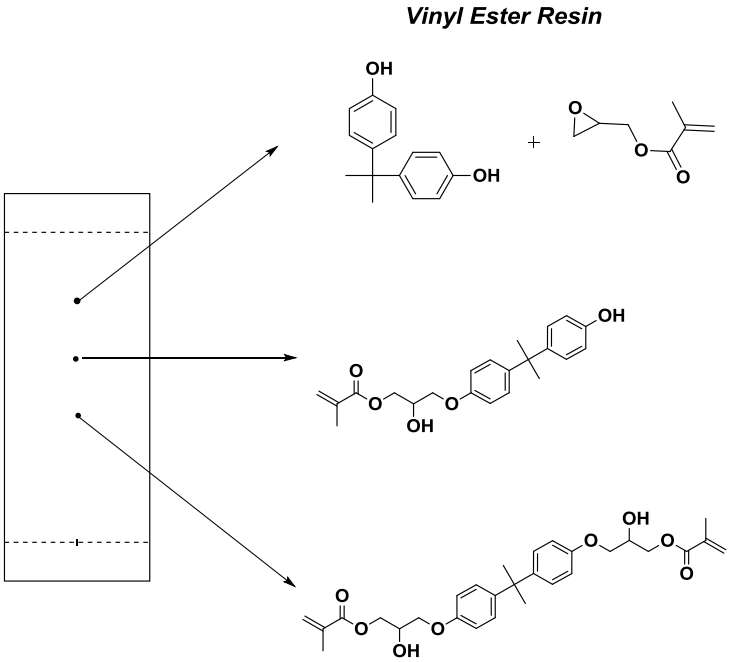

Figure 6. TLC of vinyl ester resin mixture in ethyl acetate and hexane in 3:7 ratios.

After confirming the presence of three different products in the reaction mixture; all fraction were separated by column chromatography using a 3:7 ethyl acetate: hexane ratio and analyzed using ^{1}H NMR as shown in Figure 7. The ^{1}H NMR clearly indicated the presence of non-functional BPA (NF) in the first fraction; mono-functional BPA (MF), GMA-BPA, in the second fraction; and di-functional BPA (DF), GMA-BPA-GMA, in the third fraction. The data clearly suggested that a 2 h reaction time was insufficient to obtain the maximum amount of DF. In order to increase the yield the reaction time was increased up to 6 h and sample was taken out at periodic interval of time, and the molar ratio of the GMA: BPA was increased to 4:1.

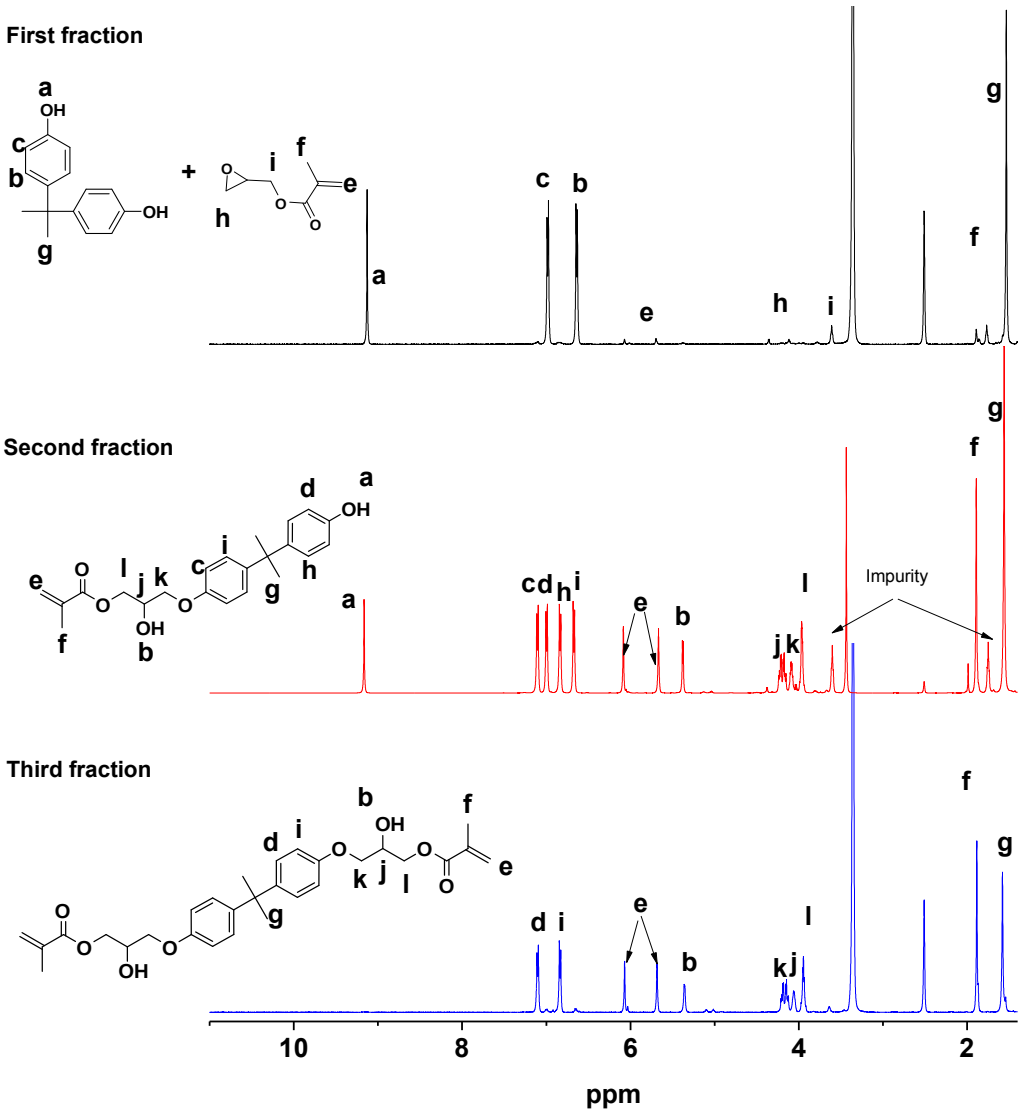

Figure 7. ^{1}H NMR of each fraction from column separation.

In order to determine the kinetics of the reaction, the quantification of NF, MF and DF in the reaction mixture is very essential. Such quantification can be obtained by high performance liquid chromatographic (HPLC) separation of the mixture. Therefore, preliminary work was conducted to develop a HPLC method for the separation and determination of BPA and reaction products in the synthesis of a VER. The ultimate goal was to separate each fraction without overlapping retention time.

Chromatograms shown in Figures 8 clearly demonstrate that the 3 compounds have very different retention times on the diol column with 7:3 hexane: ethyl acetate and should be easily separated and determined in a reaction mixture. The first fraction (NF), second fraction (MF) and third fraction (DF) exhibited retention time of 5.218, 7.946, and 13.686 min respectively.

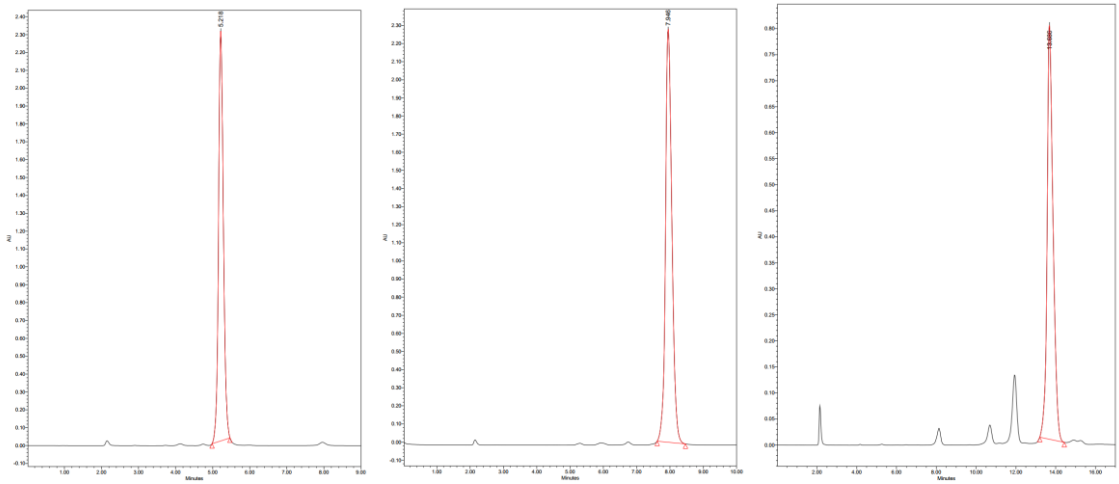

Figure 8. Chromatogram of (a) first fraction (b) second fraction, and (c) third fraction isolated during column purification of the VER-monomer.

Table 1. Percentage of various components in VER-reaction mixture at different time intervals.

Reaction time (h)	Different functional BPA		
	Non	Mono	Di
2h	32.00	49.24	18.76
3h	20.79	46.28	32.93
4h	14.13	40.63	45.23
5h	13.38	28.27	58.34
6h	12.70	18.05	69.26

We quantified the NF, MF, and DF BPA by calculating and comparing the area under the peak of the chromatogram obtained at different time intervals as shown in Table 1. The results suggested that reaction proceeds well as time progresses. However, it did not attain completion at 6 h, 69.26 % of the DF VER monomer was obtained. Experiments are in progress and the results will be published in near future with additional work to further improve the yield of this synthesis.

The entire synthetic route of glycerin to green vinyl ester resin is summarized in Figure 9. We have started with crude glycerin obtained during biodiesel production and succeeded in synthesizing green vinyl ester resin.

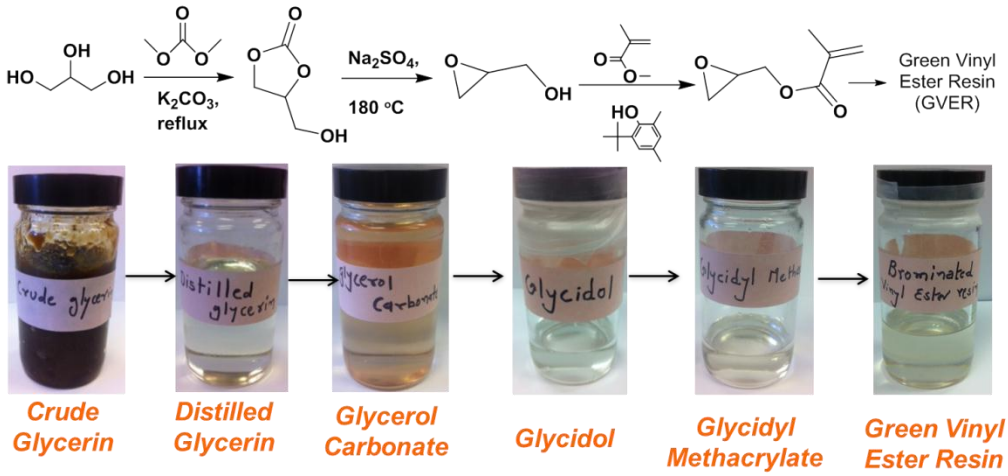

Figure 9. Summary of entire synthetic route starting from biowaste glycerin to green vinyl ester resin.

3. What are the novel aspects of your invention and how does it improve upon prior art? Does your invention overcome any deficiencies or limitations in the prior art?

- Our synthetic strategy utilizes a commercial waste material, glycerin from biodiesel manufacturing, and converts it into a value added commercially attractive GVER resin.
- The current manufacturing process of VER is based upon starting materials from petroleum feed stock. Our synthetic protocols utilize biowastes obtained during the production of biodiesel from renewable sources.
- The current manufacturing process of VER requires the use of epicholorhydrin, which is a highly toxic and carcinogenic chemical. Our developed strategy completely eliminates the use of epichlorohydrin and any halogen containing compounds that are both toxic and carcinogenic.
- Solvent-less synthetic protocols are utilized, which makes our strategy more cost-effective and environmentally benign.

4. Does there exist an earlier, dated record of the invention's conception--a sketch, report, laboratory notebook entry, or the like-which:

a.) describes your invention, and b.) can be independently corroborated?
(Note: This can be important in asserting and defending the claim to patent.)
If so, what is it, and where is it?

We have proposed entirely new synthetic route for synthesis of different kinds of VER starting from biowaste. We have laboratory notebook pages, internal monthly progress reports, and quarterly progress reports to SERDP as documented works.

5. a. Is this disclosure related to any earlier invention disclosure? If yes, identify and list showing docket number and title.

No.

5. b. Is this disclosure related to any earlier invention disclosure at another institution?
No

6. What do you see as commercial uses of your invention?

Different kinds of VER have large number of applications in various fields. The fiber reinforced composites with VER as the thermoset matrix are utilized as building blocks in the construction, automotive as well as the aviation industry. We are preparing brominated VER, which will be used by US Navy in building hull of ships.

7. What firms do you think may be, or are, commercially interested in this technology; and why?

(a) VER producing companies as they are looking for alternative, greener and cost effective newer approaches. (b) Fiber reinforced composite manufacturing firms, as they would be interested in cost-effective VER resin.

8. Do you have a relationship, formal or informal, with any of these companies? What is the nature of the relationship?

Ashland Inc., a Fortune 500 company, are our industrial teaming partner on the current program. They are currently producing VER and looking for less toxic approach

9. What do you see as the greatest impediment to the commercial adoption of your invention?

Purification of the biodiesel based glycerin is currently an energy consuming process.

10. Is further development of your invention now in progress? Scheduled? Dependent on commercial or federal sponsorship?

YES- We have two more years funding coming on the project so we will continue our research. We have a possibility to secure a subsequent bigger funding through ESTCP.

11. Has any aspect of this invention been published, been presented at a scientific meeting, been discussed with non-UMass individuals, part of a student dissertation or otherwise disseminated?

❑ YES √ NO

If yes, please identify, list dates and circumstances. (Dates are important. If published, list the date recorded on microfilm or in a library.)

12. Are there any plans to publish or otherwise publicly disseminate any aspect of this invention in the future?

√ YES ❑ NO

If yes, please identify and list dates.

13. Are you aware of related developments by other institutions or companies?

❑ YES √ NO

If yes, please identify.

14. Has the research that led to the invention been sponsored or funded by industry, or funded by a grant from a government agency or private foundation?

√ YES ❑ NO

If yes, you must provide CVIP with information on <u>all</u> funding sources for research that resulted in this invention. Please note that failure to report a funding source may result in a significant delay in proceeding with this disclosure, or may result in not being able to license the invention.

INDUSTRY OR FOUNDATION SPONSOR	GRANT #	CONTRACT #

SERDP-Sustainable green vinyl ester resin from renewable resources.

Fund	Dept. ID	P/G #	Speed Type
53106-L	L630300401-L	S51300000024869-L	114132-L

(Case Manager's Initials _____) Verified that the grant information shown above is complete as listed with the University's offices of Sponsored Programs and/or Offices of Grants and Contracts.

15. Did the research that led to the invention use any information or materials (e.g., cell lines, DNA, protein, antibodies) provided by another institution or a company?

❑ YES √ NO

If yes, was a transmittal letter or agreement (e.g., Confidential Disclosure Agreement [CDA] or Materials Transfer Agreement [MTA]), used in connection with receipt of the information or materials?

❑ YES ❑ NO

If yes to either, attach a copy of the CDA or MTA, or provide the name of the Investigator and address of the company.

16. Our technology evaluators or patent attorneys may wish to contact the Investigators with questions or to seek clarification. Please identify the primary Investigator Contact:

NAME:	PHONE:
Yongwoo Lee	978-934-3792

17. Mailing address(es) for each Investigator(s) in order listed on page 1:

Please provide your LOCAL or your HOME ADDRESS--where you are living now, not your University (i.e., Departmental P.O. Box) address. If you are a citizen of another country, then please indicate which country.

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Signature(s) of Investigator(s)

The undersigned agree(s) to cooperate with CVIP in the assessment, protection and commercialization of the invention. Further, each Covered Individual (as defined in the University Intellectual Property Policy (BOT T96-040)) does hereby assign, transfer and convey to University the entire right, title and interest in the invention and agrees to execute and deliver all documents requested by CVIP (including a Participation Agreement if not already executed) to record the assignment of rights to the University.

Name Typed	Signature	Date
1. Yongwoo Lee		11-06-14
2. Robert F. Kovar		11-06-14
3. Priyank N. Shah		11/06/14
4. Namjoon Kim		11/06/2014
5. Akshay Kokil		11/06/2014
6. Edwin Jahngen		07. Nov. 14.

18. Any other comments you believe are important for the evaluation of this technology.

We are planning to open dialogue with Ashland Inc. for filing patent on the current ID.

Appendix I

Journal of Applied Polymer Science

Processing and mechanical properties of bio-derived vinyl ester resin-based composites

Priyank N. Shah,[1] Siddharth Dev,[2] Yongwoo Lee,[1] Christopher J. Hansen[2]
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P. Shah and S. Dev contributed equally to the manuscript.
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ABSTRACT: A "green" vinyl ester resin (GVER) is investigated for use in structural applications. The GVER was formulated using a monodisperse vinyl ester created via a novel synthetic route capable of using bio-waste material from paper and biodiesel industries. The GVER was used either as a neat resin or as blended with a commercial vinyl ester resin. The processing viscosity and gel times are investigated. The GVER reaches a similar viscosity as the commercial resin with only half the styrene monomer content, thereby reducing the volatile organic compounds associated with manufacturing. Composites of the GVER matrix reinforced by carbon fabric were tested for their tensile and flexural properties. The mechanical performance of the GVER compares favorably with commercial resin and provide a route for composites manufacturing from sustainably sourced vinyl ester matrix. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44642.

KEYWORDS: composites; mechanical properties; resins; thermosets; viscosity and viscoelasticity

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DOI: 10.1002/app.44642

INTRODUCTION

Vinyl ester resins (VERs) are one of the primary classes of thermoset resins used to manufacture modern polymer matrix composites.[1] VERs offer increased toughness, thermal stability, and chemical resistance relative to their polyester counterparts, while retaining the advantages of processing under ambient temperatures using vacuum-assisted resin transfer molding (VARTM) to form small to large-scale fiber-reinforced structures.[2] VER matrix-based composites are used in diverse applications in the transportation and civil infrastructure,[3] marine,[4,5] and wind energy industries.[6]

Commercialized vinyl ester prepolymers are synthesized by the reaction of diglycidyl ether of bisphenol A (DGEBA) with unsaturated carboxylic acids. DGEBA is produced by the reaction of epichlorohydrin and bisphenol A in the presence of sodium hydroxide.[7] One disadvantage to this commercial synthesis approach is its current usage of petroleum feedstock. Recently, significant research efforts have focused on the development of bio-based thermosetting resins as a route toward more sustainable polymer matrices.[7–10] Bisphenol A has been replaced by various bio-derived hydroxy-containing aromatic compounds such as cardanol,[11–13] rosin acid,[14,15] vanillin,[16] isosorbide,[17,18] and gallic acid.[19] These molecules are subsequently functionalized with epichlorohydrin and their epoxy-based prepolymers prepared. Alternatively, unsaturated vegetable oils, such as soybean oil and linseed oil, are epoxidized as a substitute for DGEBA. Bio-based resins have been used either as neat resins—such as acrylated epoxidized soybean oil (AESO),[20] maleinated acrylated epoxidized soybean oil (MAESO),[21] and AESO blended with acrylated epoxidized linseed oil (AELO) for bulk molding compounds[22]—or as blends with petroleum-based feedstocks.[23,24]

Whereas bio-based thermoplastics such as poly(lactic acid),[25] polyhydroxy-alkanoates,[26] and poly(butylene succinate)[27] have been commercialized successfully, there has been limited commercial penetration of bio-based thermosetting resins. Solvay and Dow have commercialized epichlorohydrin derived from biodiesel glycerin under the brand name of Epicerol® and by a glycerin-to-epichlorohydrin (GTE) technology, respectively.[28] Arkema has commercialized epoxidized soybean oil (EBSO) and epoxidized linseed oil (ELO) under the Vikoflex® brand, which can be subsequently acrylated.[29] Dixie Chemical offers maleinated acrylated epoxidized soybean oil (MAESO) and linseed oil (MAELO) designed to compare favorably with unsaturated polyester resins.[30]

Beyond the use of petroleum feedstocks, a disadvantage to current commercial syntheses is the use of the reactant

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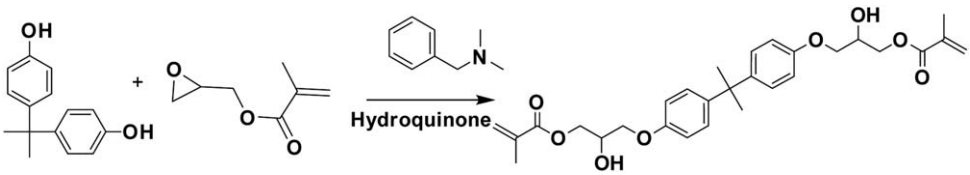

Figure 1. Synthesis of vinyl ester polymer by reaction of glycidyl methacrylate and bisphenol A.

epichlorohydrin, which is a known environmental and health hazard that produces acute toxicity in case of inhalation, oral, and dermal exposure and is a probable carcinogen.[31] In all previous studies, epichlorohydrin has been used as a reactant. Completely bio-derived VER via less hazardous routes presents a significant synthetic challenge.

Commercial vinyl ester prepolymers are sufficiently viscous to preclude composites processing as a neat material. VER formulations are thus formulated as a blend of the vinyl ester prepolymer and a reactive diluent, typically 35–50 wt % styrene monomer. However, styrene is reasonably suspected to be a carcinogen by the U.S. Department of Health and Human Services,[31] and the National Institute for Occupational Safety and Health (NIOSH) and Occupational Health and Safety Administration (OSHA) define the permissible exposure limits as 50 or 100 ppm (time weighted average), respectively.[32] Recently, bio-based styrene replacements have been evaluated, including methacrylated fatty acid (MFA),[30,33] vinyl levulinate,[34,35] and benzoxazines.[36] However, these alternatives have seen limited market penetration due to their increased cost, their reduced diluent capability caused by higher molecular weights, and lower mechanical properties.

In a recently published article, we demonstrated an alternative vinyl ester synthesis route based on bio-waste from the biodiesel and paper industries that avoids the use of epichlorohydrin.[37] The environmentally benign vinyl ester prepolymer synthesis uses glycidyl methacrylate (GMA) and bisphenol A (BPA) as the input materials. GMA was synthesized from glycerin obtained in the waste stream of the biodiesel industry. BPA can be synthesized by phenol obtained by pyrolysis of lignin, which is a waste product in paper industry. The GMA and BPA could be derived from these and other readily available renewable resources. This route successfully eliminates the usage of epichlorohydrin in vinyl ester prepolymer synthesis and enables a fully bio-sourced synthesis.

In the present work, we present the scaled synthesis of vinyl ester resins (GVER), which can be synthesized from these bio-derived feedstocks, and its suitability for processing and performance in carbon fiber-reinforced composites. The synthesis of vinyl ester prepolymer product is scaled using commercial GMA and BPA, and this product is purified. A resin is formulated by the dilution of the synthesized polymer with the reactive diluent styrene. The resulting GVER is blended with a commercial resin (Derakane Momentum 411 350) to establish benchmarks for formulations that span the transition from petroleum-based to bio-sourced feedstocks, as well as to determine the scope for styrene reduction. Carbon fiber-reinforced composites are fabricated by infusion with GVER and blends thereof and subsequently investigated for their processing and mechanical performance.

EXPERIMENTAL

Materials

The chemicals used to synthesize the VER were bisphenol A (99%, Sigma-Aldrich), glycidyl methacrylate (97%, Sigma-Aldrich), hydroquinone (99.9%, Sigma-Aldrich), cumene hydroperoxide (80%, Sigma-Aldrich), cobalt naphthenate (Sigma-Aldrich), styrene (>99%, Sigma-Aldrich) and *N*,*N*-dimethylbenzylamine (≥99%, Sigma-Aldrich). These chemicals were used as received.

The composite specimens were fabricated by infusion of an AS4-GP-3K carbon plain weave fabric of 192 g m^{-2} (Style 4147, Textile Product Inc., CA). The commercial vinyl ester resin used was Derakane Momentum 411–350 (Ashland, Inc.). Standard vacuum assisted resin transfer molding (VARTM) consumables were purchased from Fibre Glast, Inc.

Synthesis and Formulation of Vinyl Ester Resin

The synthesis and purification of the vinyl ester polymer (Figure 1) was performed per the previously detailed procedure[37] and scaled to a 400 g batch size. A 500-mL three-neck round bottom flask was charged with BPA (114 g, 0.5 mol), GMA (142 g, 1.0 mol) and *N*,*N*-dimethylbenzylamine (0.65 g, 5 mmol). The flask was heated to 70 °C for 6 h under a continuous flow of argon. After the reaction, resin was purified by column chromatography using silica gel as a stationary phase and hexane:ethyl acetate (7:3) mixture as a mobile phase. The isolated pure fraction of the product was analysed by ^{1}H NMR and FT-IR.

This vinyl ester fraction was mixed with 40 wt % of styrene to create the baseline bio-derived vinyl ester resin (GVER-1). This resin was then blended with a commercial resin (Derakane Momentum 411–350) at a fraction of 20–80 wt % for structural equivalence testing. The seven resin formulations that were studied are shown in Table I.

Neat Resin Characterization

NMR Spectroscopy. ^{1}H NMR spectra of the synthesized materials were recorded at 25 °C on a Bruker 500 MHz spectrometer (Cambridge Isotope Lab., Inc.) using DMSO as the solvent and tetramethylsilane (TMS) as the internal reference (δ H 0.00).

FTIR Spectroscopy. ATR-FTIR spectroscopy was conducted on resin compositions using a Bruker Tensor 27 FTIR spectrometer (Bruker Corporation) with 64 scans performed at a resolution of 2 cm^{-1} per specimen.

Rheology. The non-activated and activated resin rheologies were measured on a rotational rheometer (ARES-G2, TA Instruments). The non-activated formulation was measured with a 40 mm diameter 2° truncated cone geometry under steady

Table I. Formulations of Bio-Derived Vinyl Ester Resin Investigated

Name[a]	Formulated GVER (wt %)	Derakane momentum 411 350 (wt %)	Styrene fraction (wt %)
CVER	—	100.0	40.0
FVER-1	20.0	80.0	40.0
FVER-2	50.0	50.0	40.0
FVER-3	80.0	20.0	40.0
GVER-1	100.0	—	40.0
GVER-2	100.0	—	30.0
GVER-3	100.0	—	20.0

[a] CVER-Commercial Vinyl Ester Resin, FVER-Formulated Vinyl Ester Resin, GVER-Bio-Derived Vinyl Ester Resin

shear using a shear rate, $\dot{\gamma}$, of 0.1 s^{-1}. The activated resin was measured using a parallel-plate equipped with 25 mm diameter parallel discs with a 0.8–1.0 mm separation gap. All experiments were conducted at 25 °C.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) was conducted using a TA Instruments Dynamic Mechanical Analyzer Q800. The specimens were approximately 12-mm wide, 3-mm thick, and were clamped using a dual cantilever fixture with a support span of 35 mm. A sinusoidal transverse displacement was applied with a 6 N amplitude load at 1 Hz. The experiments were ramped at 5 °C min^{-1} from 0 to 150 °C.

Flexural Properties. Flexural properties for neat resin specimens were tested per ASTM D790. The specimens were manufactured using a modified injection molding technique to minimize surface defects. The specimens were approximately 3 mm thick × 12 mm wide and were tested using a support span of 53 mm, which corresponds to a span-to-thickness ratio of 20:1. All specimens were tested to failure using an Instron 8511 test frame with a loading rate of 5 mm min^{-1}.

Composite Manufacture

Composite plates were prepared using vacuum-assisted resin transfer molding (VARTM). The resin was activated with 0.20 wt % cobalt naphthenate (CoNaph) as promoter, 1.00 wt % cumene hydroperoxide (CHP) as initiator, and 0.30 wt % 2,4-pentanedione (acetylacetone) as retarder. The preform stack-ups were 12, 18, and 34 layers for the tensile, flexural, and short beam shear coupons, respectively. Resin was infused under vacuum at a gage pressure of −90 kPa. The composite plates were cured at room temperature for 24 h, followed by a post-cure at 120 °C for 2 h.

Composite Characterization

The composites were assessed for their tensile, flexural, and short beam shear properties. Tensile testing was performed per ASTM D3039, with specimens having a 2.54-mm thickness and 125-mm gauge length. The tensile specimens were tested using a universal testing machine (Instron 1332) with a 90 kN load cell and strain gage voltage and resistance data was collected (Agilent 34970A and Agilent 34902A). Flexural and short beam shear properties were tested per ASTM D7264 and ASTM D2344, respectively, using an Instron 8511 servo-hydraulic testing machine with a 20 kN load cell. Flexural specimens had a 3.55-mm thickness and a span-to-thickness ratio of 20:1. Short beam strength specimens had a 6.35-mm thickness. A total of three specimens were tested per test condition.

RESULTS AND DISCUSSION

Vinyl Ester Polymer Synthesis Scale-Up and Resin Formulation

The ultimate goal to manufacture composites with a bio-sourced vinyl ester matrix requires a scalable synthesis process to produce a sufficient quantity of prepolymer to enable analysis of the resin, matrix, and composite material properties. The source materials for synthesis are renewable, low-cost, have potential for industrial scalability, and thus are expected to significantly reduce the dependence on petroleum feedstock. While the bio-sourced materials used in the previous work to synthesize the GVER in gram-scale quantities are becoming increasingly abundant, in this work scaling the synthesis to 400 g batches required the use of commercially sourced chemicals.

The purified vinyl ester prepolymer was analysed using 500 MHz ^{1}H NMR and DMSO as a solvent. The chemical shift δ (ppm) was observed as follow: 6.09, 5.72 (2H, —C═CH_2), 4.48, 3.92 (2H, —CH_2—CH—), 3.25 (1H, —CH$_2$—CH—), 2.82, 2.67 (2H, —O—CH_2), 1.56 (3H, —C—CH_3), and 1.90 (3H, —CH$_2$═C—CH_3). The peak position and integration value confirmed the structure of the prepolymer as described in Figure 2. In addition, the FT-IR analysis of the prepolymer exhibited peaks at 3424 (-OH stretching), 2963, 2926 (—CH stretching aliphatic), 1724 (—C═O stretching), 1634, 1607, 1597, 1403, 1362 (—CH bending).

In addition to verifying the chemical structure of the vinyl ester, the results from NMR were used to determine the molecular weights and the ratio of styrene to methacrylate groups in the seven resin compositions as shown in Table II.

The vinyl ester prepolymer is monodisperse (polydispersity index (PDI) = 1.0) and has a low molecular weight (MW = 512.60 g mol^{-1}). Within polydisperse systems, the polymer fraction with higher molecular weights dominate the melt viscosity, as the viscosity is proportional to either molecular weight with a power–

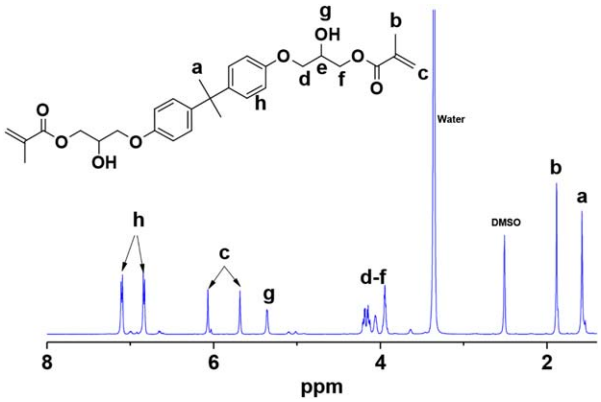

Figure 2. ^{1}H NMR spectrum of the column purified vinyl ester prepolymer. [Color figure can be viewed at wileyonlinelibrary.com]

Table II. Parameters Obtained from NMR that Describe the Composition of Each Resin System

Resin	Oligomer MW (g mol^{-1})	Ratio of styrene: methacrylate	Methacrylate in oligomer (mol g^{-1})	Methacrylate in resin (mol g^{-1})
CVER	948	3.84:1.27	2.11×10^{-3}	1.27×10^{-3}
FVER-1	861	3.84:1.39	2.32×10^{-3}	1.39×10^{-3}
FVER-2	730	3.84:1.64	2.74×10^{-3}	1.64×10^{-3}
FVER-3	600	3.84:2.00	3.33×10^{-3}	2.00×10^{-3}
GVER-1	513	3.84:2.34	3.90×10^{-3}	2.34×10^{-3}
GVER-2	513	2.88:2.73	3.90×10^{-3}	2.73×10^{-3}
GVER-3	513	3.12:1.92	3.90×10^{-3}	3.00×10^{-3}

law exponent of either 2 or 3.4 if below or above the entanglement molecular weight, respectively. La Scala *et al.* have reported power–law exponents as high as 5 to 10 in similar systems.[38] As compared to the typical polydispersity PDI ~2 for commercial polyester resins, the monodisperse vinyl ester prepolymer possesses a significantly lower viscosity than commercial polyesters.

Resin infusion times during composites processing is directly related to the formulation viscosity, which is typically ~500 cps. Commercial resins commonly contain 40–50 wt % of the reactive diluent styrene to achieve this viscosity range; the baseline commercial resin chosen for this project—Derakane Momentum 411–350—is a BPA-based vinyl ester resin that contains a polymer with a molecular weight of 512 g mol^{-1} and formulated with 40 wt % styrene. This commercial formulation exhibited an initial viscosity of 458 cps. Despite the availability of lower viscosity resins on the market (e.g., Ashland's Aropol 914), Derakane Momentum 411 350 has been chosen as the benchmark resin because this study aims to investigate if the bio-based GVER has the ability to match the performance of the Derakane resin in specific end use applications, such as the manufacturing of hulls of large scale naval vessels. The bio-derived vinyl ester resin (GVER), by contrast, can be formulated to reach this viscosity target with less reactive diluent due to its monodisperse, low molecular weight composition. The GVER is formulated by combination of the vinyl ester material with 20, 30, and 40 wt % styrene. These formulations had viscosities of 427, 108 and 68 cps, respectively. For a comparable styrene fraction of 40 wt %, the GVER formulation has a viscosity seven times lower than its commercial VER counterpart. Alternatively, a comparable viscosity to the commercial VER (40 wt % styrene) can be achieved with a GVER formulation containing only 20 wt % styrene. Hence, the GVER offers a route to reduce by half the resin styrene contents and related volatile organic compound (VOC) emissions.

The large vinyl ester resin market and the difficulties of quickly scaling bio-sourced production make it imperative to investigate resin blends of bio-sourced and traditional petroleum-based materials.

Cure Kinetics

The fractional double bond conversion of both the styrene and methacrylate groups provides insight into the rate of polymerization as well as the degree of cure of the vinyl ester resin. Previous studies have demonstrated the efficacy of isothermal FTIR in determining the double bond conversion as well as the *in situ* rate of polymerization.[39–42] It has been shown that the initial rate of conversion of vinyl ester double bonds is significantly faster than that of the styrene double bonds. This behavior has been attributed to the higher reactivity of the acrylate free radicals as compared to the styrene free radicals during the early stages of the reaction. However, it was also observed that the final conversion of methacrylate double bonds was lower than that of the styrene double bonds. This result has been reasoned to be due to the formation of a microgel network during the polymerization process, thereby inhibiting the access of the vinyl ester double bonds to the active free radicals within the system.[39,42,43] In addition to the decreasing reactivity of the vinyl ester as the reaction progresses, homopolymerization of styrene to form linear polystyrene chains continues to occur even towards the end of the reaction, further adding to the significant difference in double bond fractional conversion of styrene relative to the vinyl ester.

ATR-FTIR studies were conducted on the seven resin formulations to determine the fractional conversion of the styrene and vinyl ester double bonds as separate populations, as well as the overall double bond conversion. Conversion rates were determined by comparing the peaks in the FTIR spectra for the neat resin compositions to the FTIR spectra of specimens cured for 24 h at 25 °C followed by a post-cure for 2 h at 120 °C. Figure 3 shows an example spectra for GVER-1 from 650 to 1000 cm^{-1}.

The peaks at 910 and 945 cm^{-1} correspond to the bending of the carbon-hydrogen bond in the vinyl group, while the peaks at 830 and 700 cm^{-1} correspond to the bending of the aromatic carbon-hydrogen in the vinyl ester and styrene groups. (1) and (2) have been adopted from previous studies to calculate the fractional conversion of the vinyl ester and styrene double bonds respectively,[39,42,44]

$$\alpha_{VE} = 1 - \left(\frac{ABS(1)_{945\,cm^{-1}}}{ABS(0)_{945\,cm^{-1}}}\right)\left(\frac{ABS(0)_{830\,cm^{-1}}}{ABS(1)_{830\,cm^{-1}}}\right) \quad (1)$$

$$\alpha_{styrene} = 1 - \left(\frac{ABS(1)_{910\,cm^{-1}}}{ABS(0)_{910\,cm^{-1}}}\right)\left(\frac{ABS(0)_{700\,cm^{-1}}}{ABS(1)_{700\,cm^{-1}}}\right) \quad (2)$$

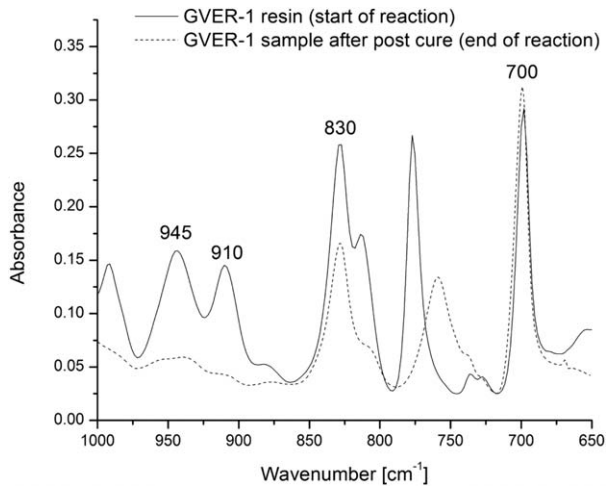

Figure 3. FTIR spectra of GVER-1 resin. The solid and dashed lines represent the uncured resin and the post-cured polymer, respectively.

where ABS (0) and ABS (1) are the peak heights at the specified wavenumber for the resin and the post-cured specimens, respectively. Table II summarizes the fractional conversion of the styrene and vinyl ester for all seven resin compositions.

The total double bond conversion for all resin compositions was obtained by mulitplying the fractional conversion of the vinyl ester and styrene double bonds by their respective mole fractions.

The fractional conversion of the CVER is slightly lower as compared to values reported in previous studies that have determined the conversion rates of the Derakane 411 series resin.[39,40] As expected, the conversion of the methacrylate bonds is signficantly lower than the fractional conversion of the styrene bonds for all resins. The methacrylate conversion rate increased significantly to greater than or equal to 0.6 for GVER-1, GVER-2, and GVER-3 as compared to 0.30 for CVER. As shown in Table III, the CVER has a significantly higher molecular weight as well as fewer moles of methacrylate per gram of resin than the GVER-1. For vinyl ester resins containing the same weight fraction of styrene (CVER and GVER-1), a decrease in molecular weight has two effects: (1) a decrease of molecular weight between crosslinks and (2) an increase in the number of available vinyl ester terminal double bonds, which serve as crosslinkers for the polymerization reaction, per unit mass of resin.[41] Therefore, it is expected that the lower VE conversion fraction should correlate to lower crosslink density and result in a lower storage modulus in the CVER.[38] For the resins with the same molecular weight but decreasing styrene concentration (GVER-1 to GVER-3), the methacrylate conversion is the highest for GVER-1. This agrees with a previous study that has shown that increasing styrene concentration increases ultimate vinyl ester conversion.[42] This occurs because the presence of a higher styrene concentration leads to greater molecular mobility and allows the vinyl groups to more easily diffuse to reach reactive sites after gelation occurs. The results also show that as the styrene fraction decreases for the same molecular weight resin, the styrene conversion increases and is consistent with observations in literature[38]. This lower conversion of vinyl ester bonds in a resin with a lower styrene content is explained by the styryl radicals being restricted to homopolymerization once vinyl ester double bonds have achieved maximum fractional conversion. Therefore, the highest fractional conversion of styrene double bonds occurs in GVER-3, which has the lowest styrene content of the seven resin compositions.

Table III. Fractional Conversion of Methacrylate and Styrene Double-Bonds after Resin Post-Cure

Resin	Methacrylate conversion	Styrene conversion	Total double bond conversion
CVER	0.30	0.88	0.74
FVER-1	0.39	0.91	0.77
FVER-2	0.54	0.91	0.80
FVER-3	0.58	0.90	0.79
GVER-1	0.67	0.89	0.81
GVER-2	0.62	0.93	0.78
GVER-3	0.60	0.96	0.82

Chemorheology Characterization

Resin infusion processes depend upon the chemorheological behavior of the resin formulation. The initial viscosity η_0, discussed in Vinyl Ester Polymer Synthesis Scale-up and Resin Formulation, dictates the initial infusion rate. However, the viscosity dynamically increases with the formation of polymer networks in the matrix. The time to gelation is a critical processing parameter, as resin infusion slows dramatically near the gel point and no additional resin infusion occurs after gelation. However, excessive gel times slow throughput of manufacturing and cost valuable mold time. Hence, manufacturers value a resin cure that offers a gel point minimally longer than the anticipated infusion time; typical industrial infusion times range from 30 min to 2 h.

The time to gelation for formulations of CVER and GVER were first investigated. The formulation gel points are measured by oscillatory rheology and the crossover between the storage modulus (G') and loss modulus (G'') is used to approximate the gel point. Neat commercial VER (CVER), bio-derived VER (GVER-1), and a mixture of equal parts commercial and bio-derived VERs (FVER-2) are formulated with 40 wt % styrene and with the same promoter, initiator, and retarder concentrations. The time varying rheology measured at room temperature is shown in Figure 4(a). The resulting gel points for the CVER, FVER-2, and GVER are 67, 183, and 675 min, respectively. The gel time for the FVER-2 formulation of equal parts CVER and GVER is double that of the pure CVER, yet still offers a reasonable infusion time for certain manufacturers. The GVER-1 gel time, however, is excessively long at ~11 h. A sample of GVER-1 resin with no retarder was subsequently activated; however, the gel time still exceeded 7 h. This significantly higher gel time is due to the presence of added inhibitor (hydroquinone), leading to a higher concentration in the GVER-1 as compared to the CVER. Beyond reduction of the inhibitor concentration, increases in initiator or promoter concentrations were not investigated but

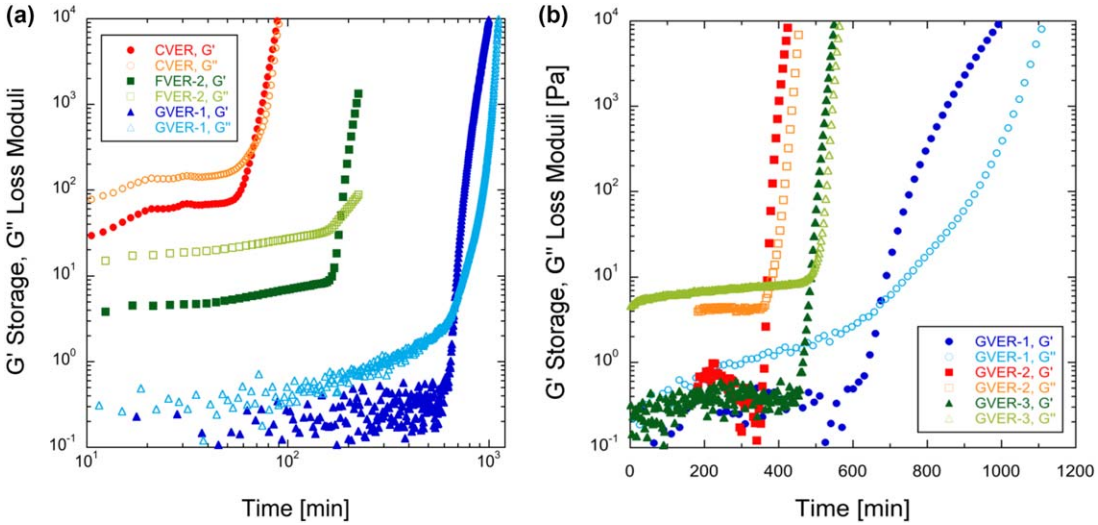

Figure 4. (a) G' storage modulus and G'' loss modulus for commercial resin (CVER), 50 wt % commercial and 50 wt % bio-derived vinyl ester resin (FVER-2), and neat bio-derived vinyl ester resin (GVER-1) as a function of cure time. (b) G' storage modulus and G'' loss modulus for bio-derived vinyl ester resins with 40 wt % (GVER-1), 30 wt % (GVER-2), and 20 wt % styrene (GVER-3). [Color figure can be viewed at wileyonlinelibrary.com]

offer future avenues to further reduce the gel time by activator concentration modifications.[45,46]

A second test of the GVER-1 chemorheology was performed at 45 °C; this temperature increase of 20 °C significantly decreased the gel time to 23 min. Thus, the GVER-1 demonstrates a sufficiently long pot life (>10 h) and an ability to cure with a minor temperature increase, which accelerates the manufacturing process with minimal energy input.

The chemorheological dependence on styrene fraction for the GVER is investigated. The evolution of the G' and G'' moduli and the gel time for the vinyl ester polymer formulated with 40 wt % (GVER-1), 30 wt % (GVER-2), and 20 wt % (GVER-3) styrene monomer were measured [Figure 4(b)]. The gel times were 675, 367, and 487 min for 40, 30, and 20 wt % styrene, respectively. Literature reports have observed that the reaction of vinyl ester resins proceeds more quickly at reduced styrene fractions[40] because the addition of styrene diluent enhances molecular mobility and this diffusive enhancement can compensate for the reduced reaction rate.[42] However, the impact of styrene on the molecular mobility is only observed after the gel point, that is, after which a microgel network has formed and the accessibility of vinyl ester double bonds to free radicals is greater for a resin with an initially lower viscosity. In this case, the longer gel times of the GVER-2 and GVER-3 are due to the higher concentrations of the hydroquinone inhibitor.

Matrix Physical and Mechanical Properties

The cured GVER material exhibits a minor increase in bulk density. The commercial resin has a post-cure density of 1.135 g cm^{-3}, while the GVER-1 (GVER with 40 wt % styrene) has a density of 1.167 g cm^{-3}, an increase of approximately 3%. The density varies according to a rule of mixtures approach for formulations blended from the CVER and GVER-1. Reduction in the styrene content further increases the post-cure density to 1.174 and 1.195 g cm^{-3} for 30 and 40 wt % styrene content, respectively.

The neat matrix mechanical properties were assessed by dynamic mechanical analysis (DMA). All compositions were tested at room temperature (Figure 5), as well as up to 150 °C (Figure 6). In addition, flexural testing in a three-point bend configuration was conducted to determine the elastic modulus of the resin compositions. At room temperature, the elastic storage modulus increases by 20% for the GVER-1 relative to the CVER. The increase in storage modulus is in line with observations seen in literature and can be attributed the fact that the GVER-1 has a lower molecular weight vinyl ester monomer than the CVER. The lower molecular weight decreases the distance between crosslinks and results in a more densely crosslinked network that is more rigid.[38] Despite the higher storage modulus values for GVER-1 compared to CVER, no discernible linear trend was observed across the resin blends between these two compositions [Figure 5(a)]. The flexural modulus on the other hand, showed a significantly stronger linear trend for formulations intermediate to the CVER and GVER-1 compositions. Previous studies have shown that the support span to thickness ratio can significantly affect the accuracy of the data and the discrepancy in the storage and flexural moduli might be related to the relatively low span to thickness ratio for the DMA specimens.[47] In both sets of results, there is no statistically significant difference observed in GVER modulus as a function of styrene fraction.

The glass transition temperature (T_g), as defined by the temperature of maximum tan δ, increases linearly with GVER content, from 128 °C for CVER to 138 °C for GVER-1 as seen in Figure 6. No discernible trend is observed as a function of styrene monomer content in the GVER-1, −2, and −3 formulations, with a T_g ranging from 134 to 138 °C. An increase in styrene content while keeping the VER molecular weight constant should theoretically increase the crosslink density as well as the

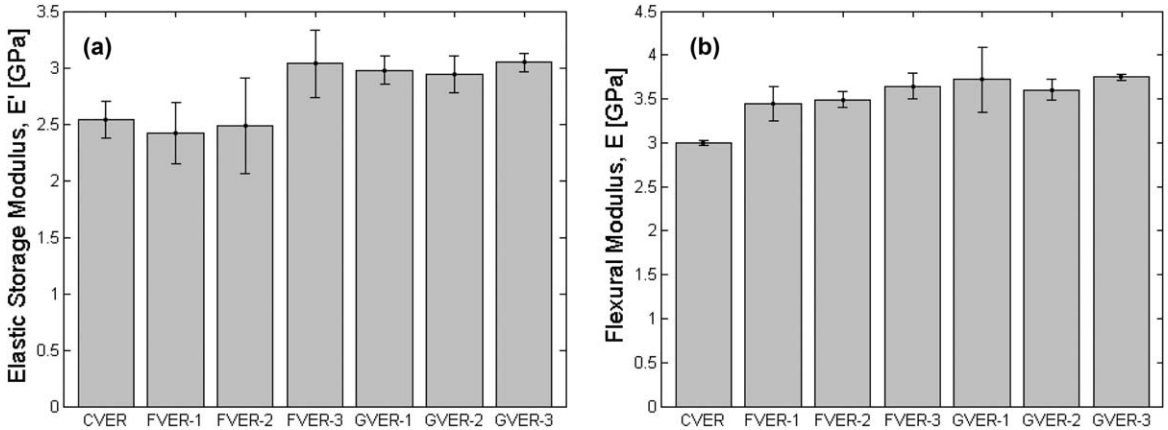

Figure 5. (a) Elastic storage modulus (E') at room temperature for VER compositions. (b) Flexural modulus (E) at room temperature for VER compositions.

T_g, because the higher styrene content provides the double bonds with greater accessibility to free radicals within the system. However, literature reports have found mixed effects of styrene content on the glass transition temperature, including (1) a maximum observed at 30–40 wt % styrene,[40] (2) a decrease as styrene content increases,[43] or (3) a less pronounced impact of styrene content on the T_g for resins with higher molecular weight vinyl ester monomers[38] as is the case with GVER-1, −2, and −3 resins. The 4 °C shift in T_g for the 20 wt % change in styrene content between GVER-1 to −3 is comparable to these reports.[43]

Composite Mechanical Properties

The evaluation of mechanical performance for carbon fiber-reinforced composites was next tested based on the comparable mechanical performance of the neat matrix materials. The properties of interest tested include the tensile modulus, tensile strength, and failure mode, the flexural modulus and strength, and the short beam shear strength as a matrix-dominated failure mode. Each of these properties was evaluated for the formulations listed in Table I.

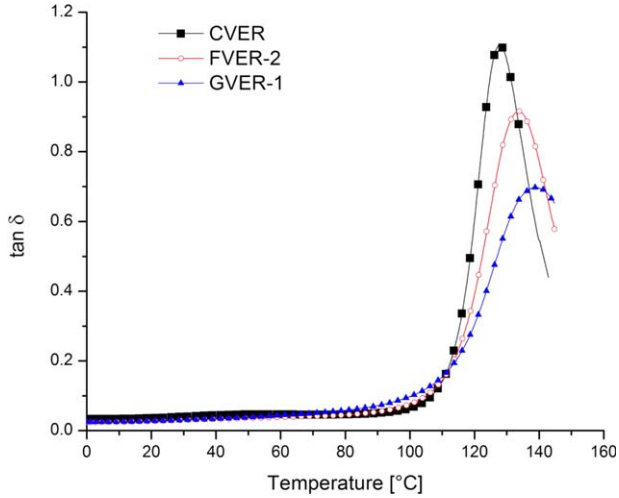

Figure 6. Tan δ as a function for temperature for CVER, FVER-2, and GVER-1. [Color figure can be viewed at wileyonlinelibrary.com]

Tensile testing was performed to evaluate and compare the composites' tensile moduli, strengths, and failure modes. Representative stress–strain curves for each formulation are shown in Figure 7. The numerical data are summarized in Table IV.

The elastic moduli range from ∼53 GPa commercial resin and pure GVER resin with 20 wt % styrene to ∼60 GPa for the FVER and GVER-1,2 composite specimens. The fiber volume fractions for all composites vary from 0.48 to 0.59 with the exception of CVER which has a fiber volume fraction of 0.41. This substantially lower fiber volume fraction could be attributed to the significantly faster kinetics of polymerization as compared to the other resin compositions. The rheological results previously discussed show the gel time for FVER-2 is at least twice as long as that of the CVER. It is also noted that the fiber volume fractions, and the corresponding modulus values, are inversely related to the resin viscosities. This trend is observed both for the formulated resins, as well as the increased styrene

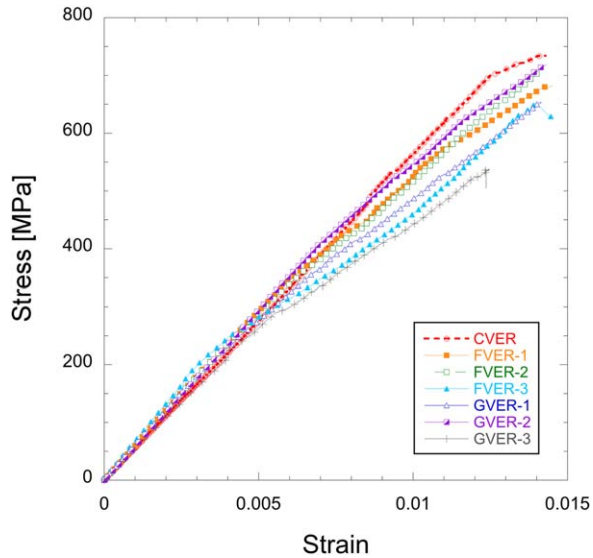

Figure 7. Stress vs. strain plot for representative tensile curves for carbon fiber-reinforced composites infused with CVER and GVER formulations. [Color figure can be viewed at wileyonlinelibrary.com]

Table IV. Tensile Properties of Carbon Fiber-Reinforced Composites of Commercial and GVER Resin Formulations

Sample (sample size)	Fiber volume fraction	Tensile modulus (GPa)	Ultimate tensile strength (MPa)
CVER ($n = 4$)	0.41	53.0 ± 1.2	691 ± 41
FVER-1 ($n = 3$)	0.56	61.4 ± 2.9	669 ± 14
FVER-2 ($n = 3$)	0.59	60.5 ± 1.4	683 ± 22
FVER-3 ($n = 3$)	0.55	59.7 ± 2.8	684 ± 26
GVER-1 ($n = 3$)	0.55	59.0 ± 1.2	681 ± 35
GVER-2 ($n = 3$)	0.50	57.9 ± 1.4	692 ± 19
GVER-3 ($n = 3$)	0.48	52.3 ± 1.8	558 ± 14

fraction. The higher viscosity of the CVER coupled with a faster rate of polymerization means that the resin infuses more slowly and the viscosity quickly increases following full infusion, preventing compaction of the fiber reinforcements. By contrast, the lower viscosity resin quickly infuses and is able to bleed out of the textile into the surrounding bleeder material resulting in a higher fiber volume fraction for the GVER compositions. In the case of GVER 3, the modulus and strength are significantly lower despite having a similar fiber volume fraction to GVER-2. One possible factor is that the tensile specimens for the GVER 3 were fabricated during the summer when the ambient humidity was significantly higher, such that moisture-induced voids adversely affected the strength and modulus of the composite.

Flexural modulus and strength of composites made from the VER formulations were tested under three-point bend loading. Representative flexural stress–strain curves for each formulation are shown in Figure 8, and the numerical data are summarized in Table V.

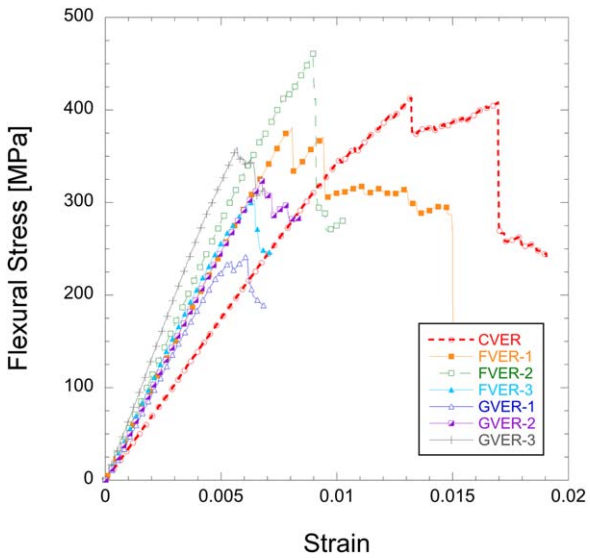

Figure 8. Flexural stress vs. strain plot for representative curves for carbon fiber-reinforced composites infused with CVER and GVER resin formulations. [Color figure can be viewed at wileyonlinelibrary.com]

Table V. Flexural Properties of Carbon Fiber-Reinforced Composites of CVER and GVER Resin Formulations

Sample (sample size)	Fiber volume fraction	Flexural modulus (GPa)	Flexural strength (MPa)
CVER ($n = 5$)	0.42	34.1 ± 1.3	422 ± 8
FVER-1 ($n = 3$)	0.54	49.7 ± 0.5	398 ± 15
FVER-2 ($n = 3$)	0.56	49.5 ± 2.5	446 ± 18
FVER-3 ($n = 3$)	0.56	46.4 ± 0.9	263 ± 9
GVER-1 ($n = 3$)	0.56	44.6 ± 2.0	190 ± 9
GVER-2 ($n = 3$)	0.57	49.8 ± 2.0	363 ± 34
GVER-3 ($n = 3$)	0.59	63.3 ± 1.9	373 ± 17

The flexural moduli range from 45 to 50 GPa for the blended FVER resins and pure GVER resins exceed that of the non-blended CVER resin. However, CVER flexural modulus is within the standard deviation of the GVER-1 resin when normalized by the fiber volume fraction. The comparable modulus values for the formulated VER mixtures (20, 50, 80, and 100 wt % GVER) indicate all blends should be equally suitable for VARTM infusion. The average flexural modulus decreases slightly with increasing fraction of the GVER, but this decrease is approximately equal to the standard deviation. The modulus normalized by fiber volume fraction increases by up to 35% as the styrene content is decreased from 40 to 20 wt % in the GVER resins. The origin of this result is unknown and will require future investigation.

By contrast with the fiber-dominated tensile and flexural properties, the short beam shear performance is dominated by matrix properties. The short beam shear strength was tested and the mean shear strength values are summarized in Table VI.

The short beam shear strength is uniform across formulations with the exception of the FVER-3 and GVER-1 specimens. These two formulations exhibited significantly weaker short beam shear strength; these same matrix materials exhibited similar decreases in flexural strength. These results indicate a poor performance with respect to shear loading of the GVER-1 and FVER-3 matrices, though it is unknown whether the origin of this compromised performance is due to processing effects (e.g., voids[48]) or weakness of the GVER material. The excess resin in

Table VI. Short Beam Shear Strength of Carbon Fiber-Reinforced Composites of CVER and GVER Formulations

Sample (sample size)	Short beam shear strength (MPa)
CVER ($n = 5$)	32 ± 3.0
FVER-1 ($n = 3$)	31.6 ± 2.0
FVER-2 ($n = 3$)	35 ± 0.6
FVER-3 ($n = 3$)	23.7 ± 1.5
GVER-1 ($n = 3$)	18.5 ± 0.4
GVER-2 ($n = 3$)	30.8 ± 2.1
GVER-3 ($n = 3$)	31.4 ± 0.9

the infusion pot occasionally showed a small quantity of liquid rejected from the cured resin. This material could represent an immiscible molecular species that requires further purification steps in future processing with high GVER content.

CONCLUSIONS

The synthesis of a "green" vinyl ester resin suitable for bio-sourced materials was successfully scaled to formulate vinyl ester resins suitable for infusion of carbon-fiber reinforced composites. A series of resins were formulated by combining the GVER with 0 to 80% commercial resin (Derakane Momentum 411 350). A similar processing viscosity to the commercial VER (40 wt % styrene) was achieved for the GVER with 20 wt % styrene, thereby reducing the styrene content by up to half. The activated resin rheology shows an extended pot life at room temperature which can be shortened on demand with minimal 20 °C temperature increase. Resin formulations ranging from 20 to 80 wt % GVER, and pure GVER with 30–40 wt % styrene content, exhibited similar tensile strength, flexural strength, and short beam strength to those of the commercial resin. However, GVER formulated with only 20 wt % styrene demonstrated compromised mechanical properties. These results provide a pathway to transition from petroleum-based vinyl ester resins to their bio-based counterparts, while maintaining existing processing conditions and comparable mechanical performance. Future work will investigate further scale-up of the resin synthesis and purification, as well as extensive flammability testing of brominated resins for naval applications.

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Appendix J

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Environmentally benign synthesis of vinyl ester resin from biowaste glycerin†

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We present here for the first time a novel environmentally benign protocol for the synthesis of vinyl ester resin (VER). Our synthetic strategy utilizes a commercial waste material, glycerin, from biodiesel manufacturing and converts it into a widely utilized resin. The VER was synthesized using bisphenol A (BPA) and glycidyl methacrylate (GMA) as precursors. GMA was synthesized *via* a multistep synthetic protocol using glycerin obtained from a biodiesel manufacturing waste stream. The structure of the intermediates was confirmed by ^{1}H NMR, HPLC and FT-IR spectroscopy.

Introduction

Vinyl ester resin (VER), introduced in the late 1960s, is a low-cost material that can be processed to form a matrix of fiber-reinforced composites that are excellent materials for hulls, transportation vehicles, and many other structural composites.[1] Fiber-reinforced composites produced from VER have in particular become the materials of choice for marine applications. VER is therefore finding increasing applications in transportation, construction, marine, and wind energy industries.[2–5] According to recent investigations, BPA has been shown as an endocrine disrupter, has been found to bind to estrogen receptors and have estrogenic effects.[6] Humans are exposed to BPA majorly through their diet as the food might be in contact with containers or food packaging made with un-crosslinked polymers containing BPA as the repeat units. Vinyl ester resin typically contains BPA, because the chemical structure has displayed to yield the best mechanical performance of the composites used mostly in the marine industry for fabrication of hulls. We chose to utilize BPA as a building block for the environmentally benign synthesis of VER resin to display the feasibility of this approach, which will be extended to other non-BPA building blocks.

VER can be processed at ambient temperature using vacuum-assisted resin transfer molding (VARTM) into massive carbon-fiber-reinforced composites.[5] The synthetic protocols used for manufacture of VER has two main disadvantages. First, VER is currently synthesized from petroleum feedstock, which reduces the sustainability. Second, VER is synthesized from epichlorohydrin which is a known environmental hazard that produces acute toxicity in case of inhalation, oral, and dermal exposure.

Hence, for reducing the environmental impact, it is essential to develop VER synthesis routes that are not dependent on petroleum based feedstock. Moreover, investigations of the VER synthesis routes that lead to elimination of the use of hazardous chemicals, such as epichlorohydrin, are necessary. To assure sustainability of the new processing route, starting materials should be derived from readily available renewable resources.

Recently, significant advances have been made for obtaining biodiesel, a renewable biofuel for use in diesel engines and heating applications. Biodiesel can be produced by base catalyzed hydrolysis of rapeseed oil,[7] soybean and wastes of cooked oil,[8] rice straw,[9] vegetable oil mixtures of cottonseed, soybean and castor oils,[10] jatropha oil,[11] and crude palm oil.[12] Biodiesel is environmentally beneficial because it is biodegradable, nontoxic and has low emission.[13] During manufacturing of biodiesel, approximately a 10% volume of glycerin is produced as a by-product or waste.[14] Therefore, the effective utilization of glycerin enlarges the economy of biodiesel production; moreover, the conversion of glycerin to value added chemicals can expand the scope of green chemistry.[15] Although biodiesel uses non-petroleum feedstocks, it is still subject to the price fluctuations of the petroleum liquid fuels market. Subsidization also plays an important role in the overall market price of biodiesel.

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These two market factors often make it very important for biodiesel manufacturers to sell as many of their byproducts as possible.

Only limited systematic investigations are reported on the use of functional vinyl monomer such as glycidyl methacrylate (GMA),[16] which is a versatile bidentate monomer capable of imparting oxirane functionality to VER. It is also worth mentioning that bisphenol A (BPA) is an important chemical used to manufacture polycarbonate plastic, epoxy resin, flame retardants, and other specialty products,[17] and is manufactured by acid catalyzed condensation of acetone and phenol.[18]

In the present work, we focused on the synthesis of the green vinyl ester resins (GVER) from renewable sources using three steps (Fig. 1): (1) synthesis of GMA from waste glycerin; (2) conversion of phenol into BPA using environmentally benign conditions, and (3) synthesis of GVER from BPA and GMA.

Experimental section

Materials

Crude glycerin (Maine Standard Biofuels), potassium carbonate (99% Sigma-Aldrich), dimethyl carbonate (99% Alfa-Aesar), sodium sulfate (99.9% Alfa-Aesar), methyl methacrylate (99.9% Alfa-Aesar), potassium cyanide (Sigma-Aldrich), 2,4-dimethyl-6-*tert*-butyl phenol (Alfa-Aesar), phenol (99% Sigma-Aldrich), acetone (99.9% Sigma-Aldrich), Amberlyst® 15 hydrogen form (Sigma-Aldrich), 2-diethylaminoethanethiol hydrochloride (95% Sigma-Aldrich) and *N*,*N*-dimethylbenzylamine were used as received.

Characterization

NMR spectroscopy. ^{1}H NMR spectra of the synthesized materials were recorded at 25 °C on a Bruker 500 MHz spectrometer using DMSO (Cambridge Isotope Lab., Inc.) as the solvent and tetramethylsilane (TMS) as the internal reference (δ H 0.00).

Fig. 2 Small scale biodiesel reaction at Maine Standard Biofuels (MSB). Biodiesel/methyl esters (top), soaps (middle), crude glycerin (bottom).

Chromatographic system. The liquid chromatograph (Water's Alliance system model 2695 HPLC system) is equipped with a photodiode array (PDA) detector (Water's model 2996) monitored at 277 nm and a 4.6 mm × 15 cm column that contains 3 μm packing (Polar – Diol). The column temperature is maintained at 25 °C with a flow rate of 1.0 mL min^{-1} and an injection volume of 1 μL. The system was run isocratic with a 70 : 30 mixture of hexane and ethyl acetate. Samples were prepared in ethyl acetate.

Synthesis of glycidyl methacrylate (GMA) from glycerin. GMA was synthesized by a multistep synthesis. The first intermediate, glycerol carbonate, was synthesized from glycerin and dimethyl carbonate under basic condition. The second

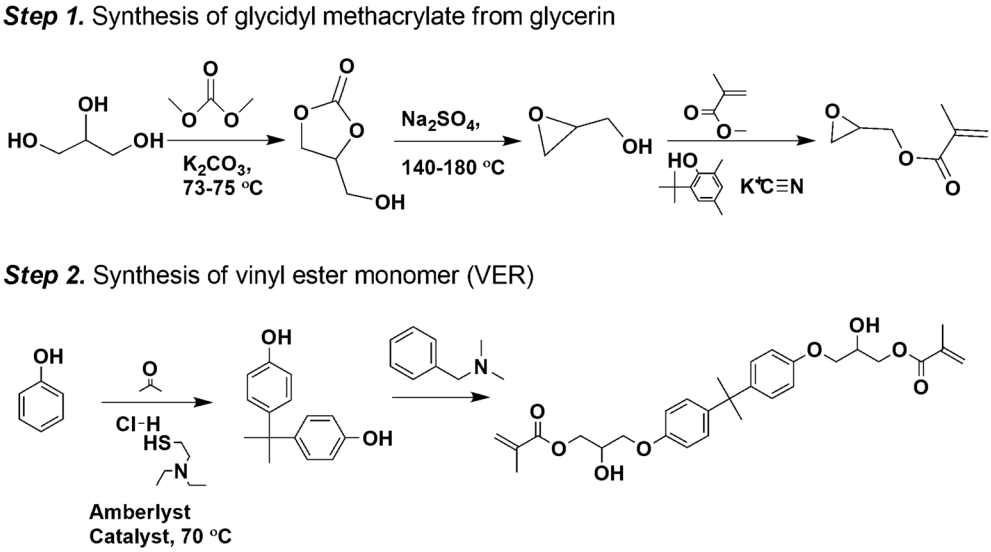

Fig. 1 Synthesis of vinyl ester oligomer from phenol and glycerin.

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intermediate, glycidol, was synthesized by decarboxylation of glycerol carbonate in the presence of sodium sulfate at high temperature. Finally, the GMA was synthesized by reaction of glycidol and methyl methacrylate as described in Fig. 1. Following is the procedure for synthesis of each intermediate.

Glycerol carbonate. In a typical setup, a 250 mL flask equipped with a magnetic stirrer, condenser and thermometer was charged with glycerin (40.05 g, 0.435 mol), dimethyl carbonate (117.45 g, 1.305 mol) and K_2CO_3 (1.8 g, 13.05 mmol). The reaction mixture was refluxed (73–75 °C) for 3 h. After completion of the reaction, methanol and the excess of dimethyl carbonate were distilled off at 40 °C under reduced pressure. The remaining glycerol carbonate was analyzed by ^{1}H NMR and FT-IR spectroscopy. Glycerol carbonate was isolated with 98.5% conversion. Glycerol carbonate: ^{1}H NMR (DMSO, 500 MHz), δ (ppm), 5.20 (1H, –O*H*), 4.80 (1H, –CH_2–C*H*–), 4.49, 4.31 (2H, –O–CH_2), 3.67, 3.53 (2H, –CH_2–CH–). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 155.97 (*C*O–O–), 77.17 (–OH–CH_2–*C*H–), 65.87 (–OH–*C*H_2–CH–), 60.80 (–OH–CH_2–CH–*C*H_2). IR (cm^{-1}): 3428 (–OH stretching), 2920 (–CH stretching aliphatic), 1761 (–C=O stretching), 1480, 1399, 1277 (–CH bending).

Glycidol. A distillation apparatus with a 100 mL flask was placed in an oil bath with magnetic stirring. The flask was charged with 40.0 g of the glycerol carbonate and 4.0 g of anhydrous sodium sulphate. The reaction mixture was continuously stirred using magnetic stirrer under reduced pressure and the flask was heated to 160 °C. Glycidol was allowed to be distilled off for 3 h. The success of the reactions (*i.e.*, purity of both glycerol carbonate and glycidol) were determined by H^1 NMR and FTIR. Glycidol was isolated in pure form with 33.0% yield. Glycidol: ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm), 4.83 (1H, –O*H*), 2.99 (1H, –CH_2–C*H*–), 3.60, 3.33 (2H, –O–CH_2), 2.68, 2.53 (2H, –CH_2–CH–). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 62.13 (–OH–*C*H_2–CH–), 52.44 (–OH–CH_2–*C*H–), 44.30 (–OH–CH_2–CH–*C*H_2). IR (cm^{-1}): 3420 (–OH stretching), 2926 (–CH stretching aliphatic), 1397, 1269 (–CH bending).

Glycidyl methacrylate. A flask was charged with 50.0 g (0.5 moles) of methyl methacrylate; 7.4 g (0.1 mol) of glycidol; 0.05 grams of 2,4-dimethyl-6-*tert* butyl phenol as polymerization inhibitor; and 0.055 g (0.85 millimoles) of potassium cyanide and the mixture heated to 70–80 °C for 2 h. They were immediately vacuum distilled and two fractions were collected. Glycidyl methacrylate was isolated with 25.3% yield. Glycidyl methacrylate: ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm), 6.09, 5.72 (2H, –C=CH_2), 4.48, 3.92 (2H, –CH_2–CH–), 3.25 (1H, –CH_2–C*H*–), 2.82, 2.67 (2H, –O–CH_2), 1.90 (3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 166.35 (=C–*C*O–O–), 135.70 (–CH_2=*C*–CO–O), 125.51 (–*C*H_2=C–CO–O), 64.92 (–O–*C*H_2–epoxy ring), 48.93 (–O–CH_2–*C*H (epoxy ring)), 43.96 (–O–*C*H_2 (epoxy ring)), 17.78 (–CH_2=C–*C*H_3). IR (cm^{-1}): 2995, 2951 (–CH stretching aliphatic), 1726 (–C=O stretching), 1452, 1397, 1326, 1269 (–CH bending).

Synthesis of bisphenol A from phenol

A 50 mL flask was charged with phenol (10.0 g, 106.3 mmol), 100 mg amberlyst-15, 187.75 mg of 2-diethylaminoethanethiol hydrochloride and acetone (2.80 g, 48.31 mmol). The reaction mixture was heated to 65–90 °C for 24 h with constant stirring. After 24 hours, the reaction mixture was cooled to ambient temperature, and the product was analysed by TLC and ^{1}H NMR. The BPA was purified by column chromatography using 3 : 7 ethyl acetate : hexane ratio. The ^{1}H NMR showed that the conversion of BPA from phenol was ~27.0%, but after column purification, we could successfully isolated BPA with 9.0% yield. Bisphenol A: ^{1}H NMR (DMSO, 500 MHz), δ (ppm), 9.12 (2H, –O*H*), 6.98, 6.62 (8H, –Ar*H*), 1.54 (6H, –C–CH_3). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 155.39 (OH–*C*(ArC)), 141.57 (–CH_3–C–*C*(ArC)), 127.7 (–CH_3–C–C(ArC)–*C*(ArC)), 155.08 (OH–C(ArC)–*C*(ArC)), 41.38 (–CH_3–*C*–C(ArC)), 31.40 (–*C*H_3–C–C(ArC)). IR (cm^{-1}): 3320 (–OH stretching), 2963 (–CH stretching Ar), 1508, 1434, 1383 (–CH bending).

Synthesis of vinyl ester resins (VER)

A 25 mL RB flask was charged with BPA (1.14 g, 5 mmol), GMA (1.42 g, 10 mmol) and *N*,*N*-dimethylbenzylamine (0.0065 g, 0.05 mmol). The flask had continuous flow of argon, and the temperature was raised to 70 °C, which was maintained for 6 h. After the reaction, the highly viscous liquid was transferred to a glass vial, and the product was analysed by TLC, ^{1}H NMR, and FT-IR. By HPLC, the conversion of difunctional VER was observed to be 69.3%. Difunctional bisphenol A: ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm), 6.09, 5.72 (2H, –C=CH_2), 4.48, 3.92 (2H, –CH_2–CH–), 3.25 (1H, –CH_2–C*H*–), 2.82, 2.67 (2H, –O–CH_2), 1.90 (3H, –C–CH_3). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 167.09 (=C–*C*O–O–), 156.58 (–CH_2–O–*C*(ArC)), 143.25 (–CH_3–C–*C*(ArC)), 136.13 (–CH_2=*C*–CO–O), 127.78 (–*C*H_2=C–CO–O), 126.45 (–CH_2–O–C(ArC)–*C*(ArC)), 114.10 (–CH_3–C–C(ArC)–*C*(ArC)), 69.27 (CO–O–*C*H_2–CH– CH_2), 67.35 (CO–O–CH_2–*C*H–CH_2), 66.01 (CO–O–CH_2–CH–*C*H_2), 39.48 (–CH_3–*C*–C(ArC)), 30.78 (–*C*H_3–C–C(ArC)), 18.35 (–CH_2=C–*C*H_3). IR (cm^{-1}): 3424 (–OH stretching), 2963, 2926 (–CH stretching aliphatic), 1724 (–C=O stretching), 1634, 1607, 1597, 1403, 1362 (–CH bending).

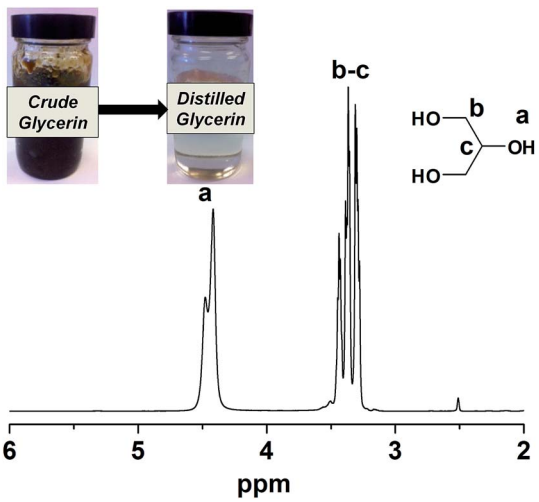

Fig. 3 ^{1}H NMR of the distilled glycerin.

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Results and discussion

Here we demonstrate the sustainable, environmentally benign synthesis of 'green' vinyl ester resin (GVER). The GVER was synthesized predominantly from a bio-waste, namely glycerin, recovered from biodiesel waste stream. Such source materials are renewable, low-cost, and are becoming increasingly abundant and thus are expected to significantly reduce the dependence on petroleum feedstock.

Synthesis of glycidyl methacrylate from glycerin

GMA was synthesized using glycerin as the main precursor. Glycerin is a side-product of the transesterification of triglyceraldehyde in manufacturing of biodiesel or the hydrolysis of triglyceraldehyde during saponification. Fig. 2 demonstrates the mixture of products generated during the synthesis of biodiesel at Maine Standard Biofuels (MSB), which has biodiesel in the top layer, soaps in the middle, and waste glycerin in the bottom. We obtained the glycerin from waste stream of a biodiesel production facility of MSB. The crude glycerin was purified using vacuum distillation at 190 °C, and isolated in pure form as shown in Fig. 3.

Glycerol carbonate (GC), a first intermediate in the synthetic route to GMA from the distilled glycerin, is an attractive intermediate having a large number of applications in various fields. Various approaches had been adopted by different groups for the synthesis of the GC; such as, using (a) Novozyme 435 catalyst and dimethyl carbonate as a precursor,[17] and (b) metal oxide as a catalyst and urea as a precursor.[18] In a new approach, GC was synthesized by reaction between glycerin and dimethyl carbonate at 73 °C for 3 h in the presence of potassium carbonate.[19] The method is promising, with several challenges for example the separation of potassium carbonate from the reaction mixture. Firstly, the reaction was performed at 73 °C and the GC was synthesized successfully. The product formation was confirmed by ^{1}H NMR as shown in Fig. 4. The peak integration value suggested ~98.5% conversion of glycerin to GC at 73 °C. In order to complete the reaction to 100.0%, the reaction temperature was increased to 100 °C; however, as the temperature increased to 100 °C, formation of some side product was observed and unreacted glycerin was also found in the final mixture. The FT-IR spectra of glycerol carbonate synthesized at 73 °C clearly showed peaks of –C=O at 1772.51 cm^{-1} and –OH at 3456.9 cm^{-1} as shown in Fig. S2 in ESI.†

Glycidol is the second intermediate during the synthesis of GMA from glycerin. Glycidol was obtained by decarboxylation of GC as shown in Fig. 1. In a typical setup for the synthesis of glycidol, a vacuum distillation apparatus was utilized. Glycidol was synthesized by heating the glycerol carbonate in the presence of sodium sulfate at 180 °C for 3 h.[20] The formation of glycidol was confirmed by ^{1}H NMR by matching the integration value of each proton as shown in Fig. 4. Strong evidence is provided by the FT-IR exhibiting a clear disappearance of the –C=O peak at 1761 cm^{-1} as shown in Fig. S2 in ESI.† Glycidol was isolated with 33.0% yield.

Glycidyl methacrylate (GMA) is one of the precursors for the synthesis of vinyl ester resin monomer along with bisphenol A.

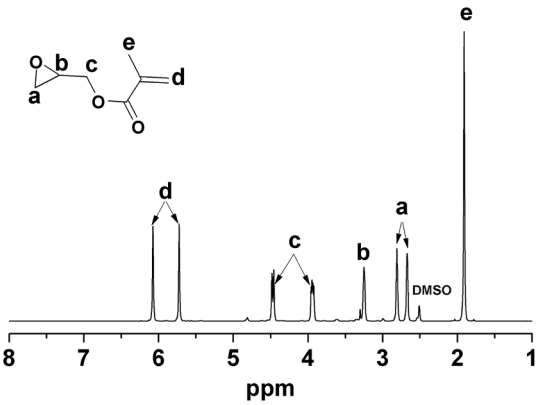

Fig. 5 ^{1}H NMR of glycidyl methacrylate.

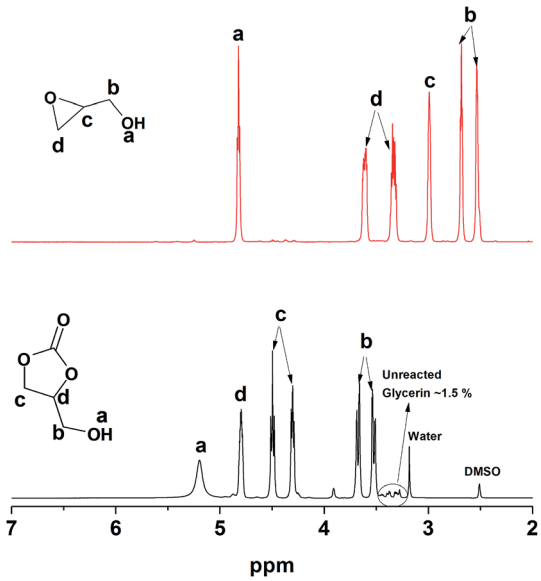

Fig. 4 ^{1}H NMR of glycerol carbonate and glycidol.

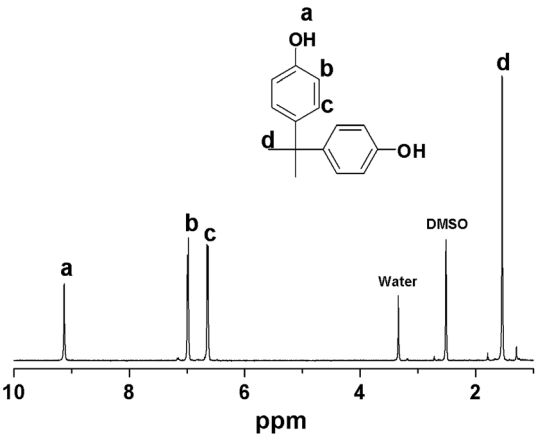

Fig. 6 ^{1}H NMR of bisphenol A.

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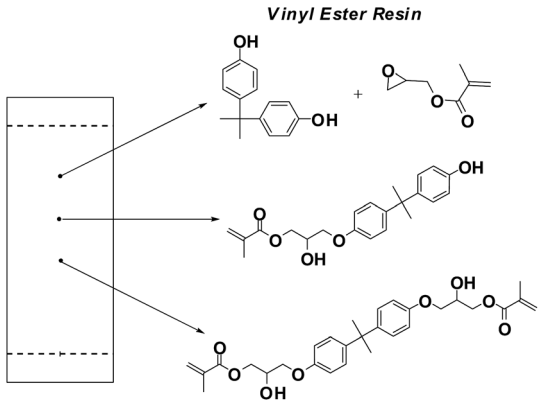

Fig. 7 TLC of vinyl ester resin mixture in ethyl acetate and hexane in 3 : 7 ratios.

GMA was synthesized by transesterfication between methyl methacrylate and the oxirane moiety in the presence of potassium cyanide as a catalyst and 2,4-dimethyl-6-tertbutylphenol.[21] First, the pressure was reduced in the reaction flask, and the temperature was raised to 70 °C. The temperature of 70 °C was maintained for 2 h, and after that unreacted methyl methacrylate and methanol were distilled off. In a second fraction unreacted glycidol was collected and in last fraction GMA was obtained. The structure of GMA was confirmed by ^{1}H NMR as shown in Fig. 5. The GMA was isolated with 25.3% yield.

Synthesis of bisphenol A (BPA)

BPA was synthesized using a solvent-free environmentally benign synthetic protocol, in which phenol was first melted in an oil bath at 60 °C then combined with acetone in the presence of Amberlyst 15 as the catalyst and 2-diethylaminoethanethiol hydrochloride as a promoter.[16] The reaction was performed in a reactor sealed with a plastic stopper. The mixture yielded a crude product subsequently identified as a mixture of BPA and unreacted phenol using thin layer chromatography and ^{1}H NMR. The synthesized BPA was purified by column chromatography using hexane : ethyl acetate in a 7 : 3 ratio as a solvent

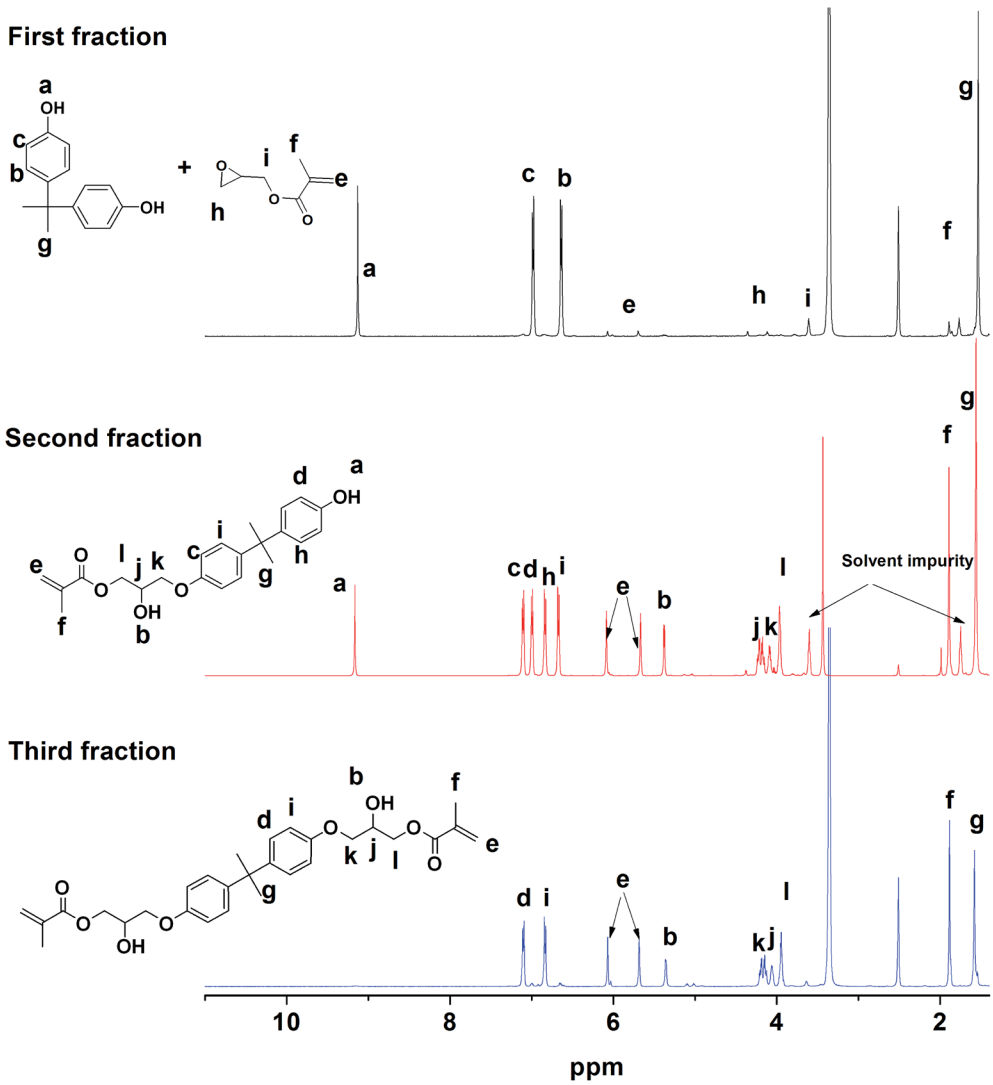

Fig. 8 ^{1}H NMR of each fraction from column separation.

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mixture. The BPA was isolated with 9.0% yield and product was confirmed by ^{1}H NMR as shown in Fig. 6.

Synthesis of vinyl ester resin (VER) monomer

VER are formulated from VER monomer using a solvent/reactive diluent, typically styrene, as well as additives to meet specific needs. In general, VER has several advantages over other polymers. For example, toughened and brominated VER produces resins with higher strengths than polyesters and lower viscosity than epoxies. This low viscosity is critical for fabricating large and intricate structures by vacuum infusion. Fiberglass-reinforced VER composites are preferred for many structural composite applications. Recent advances in compatible sizing have enabled stiffer reinforcement of VERs using carbon fiber.

The VER monomer was synthesized by a reaction between BPA and GMA in the presence of amine catalyst. The reaction was performed at 70 °C under argon.[22] The ^{1}H NMR did not exhibit the –OH peak of the BPA, so it was presumed that the reaction was 100% complete but, the integration value did not matching precisely. Thin layer chromatography (TLC) displayed three spots. The integration values in the ^{1}H NMR and the higher number of spots in TLC confirmed the presence of product in the reaction mixture as shown in Fig. 7.

After confirming the presence of three different products in the reaction mixture; all fraction were separated by column chromatography using a 3 : 7 ethyl acetate : hexane ratio and analysed using ^{1}H NMR as shown in Fig. 8. The ^{1}H NMR clearly indicated the presence of non-functional BPA (NF) in the first fraction; mono-functional BPA (MF), GMA-BPA, in the second fraction; and di-functional BPA (DF), GMA-BPA-GMA, in the third fraction. The data clearly suggested that a 2 h reaction time was insufficient to obtain the maximum amount of DF. In order to increase the yield the reaction time was increased up to 6 h and sample was taken out at periodic interval of time, and the molar ratio of the GMA : BPA was increased to 4 : 1. A very strong evidence of the formation of the vinyl ester resin can be observed in the shifting of the aromatic peaks in ^{1}H NMR of the vinyl ester resin as shown in Fig. S9 in the ESI.† The peaks for the BPA aromatic protons can be observed at 7.10 (OH–C–C*H*(ArH)) and 6.83 (C*H*–C–C–CH_3), which shift to 6.98 (–O–C–C*H*) and 6.63 (C*H*–C–C–CH_3), respectively. The peak for all four aromatic protons can be observed at 7.10 (OH–C–C*H*(ArH)), 6.98 (–O–C–C*H*), 6.83 (C*H*–C–C–CH_3), and 6.63 (C*H*–C–C–CH_3) as shown in Fig. S9 in the ESI.†

Table 1 Percentage of various components in VER-reaction mixture at different time intervals

	Different functional BPA		
Reaction time (h)	Non	Mono	Di
2 h	32.00	49.24	18.76
3 h	20.79	46.28	32.93
4 h	14.13	40.63	45.23
5 h	13.38	28.27	58.34
6 h	12.70	18.05	69.26

In order to determine the kinetics of the reaction, the quantification of NF, MF and DF in the reaction mixture is very essential. Such quantification can be obtained by high performance liquid chromatographic (HPLC) separation of the mixture. Therefore, preliminary work was conducted to develop a HPLC method for the separation and determination of BPA and reaction products in the synthesis of a VER. The ultimate goal was to separate each fraction without overlapping retention time.

Chromatograms shown in Fig. S4–S6 in ESI† clearly demonstrate that the 3 compounds have very different retention times on the diol column with 7 : 3 hexane : ethyl acetate and should be easily separated and determined in a reaction mixture. The first fraction (NF), second fraction (MF) and third fraction (DF) exhibited retention time of 5.218, 7.946, and 13.686 min respectively.

We quantified the NF, MF, and DF BPA by calculating and comparing the area under the peak of the chromatogram obtained at different time intervals as shown in Table 1. The results suggested that reaction proceeds well as time progresses. However, it did not attain completion at 6 h, 69.26% of the DF VER monomer was obtained. Experiments are in progress and the results will be published in near future with additional work to further improve the yield of this synthesis.

Conclusions

Glycidyl methacrylate, a valuable monomer in its own right, was successfully synthesized using glycerin from biodiesel waste stream and environmentally benign reaction conditions. During the novel synthetic protocol other valuable intermediates, such as glycerol carbonate and glycidol, were also obtained. The second precursor, bisphenol A was synthesised by the reaction of phenol and acetone using an environmentally benign synthetic protocol. The GVER was synthesized by reaction of BPA and GMA. This synthetic strategy opens avenues for obtaining this valuable resin using sustainable environmentally benign routes.

Acknowledgements

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Appendix K

Novel Pyrolysis Assembly with Optimized Conditions for Improved Phenolic Yields from Lignin

Priyank N. Shah,[a] Namjoon Kim,[b] Akshay Kokil,[a] Mahesh Jayamanna,[a] David K. Ryan,[a] Robert F. Kovar,[c] and Yongwoo Lee [a,]*

Lignin, a biomass that is abundant worldwide, is typically found in the waste streams from agro-based industries. The conversion of lignin to useful constituent chemicals is an attractive strategy for improving environmental sustainability. This study reports a novel pyrolysis setup that uses helium as the flow medium and can be readily scaled up. Temperature is one of the most important parameters that governs the pyrolysate yield. In this report, we also present systematic investigations on the effect of temperature on the resulting yield and composition of the pyrolysate. In a commercial setting, obtaining lignin from one pure source can be a challenge, and the lignin that is commercially available is a mixture of different sources. Hence, this study investigates the use of lignin samples obtained from commercial sources.

Keywords: Lignin; Pyrolysis; Phenolics; Phenol

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INTRODUCTION

Lignin as a biomass is abundantly available worldwide and in many cases considered to be a part of the waste streams (Phillips 1934). It is a major side-product in the pulp and paper and agro-based industries (Levine *et al.* 1935). Lignin cannot be digested by cattle and therefore is not suitable for use in animal husbandry as a feed source. Also, as a material, it possesses limited applications. As a result, the disposal of lignin is a challenge for paper and agro-based industries (Lora and Glasser 2002). Hence, the conversion of lignin biomass into commercially relevant starting chemicals is a highly important and attractive area.

Lignin is a highly branched, substituted, mononuclear aromatic polymer that is often bound to cellulose and hemicellulose fibers (Pandey 1999). It is typically obtained through the hydrolysis of wood, which removes the “waste lignin” from the cellulose and hemicellulose fibers (Brodeur *et al.* 2011). Because it has very complex structure, one of the protocols used for the decomposition of lignin into useful chemicals is pyrolysis (Panday *et al.* 2011). The use of lignin in pyrolysis is rapidly expanding for the production of useful starting chemicals.

Pyrolysis of lignin, using supercritical water conditions, is one of the well-known approaches for its decomposition into constituent chemicals (Yoshida and Matsumura 2001). Because of the high pressure conditions required in a supercritical water-based reactor setup, a limited quantity of lignin can be used. This results in a considerable challenge for scaling up this method.

Flash vacuum pyrolysis (FVP) is another technique used for the decomposition of lignin (Mohan *et al.* 2006). However, similar batch size-related limitations are faced using this technique. In FVP, the residence time of samples in the hot zone is estimated at 10 ms and the steady-state concentration of substrate is 10^{-8} to10^{-9} M (Britt *et al.* 2000). Fast bimolecular reactions, such as radical-radical couplings, can occur at low concentrations.

Hence, we developed a novel pyrolysis setup using an inert gas, which can be readily scaled up, for obtaining the constituent chemicals, *i.e.*, the pyrolysate. In the pyrolysate, typically phenols and many other commercially attractive aromatic chemicals with one or two hydroxyl groups are obtained, such as guaiacol, vanillin, butylated hydroxyl toluene, and catechol (Evans and Milne 1987).

In pyrolysis, one of the critical parameters that govern the decomposition of lignin into its constituent chemicals is the temperature. At low temperatures, slow pyrolysis occurs and long residence times are needed. The low temperatures also produce a significant amount of char as compared to volatile constituents. On the other hand, fast or flash pyrolysis, which is performed at higher temperatures, results in a high yield of volatile liquid products. Much higher temperatures, typically above 700 °C, result in the maximum gas yields (Zhou *et al.* 2013). However, a majority of the constituent chemicals also degrade at these temperatures, resulting in a higher concentration of carbon dioxide.

Product selectivity during pyrolysis is poorly understood. Most reports typically use low temperatures (< 450 °C) with long residence times (> 5 min) or slow heating rates. Hence, a systematic investigation of the effect of temperature on pyrolysis of lignin is required. Lignin that is commercially available also is structurally different form each other as they are derived from different resources. Because the obtained lignin does not originate from a single biological source, the investigation of pyrolysis of different types of commercially available lignin is important.

The objective of the present study is to perform a novel, systematic investigation of the effect of temperature on phenol production for lignin pyrolysis. The methods investigate the use of a new pyrolysis setup that was developed to use inert gas as the flow medium. This method is readily amenable to be scaled-up for larger volume production.

EXPERIMENTAL

Materials and Chemicals

Commercially available lignin of different types was procured and used as received. The different types of procured lignins were as follows: 1) FlambeauP: de-sugared lignosulfonate from Flambeau River Paper LLC (Park Falls, WI), de-sugared lignosulfonate with 4% to 12% sugars and 74% to 80% lignin based on a dry matter of 55%; 2) SA: lignin alkali form from Sigma Aldrich (St. Louis, MO, #370959), 5.0% moisture impurities; 3) TCI1: de-alkaline form from TCI America (Portland, OR, #L0082); and 4) TCI2: alkaline form from TCI America (Portland, OR, #L0045). Dichloromethane and other solvents were purchased from Sigma-Aldrich (USA) and used as received.

Pyrolysis Setup

The pyrolysis setup consisted of a Barnstead Thermolyne (Dubuque, IA) 21100 high-temperature tube furnace reactor with a thermocouple, heating mantle (500 mL) with a temperature controller, water-cooled condenser, and three Dewar flasks for cold traps. The cold traps were cooled with liquid nitrogen. Helium was used as the inert flow gas through the setup, as it would not condense in the liquid nitrogen cold traps. As shown in Fig. 1, a quartz vessel was used as the pre-heater and connected to the quartz pyrolysis furnace tube. A water condenser was introduced immediately after the pyrolysis tube, followed by liquid nitrogen cold traps. To ensure safety and complete trapping of the evolved organic compounds, three scrubbers containing highly basic aqueous NaOH solutions were added after the cold traps.

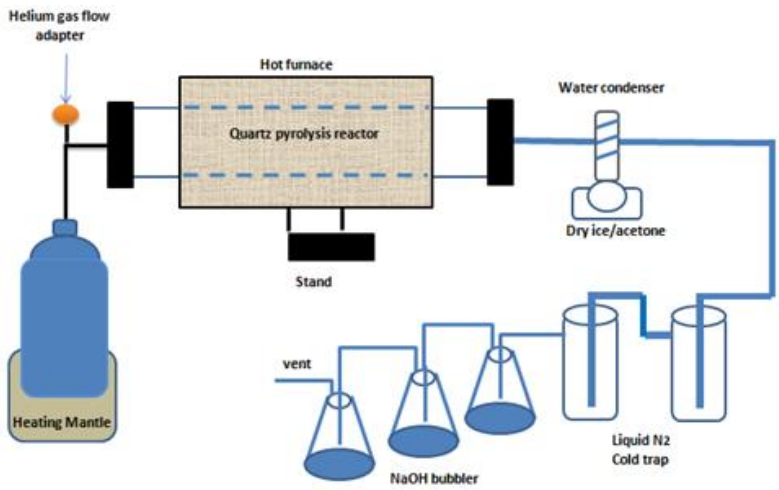


Fig. 1. Schematic of the pyrolysis setup with helium as the inert flow gas

Pyrolysis of Lignin

In a typical pyrolysis run, the tube furnace was first preheated to the desired temperature. Then, lignin was weighed (100 g) and introduced into the preheated quartz flask and the mantle was heated to the desired temperature. The setup was continuously purged with the helium flow gas throughout the pyrolysis run. After the preheater reached the desired temperature, the evolution of the organics could be visually observed with the generation of copious amounts of yellow-white mist. This mist was transferred to the quartz furnace using the helium flow gas. The pyrolysate was then condensed in the water condenser and the liquid nitrogen cold traps. The run was considered complete after a predetermined time of 1 h. After the run, the pyrolysate was carefully collected, weighed, and analyzed using gas chromatography-mass spectrometry (GC-MS).

GC-MS Analysis

The pyrolysate samples were analyzed by a previously reported modified method (Du *et al.* 2013). The general conditions for all of the measurements were:

- GC-MS: Agilent (Santa Clara, CA) 7890 GC with 5973 MS
- Column: Restek Corporation (Bellefonte, PA) Rtx Wax 30 m x 0.25 mm
- SP1Temp Program: 40 °C for 3 min then 4 °C/min ramp to 100 °C and hold for 3 min; then 6 °C/min ramp to 240 °C and hold for 10 min; total run time 54.3 min
- Injection Mode: Splitless

- Injection Volume: 2.0 µL
- Column Flow: 1.0 mL/min UHP He
- MS Library: NIST Mass Spectral Library 2008

A revised, semi-quantitative GC-MS data analysis method was applied to analyze the extraction yield of phenol. Percentage information was calculated based on the peak area calculation using the GC software (Chemstation software from Agilent, Santa Clara, CA). Eleven major phenolic standard samples were analyzed, and the relative output of each standard was compared on a percentage basis. The conditions for pyrolysis were changed in order to maximize phenol production.

RESULTS AND DISCUSSION

The pyrolysis setup was designed such that it could be readily scaled-up to accommodate the pyrolysis of large quantities of lignin. Inert conditions were necessary during pyrolysis to limit the excess oxidation reactions resulting in the formation of carbon dioxide and carbon monoxide gases. Because liquid nitrogen cold traps were used, helium was selected as the inert flow gas because it would not condense in the cold traps. The temperature in the preheating mantle was 400 °C, while a temperature of 500 °C was maintained in the pyrolysis quartz reactor furnace. The reaction time was set at 1 h.

In the investigations reported here, commercially available lignin samples contained a mixture of lignin from different source materials. However, the investigations yielded valuable information that could be directly applied for the pyrolysis of commercially available lignin. Typical pyrolysis of lignin results in the formation of char and evolution of small organic molecules. To systematically investigate the thermal decomposition of the commercially sourced lignin, mass balance investigations were conducted.

Table 1. Mass Balance and Phenolic Yields for Different Lignin Starting Materials

Pyrolysis product	Vacuum Setup (SA)	Helium Setup		
		SA	TCI (alk)	TCI (dealk)
Char (Solid) (wt. %)	55.0	54.9	62.6	54.9
Phenolics (Liquid) (wt. %)	7.1	12.6	11.5	3.2
(Gases) (remainder wt. %)	37.9	32.5	25.9	41.9

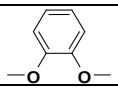
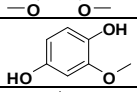
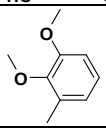
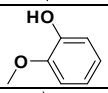
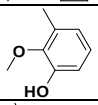
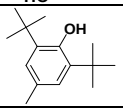
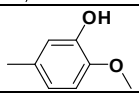
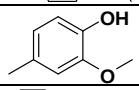
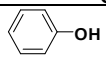
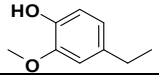
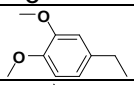
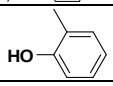
The mass balance for the lignin pyrolysis was performed by carefully weighing each component of the pyrolysis setup before and after the pyrolysis run. This was performed for three different types of lignin, and the results are summarized in Table 1. Pyrolysis of lignin was also performed under conventional flash vacuum conditions as a control. As seen from Table 1, the helium-based methods resulted in much higher amounts of the pyrolysate.

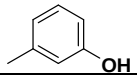
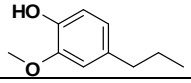
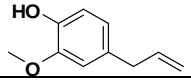
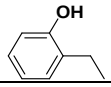
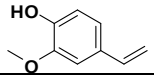
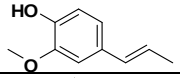
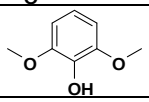
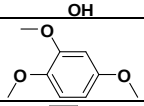
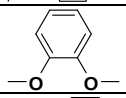
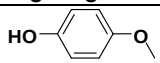
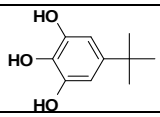
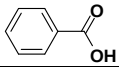
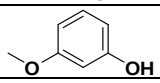
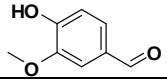
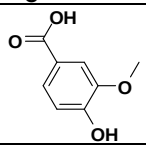
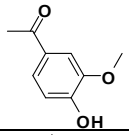
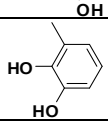
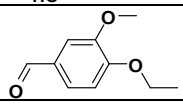
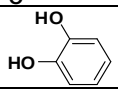
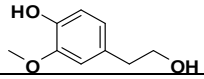
Because the residence time of the degraded lignin fractions during the conventional vacuum-based setup in the quartz furnace is significantly shorter, complete decomposition to constituent chemicals might be hindered in this setup, as seen in Table 1. On the other hand, the collection of the pyrolysate in the cold traps was also reduced upon application of the vacuum. As seen from Table 1, the alkaline commercial lignin samples resulted in a much higher pyrolysate fraction, as compared to the neutralized

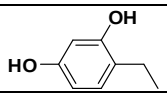
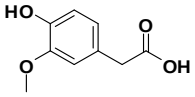
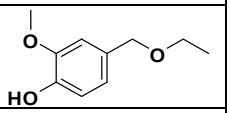
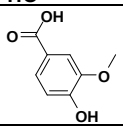
lignin samples. This could be attributed to the base catalyzed degradation of the complex cross-linked lignin structure. The mass balance of lignin was calculated based on the weight measurement of the char and the trap samples after pyrolysis. The unrecovered weight loss of lignin was attributed to the gaseous aerosol and moisture. The total recovery yield, based on char and trap samples, was 82.3% (helium flow) and 59.6% (vacuum pyrolysis).

Using GC-MS, the presence of more than 35 different phenol-based constituent compounds in the pyrolysate was identified, as shown in Table 2. In general, the percentage output yield (%) was calculated from the total peak area. In the case of diluted samples which have a higher background, we applied a semi-quantitative analysis. Among the monomeric phenolic compounds identified between the retention time range of 26 and 46 min, 11 compounds were selected, whose presence was found significantly in pyrolysates obtained under various conditions. Such compounds included phenol, catechol, and guaiacol. A complete list of phenol-based compounds is given in Table 2.

Table 2. List of Phenolic Compounds Identified in the Pyrolyzed Mixture by GC-MS, Retention Time, and Chemical Structure

No	Retention time	Name	Label	Structure
1.	25.380	1,2-dimethoxy benzene (Veratrole)		
2.	27.253	1,4-Benzenediol, 2-methoxy (2-Methoxyhydroquinone)		
3.	27.416	2,3-Dimethoxytoluene		
4.	28.471	Guaiacol	S1	
5.	28.654	2-methoxy-3-methylphenol		
6.	29.846	Butylated hydroxytoluene	S2	
7.	30.032	2-methoxy-5-methylphenol		
8.	30.289	2-methoxy-4methylphenol	S3	
9.	30.834	Phenol	S4	
10.	31.376	4-ethyl-2-methoxyphenol (4-ethyl guaiacol)	S5	
11.	32.104	1,2-dimethoxy, 4-ethyl benzene		
12.	32.563	2 methyl phenol		

13.	32.693	3 methyl phenol		
14.	33.023	4-propyl guaiacol		
15.	33.965	4-allyl guaiacol		
16.	34.110	2-ethyl phenol		
17.	34.388	2-methoxy-4-vinylphenol (4-vinyl guaiacol)	S6	
18.	35.325	4-propenyl-guaiacol		
19.	35.477	2,6-dimethoxyphenol	S7	
20.	36.757	1,2,4-trimethoxy benzene		
21.	37.312	1,2,-dimethoxybenzene		
22.	37.421	Mequinol		
23.	37.602	5-tert-butylpyrogallol		
24.	37.747	Benzoic acid		
25.	38.038	3-methoxy phenol		
26.	39.559	Vanillin	S8	
27.	40.182	4-hydoxy,3-methoxy benzoic acid		
28.	40.569	4-hydroxy-3-methoxyacetaphenone (apocynin)	S9	
29.	40.956	1,2-dihydroxy, 3-methyl benzene		
30.	41.433	4-ethoxy-3-anisaldehyde		
31.	41.523	Catechol	S10	
32.	43.228	Homovanilyl alcohol		

33.	43.469	1,3-dihydroxy,4-ethylbenzene		
34.	44.853	Homovanillic acid	S11	
35.	45.016	Phenol, 4-(ethoxymethyl)-2-methoxy		
36.	52.182	p-vanilic acid		

The yield of standard compounds (Table 2) was compared between the different lignins used in the helium flow pyrolysis. The composition of the pyrolysate from different pyrolysis runs is given in Table 3.

Table 3. Phenolic Yields with Various Lignin Starting Materials

Main phenolics identified	Vacuum Setup (SA)	Helium Setup		
		SA	TCI (alk)	TCI (dealk)
Guaiacol	31.43	10.3	9.48	2.84
2-methoxy-4-methylphenol	9.40	1.95	1.34	0.45
Phenol	6.30	9.41	20.2	4.59
4-ethyl-2-methoxyphenol	6.83	1.85	0.91	0.40
2-methoxy-4-vinylphenol	3.70	0.66	1.44	0.00
2,6-dimethoxyphenol	0.53	0.57	0.25	0.15
vanillin	0.87	0.03	0.92	0.89
4-hydroxy-3-methoxyacetaphenone	0.63	0.55	0.61	0.46
Catechol	0.10	11.7	2.27	2.02
Homovanillic acid	1.40	0.50	0.43	0.22

As shown in Table 3, the yield of standard compounds was compared between helium flow pyrolysis and vacuum pyrolysis. There were noticeable differences in catechol and guaiacol concentrations. It can be surmised that guaiacol was converted to catechol efficiently in the helium gas flow pyrolysis because of a higher residence time. Further investigation was required to determine the effect of the lignin source material and temperature conditions. Depending on the wood process, the chemical treatment of the commercial lignin differs, which results in a different chemical composition of the starting lignin. For example, paper production companies, such as Flambeau River Paper LLC (Park Falls, WI), processes wood (mostly maple and birch) to produce pulp for manufacturing paper products. Water-soluble lignosulfonate is easily separated during the acidification process with sulfur and limestone. The alkali form of lignin is obtained when the process uses magnesium and ammonia in this step. Different kinds of sugar units might be attached to lignin. Birch, for example, produces xylose that attaches to lignin. Hence, a lower pyrolysate yield is expected from such sugared lignosulfonates, as they would contain approximately 55% lignin.

Thermal-induced decomposition of polymers, such as lignin, result from the formation of radicals that recombine to eventually form undesired char. Because of its complexity and irregularity, the lignin structure is often represented by model

compounds, such as diphenylether (DPE), phenol, vanillin, anisole, guaiacol, and dimethoxyphenol (Lovell *et al.* 1989; Britt *et al.* 2000; Demirbas 2009). As a representative unit, phenylphenethyl ether (PPE) was used as a model compound mimicking the β-O-4 bond. The mechanism for the decomposition of this bond depends on the processing temperature. There is no clear consensus as to the relative importance of concerted retro-ene, free-radical, and ionic reaction pathways in the pyrolytic decomposition of lignin (Evans and Milne 1986; Antal *et al.* 1989). Extensive studies have shown that there are two dominating concerted mechanisms: 6-centered retro-ene and Maccoll elimination (Maccoll 1969). Both lead to phenol and styrene as the end products (Klein and Virk 1983). The retro-one mechanism first forms styrene and 2,4-cyclohexadiene-1-one isomerize to phenol (Beste and Buchanan 2012). Phenol, as a simplified model compound, forms cyclopentadienyl radicals by decarbonylation after its phenoxy radical formation (Scheer *et al.* 2012).

Generally, lignin decomposition occurs by several competing bond-cleavage reactions at various temperatures, depending on the bond energies. Among all different linkages, the α- and β- alkyl-aryl ether bonds are the most frequently studied because of their prominent role in lignin chemistry (Jakab *et al.* 1997). Ether-linkages in lignin can be cleaved by heat treatment, which leads to the depolymerization of lignin and formation of various phenolics (Brezny *et al.* 1983). Lignin forms volatile products upon thermal decomposition between 200 and 500 °C (Ramiah 1970). It has been demonstrated by thermogravimetric analysis that the primary pyrolysis of lignin occurs between 200 and 400 °C, with the highest degradation rate achieved at approximately 380 °C (Jiang and Argyropoulos 1998; Kawamoto *et al.* 2008; Nakamura *et al.* 2008; Ben and Ragauskas 2011). At this temperature, the primary pyrolysis takes place and the oil starts to form. The thermal scission of the α- and β- alkyl-aryl ether bonds, C−C and the C−O bonds, have bond dissociation energies of approximately 346 and 358 kJ mol^{-1}, respectively, and these bonds begin to cleave at 400 °C. During the process of cleaving, multiple reactions takes place at the same time, which includes the formation of free radicals, elimination of water, formation of carbonyl, carboxyl, and hydroperoxide groups, evolution of CO and CO_2, and eventually the production of charred residue. This suggests that different kinds of lignin possess different functional groups, which will have a significant impact on its depolymerization mechanism; however, it is strongly believed that lignin depolymerization follows a free radical mechanism (Cai and Dass 2003).

In the experiment designed, it was expected that during the preliminary pyrolysis in the heating mantle, the C-C and C-O bonds would break because of their low bond dissociation energy, and the bigger aromatic structures (more than one aromatic ring) would remain and be exposed to higher temperature for a short retention time, enabling further secondary pyrolysis to take place. During the secondary pyrolysis, the $C{-}OCH_3$ bond cleaves at higher bond dissociation energy of 410 kJ mol^{-1}, compared with other ether linkages. It is also well-known that the aromatic components start to decompose at 500 °C. Therefore, prolonged exposure to high temperatures may decrease the yield of phenolics. In addition, a short retention time at a high temperature is highly desirable and can be achieved in in our newly proposed setup. Lignin can be isolated from both softwood and hardwood because they have very high amounts of guaiacyl and syringyl units, respectively. Because our pyrolysis was aimed at the isolation of high amounts of phenol, the dissociation of $C{-}OCH_3$ linkages was desirable and can occur during the secondary pyrolysis at high temperatures resulting in more phenol being achieved. Moreover, it has been already well established that different groups of products will

dominate at different temperatures, such as low-molecular weight oxygenated products at 250 to 400 °C, phenolic compounds at 350 to 500 °C, and aromatic hydrocarbons (benzene, toluene, and styrene) at 500 to 700 °C (Kibet *et al.* 2012)

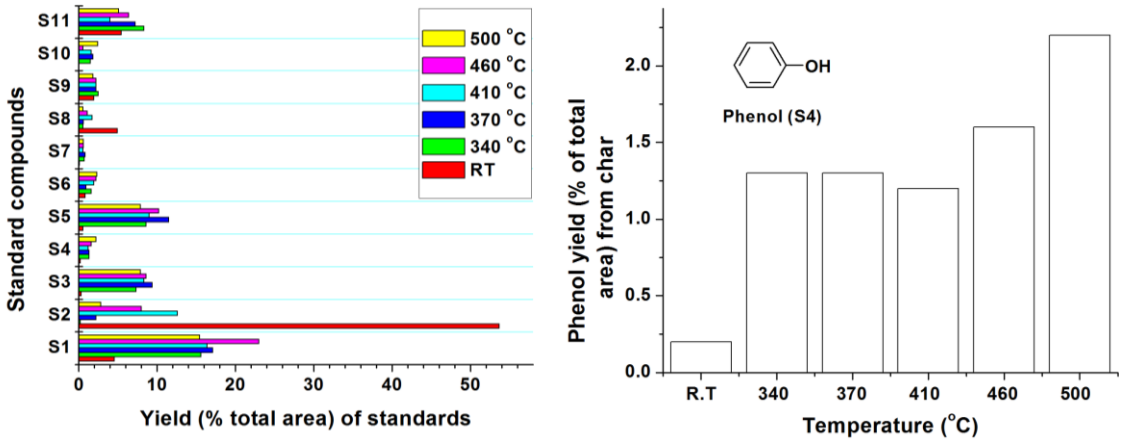


Fig. 2. The recovery yield of standards at different reactor temperatures. S1 = guaiacol; S2 = butylated hydroxytoluene; S3 = 2-methoxy-4-methylphenol; S4 = phenol; S5 = 4-ethyl-2-methoxyphenol (4-ethyl guaiacol); S6 = 2-methoxy-4-vinylphenol (4-vinyl guaiacol); S7 = 2,6-dimethoxyphenol; S8 = vanillin; S9 = 4-hydroxy-3-methoxyacetaphenone (apocynin); S10 = catechol; S11 = homovanillic acid

In this systematic investigation, six different reactor temperature conditions were set. Standard compounds were identified using GC-MS and multiple pyrolysis runs were conducted at various temperatures to produce the semi-quantitative data set shown in Fig. 2. The phenol recovery rate was highest when the pyrolysis reaction was run at 500 °C (Fig. 2). The reaction temperature was not increased beyond this point for safety considerations.

The amount of lignin that can be introduced in the quartz pyrolysis tube is limited, which introduces a big challenge in the ability to scale up the pyrolysis setup. Hence, a pyrolysis preheating chamber was introduced so that a larger quantity of lignin could be used. Also, the initial thermal decomposition of lignin occurred in the preheating chamber, resulting in a mist that was transported to the quartz pyrolysis tube by the inert flow gas.

Temperature in the preheater may significantly affect the pyrolysate obtained. Hence, the effect of temperature on lignin in the preheating unit was also investigated. The amount of lignin was weighed before and after pyrolysis. The thermal decomposition of lignin in the preheater and its effect on the pyrolysate composition was systematically performed by varying the mantle temperatures between 300 and 500 °C. The preheater was attached directly to the quartz pyrolysis reactor, which was placed inside the furnace at 500 °C. The amount of most constituent phenolic compounds decreased as preheating temperature increased (Fig. 3). This may have occurred because of the excess decomposition that was taking place in the preheater, which resulted in even further decomposition in the quartz furnace.

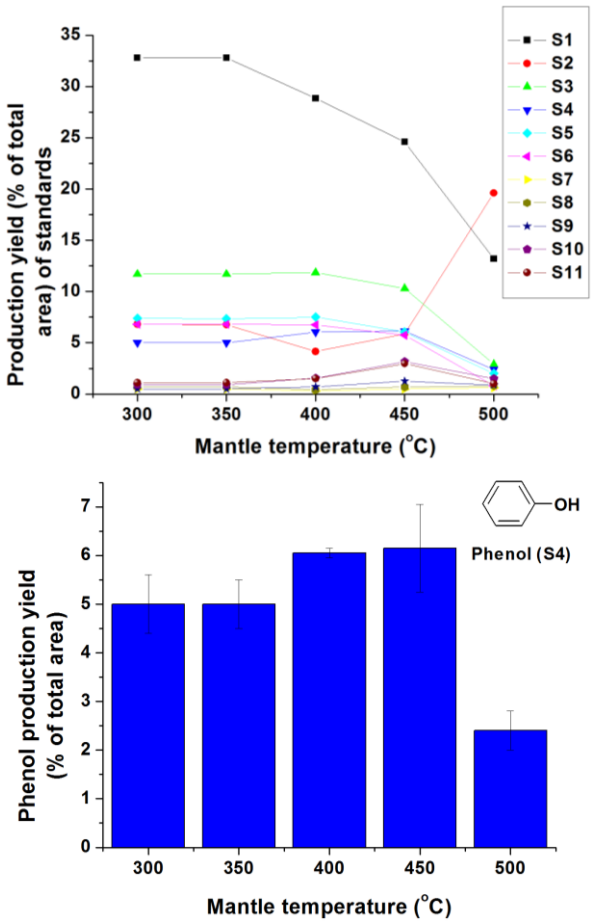


Fig. 3. Lignin preheating effect on phenol production. Pyrolysis was performed at various mantle temperatures while maintaining the reaction temperature at 500 °C . The pyrolyzed samples were collected in the cold trap unit and analyzed using GC-MS.

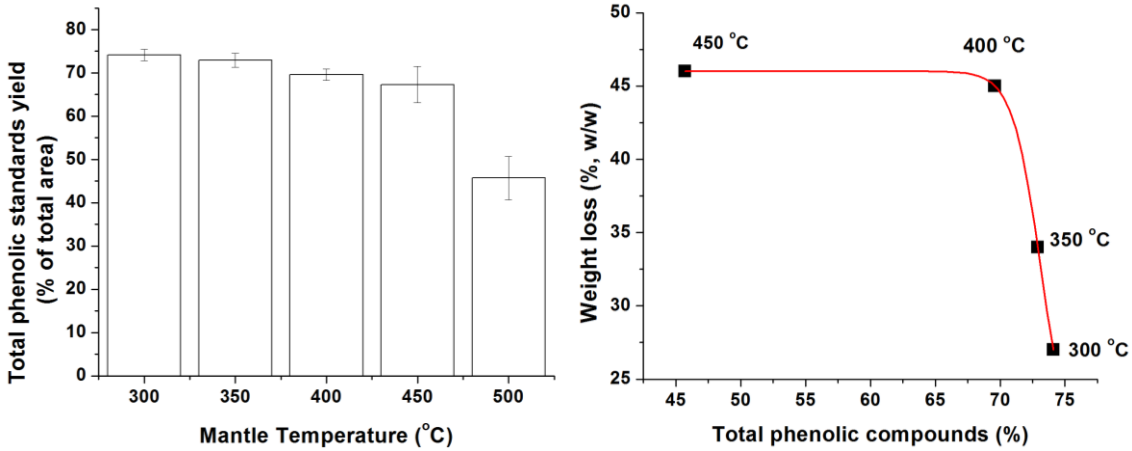


Fig. 4. The yield of total phenolic compounds at various mantle temperatures

However, the production yield of total phenolic compounds decreased as temperature increased, as shown Fig. 4. High temperatures may reduce the reaction time needed for the full thermal depolymerization of lignin. However, the production yield of

the total phenolic standard compounds decreased when the temperature reached over 400 °C. Phenol production may be directly affected under these conditions. Further investigations are required to fully understand this issue.

CONCLUSIONS

1. This study reports a novel pyrolysis setup that uses the inert gas helium as the flow medium. This setup resulted in a much higher pyrolysate yield when compared to the control pyrolysis performed in a vacuum.
2. The temperature used in the pyrolysis tube, as well as the preheating chamber, had a notable effect on the resulting amount of pyrolysate, as well as the composition of the resulting phenolic products.
3. The mechanism for the decomposition of lignin is not clearly understood. Hence, fundamental investigations that elucidate this degradation reaction would further aid in achieving selective decomposition and in maximizing the yield of pyrolysate from lignin.

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Appendix L

Synthesis and Mechanical Properties of Flame Retardant Vinyl Ester Resin from Renewable Biowaste

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ABSTRACT:

Halogen containing polymers are mainly used in fiber-reinforced polymer composites (FRPs) to improve the fire resistance properties. One such material that can be created through the incorporation of a halogen into a polymer is brominated vinyl ester resin (Br-VER). Br-VERs are economically viable, high performance materials that are widely utilized in composites for specialty applications such as the fabrication of hulls in naval vessels. It is critical that the structural components of these naval vessels are able to withstand accelerated thermal decomposition when exposed to fire for an extended period of time and the presence of bromine enables this by imparting excellent fire resistance properties to the hulls of these vessels. In this work, Br-VE monomer was synthesized using tetrabromobisphenol A (TBBPA) and glycidyl methacrylate (GMA) as precursors. It has already been demonstrated that GMA and BPA can be synthesized from the waste material from the biodiesel and wood pulp industries respectively. The Br-VE reaction products were analysed by high performance liquid chromatography (HPLC), which confirmed the presence of unreacted (nonfunctional), monofunctional and difunctional TBBPA. Br-VE monomer was purified using column chromatography and analysed by ^{1}H NMR and ^{13}C NMR. Purified difunctional Br-VE monomer was mixed with 40 wt. % of styrene to prepare a baseline formulation. This formulated resin was mixed with 20, 50 and 80 wt. % of commercial brominated vinyl ester resin (Derakane 510-40A) to prepare three formulations. Two reduced styrene content formulations of Br-VER containing 30 and 20 wt. % of styrene were also prepared. The thermomechanical properties of all six neat resin formulations and the Derakane 510-40A control were investigated using differential scanning calorimetry (DSC), rheology and dynamic mechanical analysis (DMA). The autocatalytic cure kinetics parameters and chemorheological behavior enable development of a cure cycle for the thermosetting resin. The DMA results demonstrate that all resin formulations comprising Br-VER exhibit improved mechanical performance as compared to the commercial vinyl ester resin

INTRODUCTION

Polymer matrix composites (PMCs) have seen widespread adoption in the aviation, construction, ship-building, automobile and packaging industries. Driving the substitution of these polymeric composite materials for metal components is their excellent mechanical behavior (eg. high specific strength and stiffness), chemical compatibility and corrosion resistance [1, 2]. Despite this, PMCs possess modest fire resistance performance which restricts their use in applications with flame, smoke and toxicity (FST) requirements. Extensive research over the last fifty years has led to the development of a number of novel chemistries that have been applied to polymeric materials to help improve their ability to withstand thermal degradation when exposed to fire. There are three general mechanisms that all types of flame retardant (FR) chemistries fall into; i) gas phase FRs, ii) endothermal FRs and iii) char-forming FRs [3]. The first category includes halogen and phosporous based FRs which act by reducing the heat released in the gas phase from combustion by reacting with available free radicals[4-6]. The most common halogenated FRs use chlorine or bromine rather than fluorine or iodine because the (bromine/chlorine)-carbon bond is considered to be relatively weaker and is therefore most susceptible to thermal decomposition [7]. Some of the most commonly utilized compounds based on brominated FRs include: tetrabromobisphenol-A, hexabromocyclododecane and polybrominated diphenyl ethers [8, 9]. [3].

Methods to improve flammability properties of polymers and their composites are being studied extensively with the goal of developing materials that are cost effective, environmentally friendly and have the potential to be utilized in a wide variety of industrial applications. While all FR technologies have their cons, there are a few that stand out as being the most viable options because their benefits simply outweigh those of their competitors. Halogen FRs, despite being under scrutiny for their potential environmental toxicity, are still the most widely utilized compounds for fire suppression in various applications because; 1) they are the most cost effective technology, 2) a small halogenated molecule can deliver a high amount of halogen to combat a fire and 3) they can be easily combined with other chemistries to create an even more effective FR. These are the primary reasons why this research focuses on investigating the properties of a novel brominated vinyl ester resin.

Brominated vinyl ester resins (Br-VER) are formulated from Br-VE monomer, a reactive diluent (typically styrene), and specialty additives to meet specific product needs. Br-VER can be utilized as the matrix phase of fiber-reinforced composites for applications in military and commercial systems [10]. VER has several advantages over other polymers it produces materials with greater strengths than polyesters and lower viscosities than epoxies. This low initial viscosity, η_0, is critical for fabricating large ship structures by vacuum infusion. Fiberglass-reinforced VER composites are preferred for many topside applications where low detectability and radar transmission are important. Recent advances in compatible sizings have enabled stiffer reinforcement of VERs with carbon fiber to produce yet stiffer and stronger structures.

Vinyl ester resins that are currently utilized in industry have two key disadvantages. First, VER is synthesized from petroleum feedstock and is directly susceptible to price volatility due to fluctuations in oil supplies on a global scale. Second, VER is synthesized from epichlorohydrin; widely regarded as an environmental hazard that produces acute toxicity from inhalation, oral, and dermal exposure [11, 12].The continued viability and application of vinyl ester resins are highly dependent on the synthesis of VER material through channels that are not directly reliant on petroleum feedstock as a source. In addition, it is critical to develop a two pronged approach to tackle the challenges posed by the current synthesis routes for VER material. Firstly, the use of epichlorohydrin must be eliminated from the manufacturing process and secondly resin formulations that minimize or completely phase out the use of hazardous components such as styrene must be conceived. This can be achieved by ensuring that new processing routes focus on obtaining raw materials that can be readily derived from renewable resources. Finally, the newly formulated VER must be able to retain its economic value by entering the market at a similar price point to the current resin system without having its chemical, thermal and mechanical performance compromised.

Recently, we have demonstrated the synthesis of bisphenol-A based vinyl ester resin material using bisphenol A (BPA) and glycidyl methacrylate (GMA) as precursors [13]. The BPA is obtained from the purification of phenol enriched phenolics that are created by pyrolysis of lignin which is a byproduct in the paper and pulp industry. The GMA is developed using glycerin isolated from the waste stream of a biodiesel manufacturing unit. GMA is a liquid with a high boiling point (189 °C) and therefore has a much lower vapor pressure and is less of an environmental hazard than gaseous epichlorohydrin.

In the present work, we report the synthesis, formulation and characterization of a brominated vinyl ester prepolymer synthesized from bio-derived TBBPA and GMA, which offers a route for resin synthesis based on lignin and biodiesel glycerin derived materials respectively. The prepolymer was purified using column chromatography, dried and mixed with 40 wt.% of styrene to create a brominated “green” vinyl ester resin (Br-GVER). Six different formulations were prepared by mixing Br-GVER in different ratios with commercial brominated vinyl ester resin (Br-CVER) Derakane 510-40A. The chemorheological behavior and cure kinetics of the resins were then characterized through cure rheology and differential scanning calorimetry (DSC) respectively. In addition, dynamic mechanical analysis (DMA) was conducted to determine the thermomechanical properties of cured samples manufactured from all seven resin compositions.

2. EXPERIMENTAL SECTION

2.1 Materials

Deuterated Dimethyl sulfoxide (D6-DMSO) was obtained from Cambridge Isotope Lab. Inc., glycidyl methacrylate (99%), bisphenol A (99.9%), hydroquinone (99.9%), cumene hydroperoxide (80%), styrene (>99%), cobalt naphthenate, N,N-dimethylbenzylamine (≥99%),

bromine (≥99.5%), potassium bromide (≥99%), hydrazine (≥98%), hydrazine hydrate solution(~80% in H_2O) and 2,4,-dimethyl, 6-tert-butyl phenol (97%) were obtained from Sigma-Aldrich. Sodium sulfate (99.9%) was obtained from Alfa-Aesar. All materials were used as received without further purification.

2.2 Synthesis of tetrabromobisphenol A

Tetrabromobisphenol A was synthesized by bromination of bisphenol A. In a typical procedure, a 1000 mL RB flask was charged with 71.34 g of bisphenol A and 500 mL of acetonitrile. In a 500 mL beaker, an aqueous solution of KBr_3 was prepared at room temperature by dissolving KBr (148.8 g, 1.25 mol) in water (185 mL) followed by the addition of bromine (250.1 g, 1.56 mol). The solution of KBr_3 was added to the bisphenol A solution using a 250 mL pressure-equalizing funnel within 10-12 min. The white crystals of TBBPA were obtained within 5-10 min of reaction time at 30°C. Hydrazine hydrate was added to neutralize the residual bromine. The reaction mixture was precipitated in water, filtered, and then washed three times with deionized water and dried in a vacuum oven at 100°C. TBBPA was isolated with 99.6% yield ^{1}H NMR (DMSO, 500 MHz), δ (ppm), 9.81 (2H, -O*H*), 7.35 (4H, -Ar*H*), 1.57 (6H, -C-CH_3). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 149.28 (OH-*C*(ArC)), 144.34 (CH_3-C-*C*(ArC)), 130.66 (CH_3-C-*C*(ArC)), 112.16 (OH-*C*(ArC)-Br)), 41.76 (-CH_3-*C*-C(ArC)), 30.44 (-*C*H_3-C-C(ArC)). IR (cm^{-1}): 3417 (-OH stretching), 2967 (-CH stretching Ar), 1536, 1469, 1448 (-CH bending), 566 (C-Br stretching).

2.3 Synthesis of brominated vinyl ester polymer

A 25 mL round-bottom flask was charged with TBBPA (27.2 g, 50 mmol), glycidyl methacrylate (14.2 g, 100 mmol) and N,N-dimethyl benzamine (0.065 g, 0.5 mmol) under a continuous flow of argon, and the flask temperature was raised to 70°C and the reaction proceeded isothermally. The resulting highly viscous liquid was purified using a column packed with silica gel. The mobile phase comprised THF and Hexane in a 3:7 ratio. The pure fraction was analyzed by TLC, HPLC, NMR, and FT-IR. Difunctional TBBPA: ^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm), 7.51 (4H, ArH), 6.09, 5.68 (2H, -C=CH_2), 5.39 (2H, -CH_2-CH-O*H*), 4.30 (2H, -CH_2-C*H*-OH), 4.19 (4H, -CH_2-CH-OH), 3.96 (4H, -CH_2-CH-OH), 1.89 (6H, -CH_2=CH-CH_3), 1.62 (6H, Ar-C-CH_3). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 167.12 (=C-*C*O-O-), 151.12, 142.13, 132.66, 118.99 (Ar*C*), 136.19 (-CH_2=*C*-CO-O), 125.15 (-*C*H_2=C-CO-O), 67.92 (CO-O-*C*H_2-CH- CH_2), 68.54 (CO-O-CH_2-*C*H- CH_2), 68.72 (CO-O-CH_2-CH-*C*H_2), 39.62 (-CH_3-*C*-C(ArC)), 30.92 (-*C*H_3-C-C(ArC)), 18.21 (-CH_2=C-*C*H_3). IR (cm^{-1}): 3428 (-OH stretching), 2968, 2928 (-CH stretching aliphatic), 1726 (-C=O stretching), 1645, 1596, 1426, (-CH bending), 563 (C-Br stretching).

2.4 Neat Resin Characterization

NMR Spectroscopy. ^{1}H NMR spectra of the synthesized materials measured at 25°C on a Bruker 500 MHz spectrometer using deuterated dimethyl sulfoxide (D6-DMSO) as the solvent and tetramethylsilane (TMS) as the internal reference (δ H 0.00).

Differential Scanning Calorimetry (DSC). DSC was conducted using a Discovery Series DSC (TA Instruments). The resin compositions were mixed with 0.2 wt.% cobalt napthenate (promoter) and 0.3 wt.% acetylacetone (retarder) to replicate the manufacturer recommended curing conditions used in a vacuum infusion process. The initiated resins were ramped from 0°C to 250°C at 5°C min^{-1} to obtain the ultimate heats of reaction. Isothermal DSC was conducted on the bio-derived resin, GVER1, at 50°C, 60°C and 70°C to study cure kinetics of the resin.

Fourier Transform Infrared Spectroscopy(FTIR). ATR-FTIR was conducted using a Bruker Tensor 27 FTIR spectrometer (Bruker Corporation). For each of the seven resin compositions, 64 scans at a resolution of 2 cm^{-1} were performed on films with a thickness of 125 µm.

Rheology. The non-activated and activated resin rheologies were measured on a rotational rheometer (ARES-G2, TA Instruments). The non-activated formulation was measured with a 40 mm diameter 2° truncated cone geometry under steady shear at a shear rate, $\dot{\gamma}$, of 0.1 s^{-1}. The activated resin was measured using a parallel plate equipped with 25 mm diameter parallel discs with a 0.8-1.0 mm separation gap. All experiments were conducted at 25°C.

Dynamic Mechanical Analysis (DMA). DMA was conducted using a TA Instruments Dynamic Mechanical Analyzer Q800. The specimens were approximately 12 mm wide, 3 mm thick, and were clamped using a dual cantilever fixture with a support span of 35 mm. A sinusoidal transverse displacement was applied at 1 Hz with a 6 N amplitude load. The experiments were ramped from 0 to 150°C at 5°C min^{-1}.

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RESULTS AND DISCUSSION

3.1 Vinyl Ester Polymer Synthesis

The ultimate goal to synthesize composites with a bio-sourced brominated vinyl ester matrix for composite manufacturing requires a procedure that is scalable and cost-effective. Such source materials are renewable, low-cost, and thus are expected to significantly reduce the dependence on petroleum feedstock. This section details the synthesis and characterization of chemorheological and theromechanical properties of the brominated bio-derived vinyl ester resin.

Bromination of BPA is a simple reaction performed at room temperature with a short reaction time; likewise, the procedure for the isolation of the brominated bisphenol A is also simple[1]. The TBBPA was isolated by pouring the final reaction mixture in water and filtering

and drying the product to obtain solid material with a slightly yellow color. Characterization by ^{1}H NMR proved that the material was 100% pure without any impurity or side product.

The Br-VE prepolymer was then synthesized by the reaction of TBBPA and GMA in the presence of N-benzamine catalyst as shown in Figure 1.

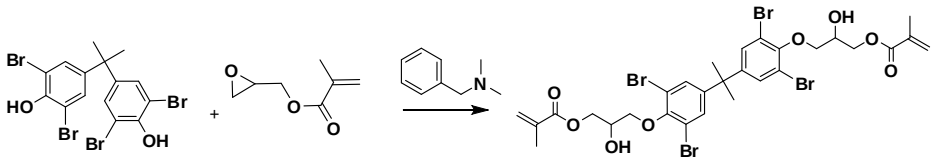

Figure 1. Synthesis of brominated vinyl ester prepolymer from tetrabromobisphenol A and glycidyl methacrylate.

The resultant product was analyzed by thin layer chromatography (TLC) using THF and hexane in a 3:7 ratio. The TLC has three peaks which are consistent with; 1) unreacted TBBPA (nonfunctional), 2) TBBPA with substitution of GMA on one –OH group (monofunctional) and 3) TBBPA with substitution of GMA on both –OH groups (difunctional). Based on TLC results, the product was purified using column chromatography with the same eluent solvent composition and the fractions were collected, concentrated and analyzed using ^{1}H NMR as shown in Figure 2. This analysis confirmed the first, second and third fractions as being nonfunctional TBBPA (with a small amount of unreacted GMA), monofunctional TBBPA and difunctional TBBPA respectively.

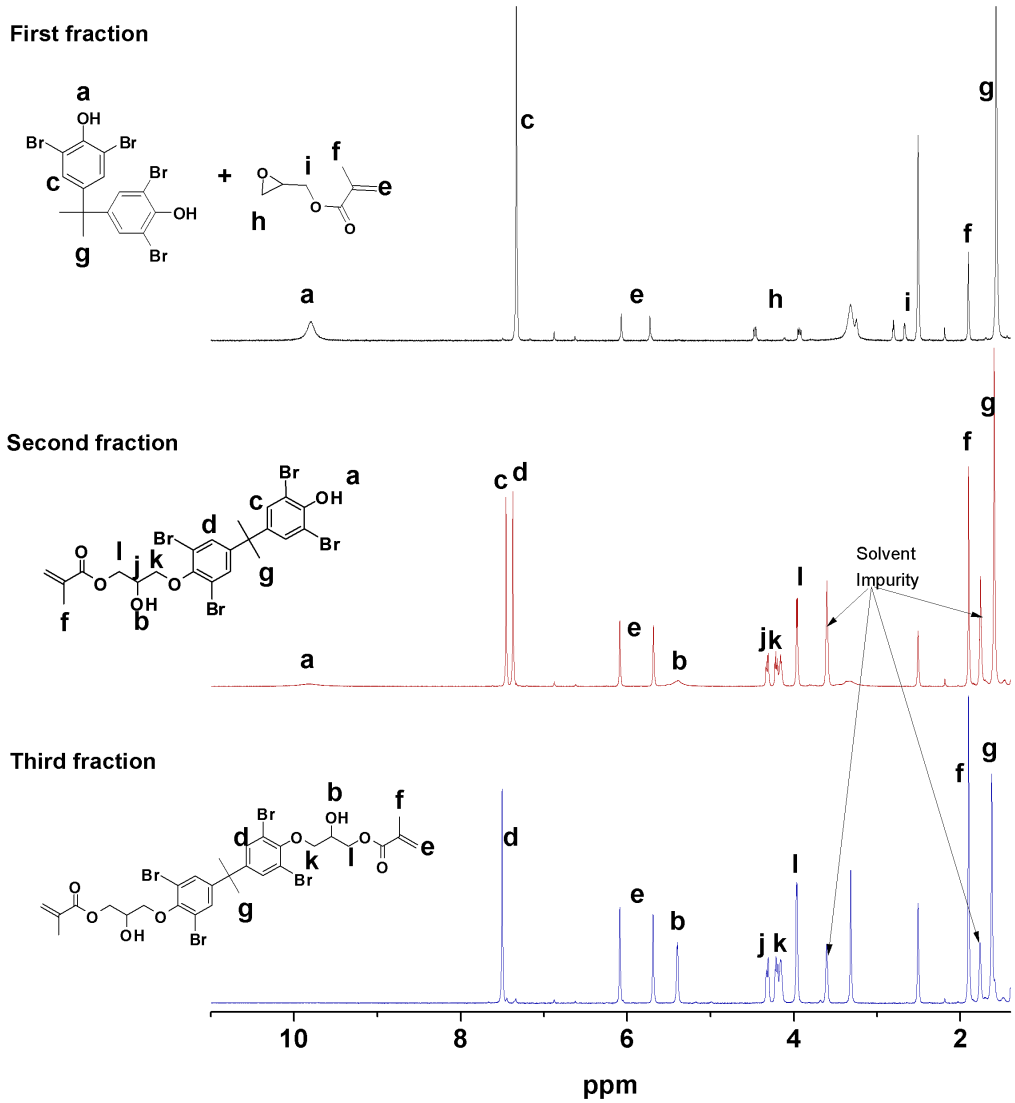

Figure 2. ^{1}H NMR of each fraction of TBBPA from column separation.

3.2 Vinyl Ester Resin Formulation

The Br-VE prepolymer is viscous liquid and mixed with reactive diluent to obtain necessary flow properties for infusion purposes. In this study, the prepolymer was mixed with 40 wt.% styrene to obtain the baseline brominated bio-derived resin (GVER-1). This resin was then blended with the commercial resin, Derakane 510-40A, in ratios of 20, 50 and 80 wt. % to investigate the performance of blends of bio-sourced and traditional petroleum-based materials. Derakane 510-40A was selected as it is presently used for naval vessels and the target goal of this work was to to develop and characterize a lower viscosity resin that could be used as a complete or partial substitute of Derakane 510-40A. In addition to these four formulations, two other formulations

of GVER with lower styrene content of 20 and 30 wt. %were also prepared. Table 1 shows the seven formulations that were examined in this study.

Table 1. Formulations of Bio-derived Vinyl Ester Resin Investigated

Name[a]	Formulated GVER (wt. %)	Derakane 510 40A (wt. %)	Styrene Fraction (wt. %)
CVER	0	100	40
FVER-1	20	80	40
FVER-2	50	50	40
FVER-3	80	20	40
GVER-1	100	-	40
GVER-2	100	-	30
GVER-3	100	-	20

[a] CVER-Commercial Vinyl Ester Resin, FVER-Formulated Vinyl Ester Resin, GVER-Bio-derived Vinyl Ester Resin

Due to variations in the molecular weight and styrene content, all seven resin formulations have different cure times. The curing of these resins occurs through free radical mechanism and the rate of the polymerization can be altered through the addition of promoters such as cobalt salts (with napthenate, octoate or hexanoate) to control the free radical production rate. Concurrently, the presence of a retarder can slow the rate of polymerization in cases where a longer gel time is desired. The experimental cure conditions for all formulations were: 0.2 wt. % cobalt napthenate as promoter, 0.3 wt. % acetylacetone as retarder and 1 wt. % cumene hydroperoxide as initiator. These amounts were chosen based on recommendations in the manufacturer's technical guidelines that would ensure the resin has a long enough pot life (>2 hours) for vacuum infusion.

3.3 Cure Kinetics

The development of a new resin requires the characterization of the reaction mechanism to better understand cure kinetics. Previous studies have shown that the curing mechanism of the thermosetting resins, including epoxy, polyester and vinyl ester resins, can be described using autocatalytic kinetics [14-20] from data fitted to isothermal DSC experiments. At the start of the reaction, a small concentration of the product is present and as the reaction progress, more product is formed and the reaction rate rises to a maximum. As all the reactant is consumed, the rate decreases till the end of the reaction. In a typical heat flow vs. time plot in an isothermal DSC test, the formation of a bell-shape curved with a flat baseline before and after the plot is indicative of the reaction following autocatalytic behavior. The most widely used model to identify cure kinetics in an autocatalytic system is the Kamal-Sourour equation [21]. In this study we use a modified version of this equation to model the behavior of the bio-derived resin as shown in Equation 1.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m) \cdot (\alpha_{max} - \alpha)^n \qquad (1)$$

where $d\alpha/dt$ is the cure rate, k_1 and k_2 are rate constants, α_{max} is the maximum achievable degree of cure at the chosen isothermal temperature and m and n are exponential parameters used to describe the order of the reaction. The value for α_{max} was obtained from Equation 2,

$$\alpha_{max} = \frac{\Delta H_{iso}}{\Delta H_{iso} + \Delta H_{res}} \qquad (2)$$

where ΔH_{iso} is the heat of reaction obtained from an isothermal experiment and ΔH_{res} is the heat of reaction obtained from a subsequent ramp from 0°C to 250°C at 10°C min^{-1} of the isothermally cured sample. The value for cure rate, $d\alpha/dt$, to be plugged into equation 1, was obtained from Equation 3,

$$\frac{d\alpha}{dt} = \frac{1}{(H_{iso} + H_{res})}\left(\frac{dQ}{dt}\right)_t \qquad (3)$$

where dQ/dt is the rate of heat generation at a given time on a plot from an isothermal experiment. In this study, the cure kinetics of the brominated bio-derived vinyl ester resin (GVER-1) were examined using isothermal DSC at a range of temperatures (50°C, 60°C and 70°C). Figure 3 shows representative plots of heat flow as a function of time for the GVER-1 cured isothermally at 50°C, 60°C and 70°C.

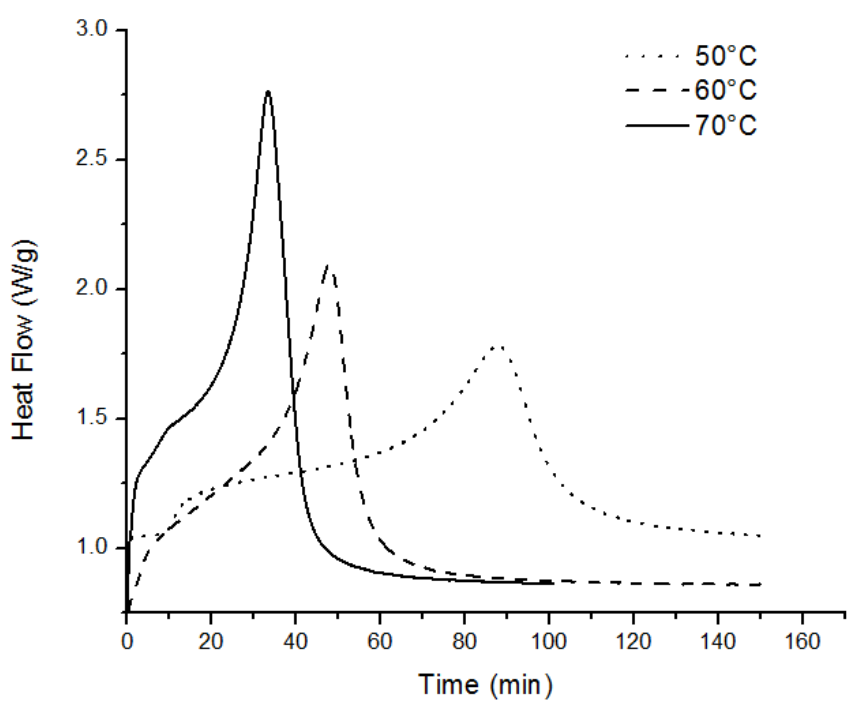

Figure 3. Isothermal plots for GVER-1 at 50°C, 60°C and 70°C

The degree of conversion for the GVER-1 at the specified temperatures was calculated using Equation 2. Figure 4 shows the degree of conversion as a function of time while Table 2 summarizes the heats of reaction obtained from the isothermal experiments.

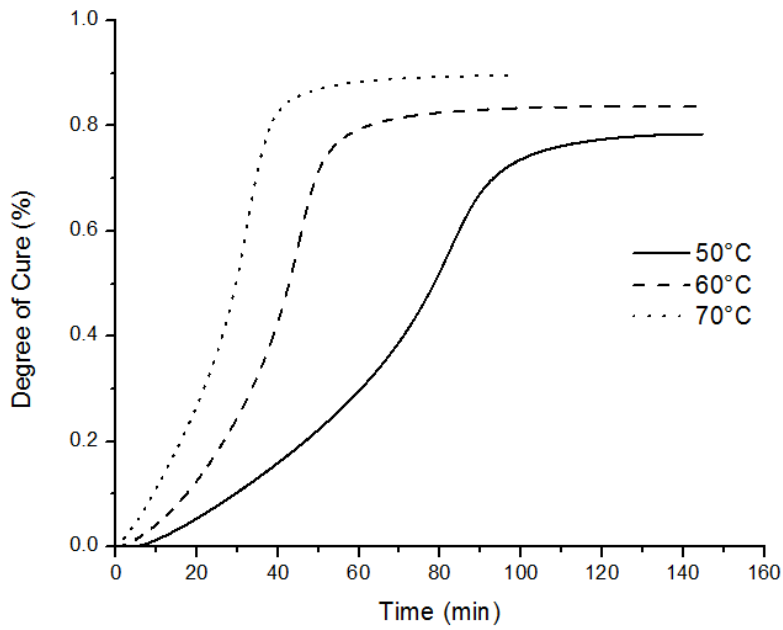

Figure 4. Experimental "degree of cure" profiles for GVER-1 at 3 different temperatures

The ultimate heat of enthalpy obtained from a scanning DSC of GVER-1 from 0°C to 250°C at 10°C min^{-1} was found to be 279 Jg^{-1}. As shown in Table 2, the sums of the isothermal and residual heats of reaction for each isothermal temperature are similar yet slightly lower than that obtained from the scanning DSC.

Table 2. Heats of reaction for GVER-1 measured by isothermal DSC

Temperature (°C)	ΔH_{iso} **(J/g)**	ΔH_{res} **(J/g)**	ΔH_{total} **(J/g)**	α_{max}
50°C	206.7	56.9	271.7	0.76
60°C	225.0	39.2	264.2	0.85
70°C	245.6	28.7	274.3	0.90

This phenomenon has been observed in previous studies [14, 15] and is attributed to increased diffusional limitations once the resin vitrifies at the tested isothermal temperature which restricts the accessibility of free radicals to vinyl ester double bonds as well as other free radicals below T_g.

The residual heats of reactions were also found to decrease as the temperature because the degree of cure usually increases with increasing temperature [22].

The kinetic parameters, k_1, k_2, m and n for the cure mechanism described previously by Equation 1 were obtained using a non-linear regression technique fitted to plots of the cure rate as a function of degree of conversion as shown in Figure 5. Previous studies have shown these values to be calculated using non-linear regression by either; 1) setting the sum of m and n to be equal to 2 (i.e. m+n=2) or 2) calculating m and n as independent parameters. In this research, m and n were calculated as independent parameters because they provided the best fit to the isothermal data obtained from DSC.

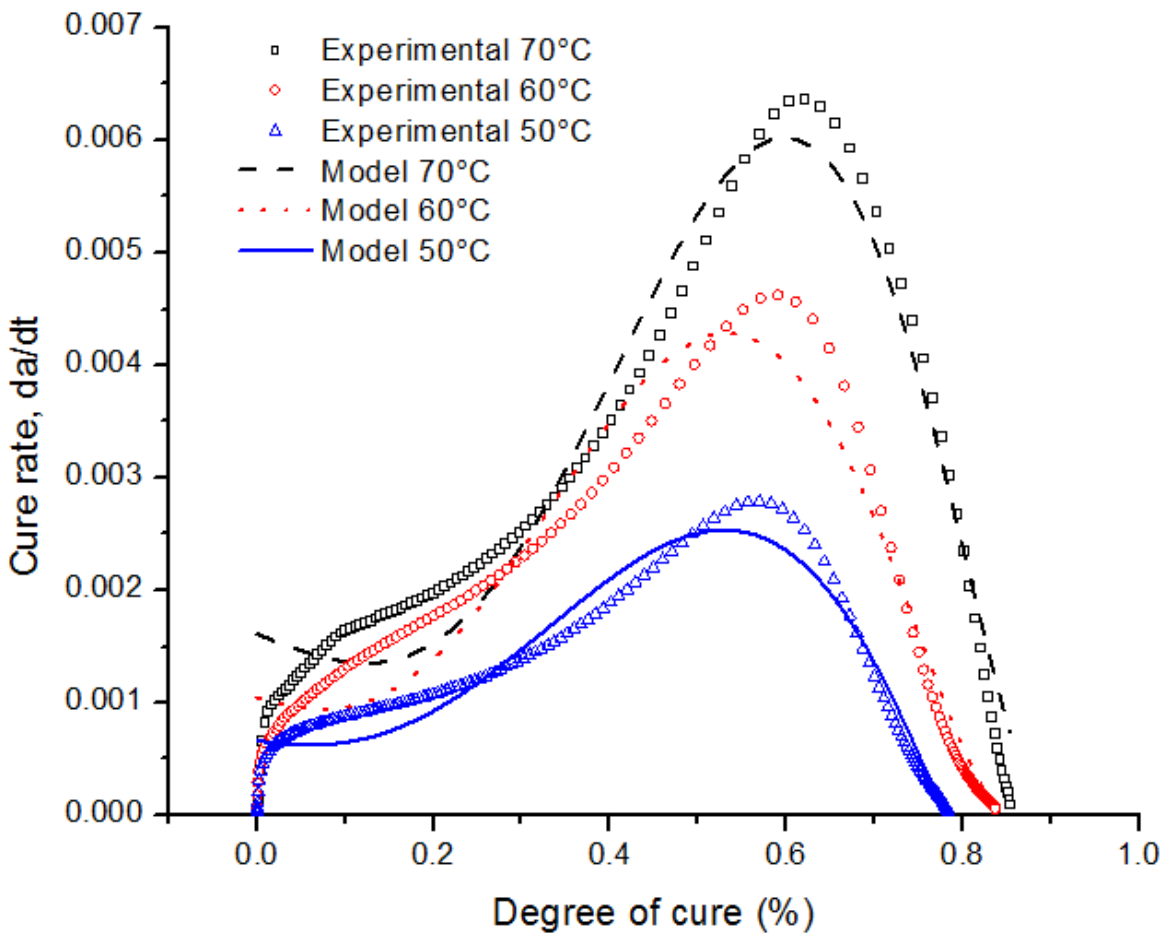

Figure 5. Comparison of isothermal data to autocatalytic model on a plot of cure rate as a function of degree of cure.

The kinetic parameters obtained from the non-linear curve fitting of the isothermal data are shown in Table 3.

Table 3. Kinetic parameters for the autocatalytic model

Temperature (°C)	k_1 (1/min)	k_2 (1/min)	m	n
50°C	0.00087	0.062	2.65	1.15
60°C	0.00137	0.187	2.99	1.69
70°C	0.00193	0.265	3.53	1.64

The values of k_1 and k_2 for each isothermal curve were used to generate Arrhenius plots to determine the pre-exponential factors and activation energies to describe the reaction mechanism of the GVER-1 resin. Figure 6 shows the plots of the natural log of the rate constants as a function of the inverse of the product of the ideal gas constant and temperature.

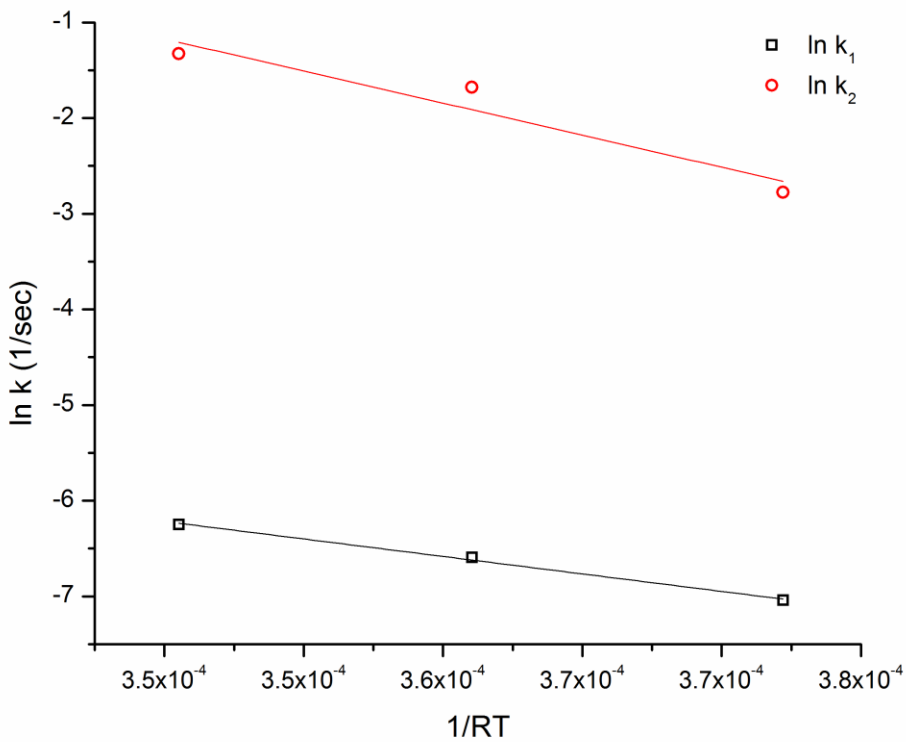

Figure 6. Arrhenius plot of rate constants for autocatalytic reaction

The linear fits of the rate constants in the Arrhenius plot shown in Figure 6 are summarized using Equations 5 and 6. The activation energies and pre-exponential factors are summarized in Table 4.

$$\ln k_1 = 2.48\left(\frac{1}{RT}\right) - 36563 \qquad (5)$$

$$\ln k_2 = 18.2\left(\frac{1}{RT}\right) - 67119 \qquad (6)$$

Table 4. Arrhenius parameters describing the autocatalytic reaction

Rate Constant	E_a (J/mol)	A (1/min)
k_1	36563	7.16×10^2
k_2	67119	4.81×10^9

In addition to determining the cure kinetics using isothermal DSC, ATR-FTIR was conducted on 125 µm thick films made from all seven resin compositions. These films were cured at room temperature for 24 hours followed by a two-hour post-cure at 120ºC per the manufacture recommended cure cycle for the commercial Br-VER resin. The double bond conversion of the vinyl ester and styrene fractions was determined using the ratio of peak heights in the uncured resin and the cured film according to methods detailed in previous FTIR studies [23-25]. The overall double bond conversion was then calculated by multiplying the respective conversion fractions by the molar ratio of vinyl ester to styrene double bonds identified from NMR data as shown in Table 5.

Table 5. Total double bond conversion for all seven resin compositions

Resin	Methacrylate conversion	Styrene conversion	Methacrylate:Styrene Functionality	Total double bond conversion
CVER	0.33	0.96	1:4.99	0.85
FVER-1	0.41	0.95	1:4.28	0.85
FVER-2	0.42	0.96	1:3.41	0.84
FVER-3	0.54	0.97	1:2.93	0.86
GVER-1	0.68	0.96	1:2.65	0.88
GVER-2	0.68	0.96	1:1.70	0.86
GVER-3	0.69	0.99	1:0.99	0.84

The total VER double bond conversion increases as the viscosity and molecular weight decrease from CVER to GVER-1. For vinyl ester resins containing the same weight fraction of styrene (CVER & GVER-1), a decrease in molecular weight has two effects: 1) a decrease of molecular weight between crosslink points, and 2) an increase in the number of available vinyl ester terminal double bonds, which serve as crosslinkers for the polymerization reaction, per unit mass of resin [26]. Therefore, it is expected that the lower VE conversion fraction should correlate to lower crosslink density and in turn a lower storage modulus in the CVER [27]. For the resins with the same molecular weight but decreasing styrene concentration (GVER-1 to GVER-3), the methacrylate conversion is almost equal for all three resin compositons. While it is expected that

increasing the styrene concentration should increase ultimate vinyl ester conversion [24], there is no discernible trend in methacrylate conversion across GVER-1 to GVER-3 seen in Table 5. The styrene conversion across all seven resin compositions is the same and independent of molecular weight. This can be attributed to the fact that at elevated temperatures, styryl radicals are able to homopolymerize whereas the vinyl ester radicals become trapped in a microgel network after the initial low temperature cure period.

ATR-FTIR was also conducted on a GVER-1 film that was cured isothermally for 2 hours at 50ºC to verify the degree of conversion data obtained from resin cured isothermally at 50ºC using DSC. Figure 7 shows the difference in peak heights between the IR spectra of the neat GVER-1 resin and the IR spectra of a film cured at for 2 hours at 50ºC.

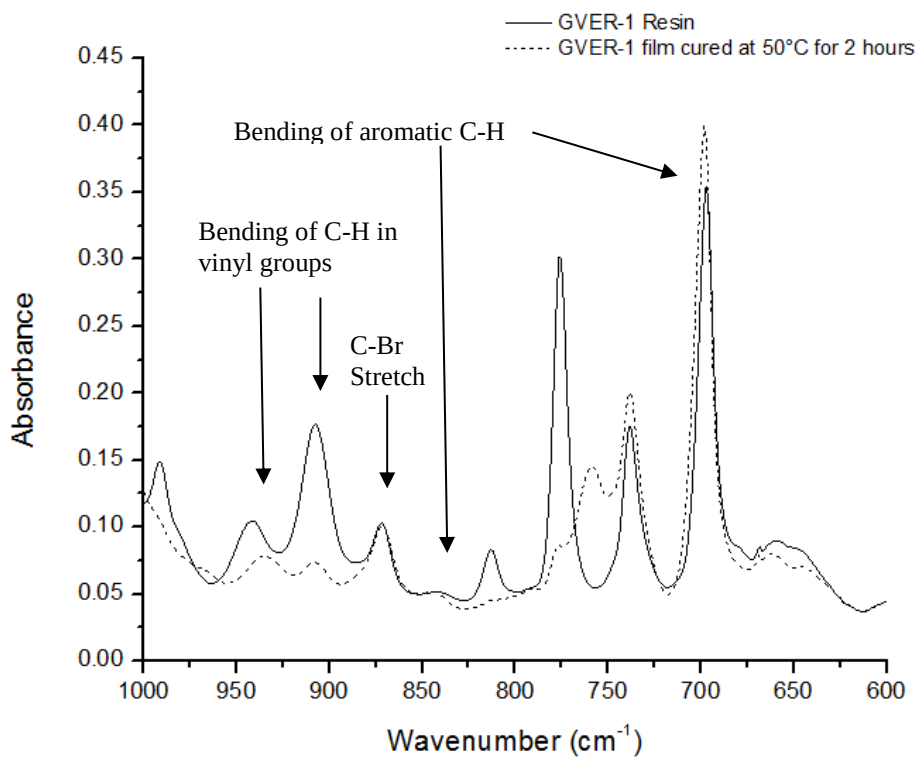

Figure 7. FTIR Plots for GVER-1 before and after 2-hr cure cycle at 50°C

The double bond conversion fractions of styrene (α_{sty}) and vinyl ester double bonds (α_{GVER}) were determined from the peaks in Figure 7. As shown in Table 5, the ratio of the functionality of styrene to vinyl ester in the GVER-1 resin was determined to be 2.65:1. Using this ratio, the overall double bond conversion was determined and compared to the conversion data obtained from the isothermal DSC conducted at 50ºC as shown in Table 6.

Table 6. Total degree of conversion for GVER-1 using DSC and FTIR

Method	Geometry	α_{GVER}	α_{sty}	α_{total}
Isothermal DSC (50°C)	Activated Resin	-	-	0.76
ATR-FTIR (50°C)	125 µm film	0.60	0.83	0.74
ATR-FTIR (24-hr 25ºC + 2-hr 120°C post cure)	125 µm film	0.68	0.96	0.88

The data for the total degree of conversion at 50ºC using DSC and ATR-FTIR are within 2%. DSC data only provides overall degree of conversion and not individual fractional conversion of the styrene and vinyl ester components and this is reflected in Table 6. When comparing the FTIR data for the 50ºC cure to that of the film cured for 24 hours at 25ºC followed by a two-hour post-cure at 120ºC, the double bond conversion for the vinyl ester is almost equal while the double bond conversion for the styrene is significantly lower. The lower styrene double bond conversion in the sample cured at 50ºC is attributed to the fact that at lower temperatures, the vinyl ester radicals favor polymerization with other vinyl ester radicals rather than with styryl radicals prior to microgel formation resulting in the loss of mobility and access of styryl radicals to terminal double bonds once a semi-rigid network is formed [23]. However, at elevated temperatures, the styryl radicals are still able to homopolymerize and as a result we see a higher conversion of styrene for the film that was postcured at 120ºC.

In summary, the cure kinetics for the bio-derived brominated vinyl ester resin are determined to follow an autocatalytic behavior. Kinetic parameters obtained using a non-linear regression fitting as well as the maximum degree of conversion for different isothermal cure profiles have been identified and provide insight into the cure behavior of the GVER-1 resin. Cure of the GVER-1 resin for 2 hours at 50°C leads to a similar vinyl ester double bond conversion as that of the same resin cured for 24 hours at 25°C followed by a post cure at 120°C. Based on these results, a curing cycle of 50°C for 6-8 hours followed by a post cure of 120°C for 2 hours is recommended if this resin is to be utilized for industrial applications. The post cure at 120°C after initial curing at 50°C ensures a higher degree of conversion for the styrene double bonds in GVER-1 in comparison to that of the 50°C cure cycle seen in Table 6.

3.2 Chemorheology Characterization

Resin infusion processing of fiber-reinforced composites depends upon the chemorheological behavior of the resin formulation. The initial viscosity, η_0, dictates the initial infusion rate. Figure 8 shows that as the fraction of GVER in the resin formulation increases progressively, the viscosity decreases. This trend is due to the lower molecular weight of the synthesized vinyl ester monomer fraction as compared to the commercial vinyl ester. Previous work has shown that the viscosity of vinyl ester resins with the same styrene content can be controlled by adjusting the

molecular weight of the vinyl ester monomer[23]. The trend across GVER-1 to GVER-3 indicates that as the styrene fraction is decreased, the viscosity increases significantly. Styrene acts as a reactive diluent and reduces the interactions such as hydrogen bonding and entanglements among vinyl ester, allowing these larger molecules to more easily slide past one another [23, 28, 29].

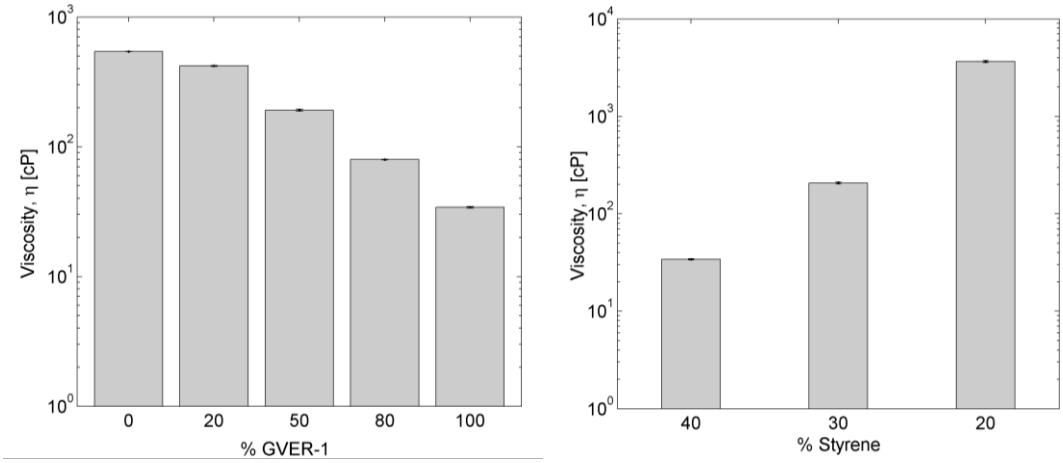

Figure 8. Zero shear viscosity of the resins as a function of GVER and styrene content.

The rheology of formulations as they cure were also examined. During the cure cycle, the viscosity dynamically increases with the formation of polymer networks. The time to gelation is a critical processing parameter, as resin infusion slows dramatically near the gel point and ceases above the gel network formation. However, excessive gel times slow throughput of manufacturing and inefficiently use mold time. Hence, manufacturers value a resin cure that offers a gel point minimally longer than the anticipated infusion time; typical industrial infusion times range from 30 minutes to 2 hours.

The time to gelation for formulations composed of CVER and GVER or "comprising" mixtures were investigated. The formulation gel points are measured by oscillatory rheology and the crossover between the storage modulus (G') and loss modulus (G'') is used to approximate the gel point. The time varying rheology measured at room temperature is shown in Figure 9. The G'/G'' crossover times for the CVER, FVER-2, and GVER are 110, 379, and 550 minutes, respectively. The gel time for the FVER-2 formulation of equal parts CVER and GVER is three times that of the neat CVER while the GVER-1 gel time is excessively long at ~9 hours. This significantly higher gel time is due to the presence of added inhibitor (hydroquinone), leading to a higher concentration in the GVER-1 as compared to the CVER.

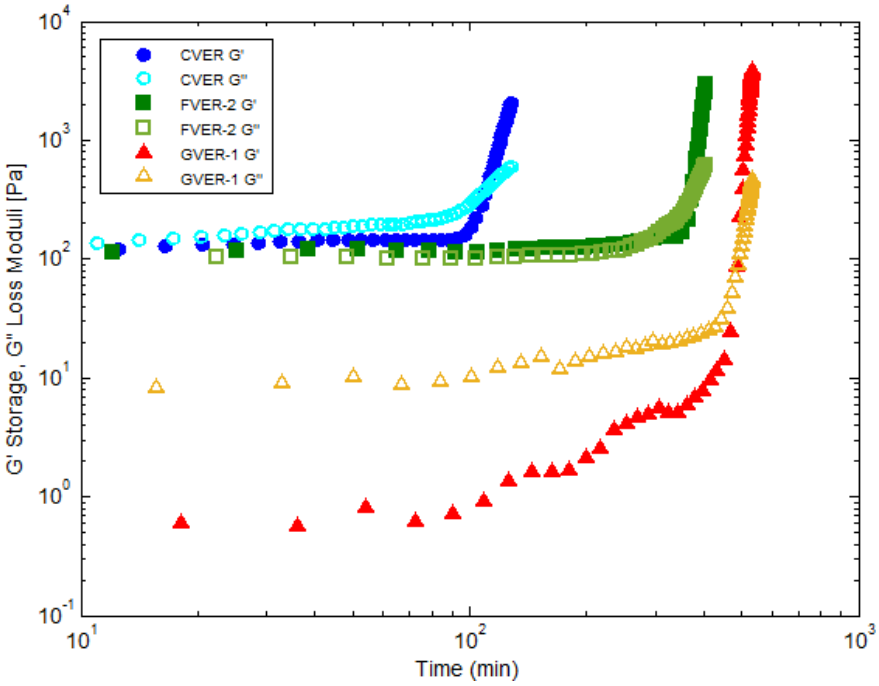

Figure 9. *G′* storage modulus and *G′′* loss modulus for commercial resin (CVER), 50 wt% commercial and 50 wt% bio-derived vinyl ester resin (FVER-2), and neat bio-derived vinyl ester resin (GVER-1) as a function of cure time.

Increases in initiator or promoter concentrations were not investigated but offer future avenues to further reduce the gel time by activator concentration modifications [30, 31].

3.4 Matrix mechanical properties

The mechanical performance of a vinyl ester polymer directly contributes to key mechanical properties of a polymer matrix composite. The neat matrix mechanical properties were assessed by dynamic mechanical analysis (DMA). Figure 10a shows the storage modulus for all resin compositions at 25°C. The data shows a monotonically increasing trend of elastic storage modulus for compositions from CVER to GVER-1.

The bio-derived GVER has a lower molecular weight than the CVER. As discussed earlier, for vinyl ester resins containing the same weight percentage of styrene (CVER to GVER-1), a decrease in molecular weight leads to a more densely crosslinked network and a higher storage modulus. This trend is clearly observed in Figure 10a where the elastic storage modulus increases steadily from CVER to GVER-1. For the same VE composition (GVER-1 to GVER-3), the decrease in styrene content leads to an increase in the percentage of vinyl ester crosslinker and this results in higher crosslink densities and a higher elastic storage modulus. This trend is also clearly seen in Figure 10a [32].

Figure 10b shows the storage modulus as a function of temperature for three compositions: CVER, FVER-2 and GVER-1. The drop in storage modulus is shifted to higher temperatures as the GVER-1 content increases. The elastic storage modulus behavior as a function of temperature is comparable between the CVER and GVER-1. The elastic plateau values decrease at the same rate, reaching 90% of their room temperature value at 53-55°C. However, the glass transition temperature (T_g), as defined by the temperature of maximum tan δ, increases linearly with increasing GVER content and is consistent with previous reports in literature [28, 32].

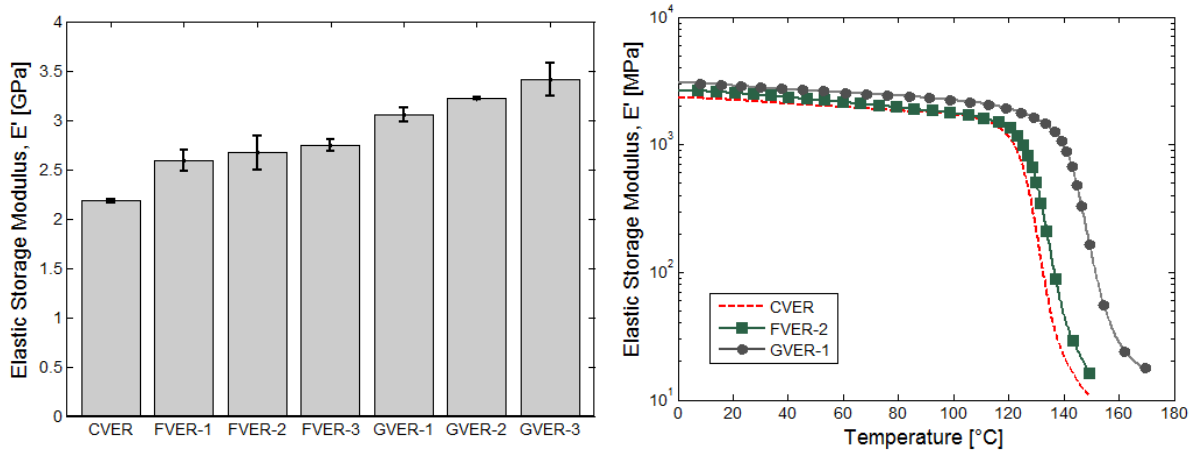

Figure 10. (a) Elastic storage modulus (E′) at 25°C for Br-VER compositions. (b) Elastic storage modulus (E′) for CVER, FVER-2, and GVER-1 as a function of temperature.

Figure 11 shows the T_g increasing linearly with GVER content, from 135°C for CVER to 150°C for GVER-1. The T_g also increases linearly as styrene content decreases across the same VE composition with the T_g increasing from 150°C for GVER-1 to 160°C for GVER-3. The increase in storage modulus is consistent with the increase in T_g and this is expected because an increase in crosslink density always results in an increase in T_g of the polymer network [32].

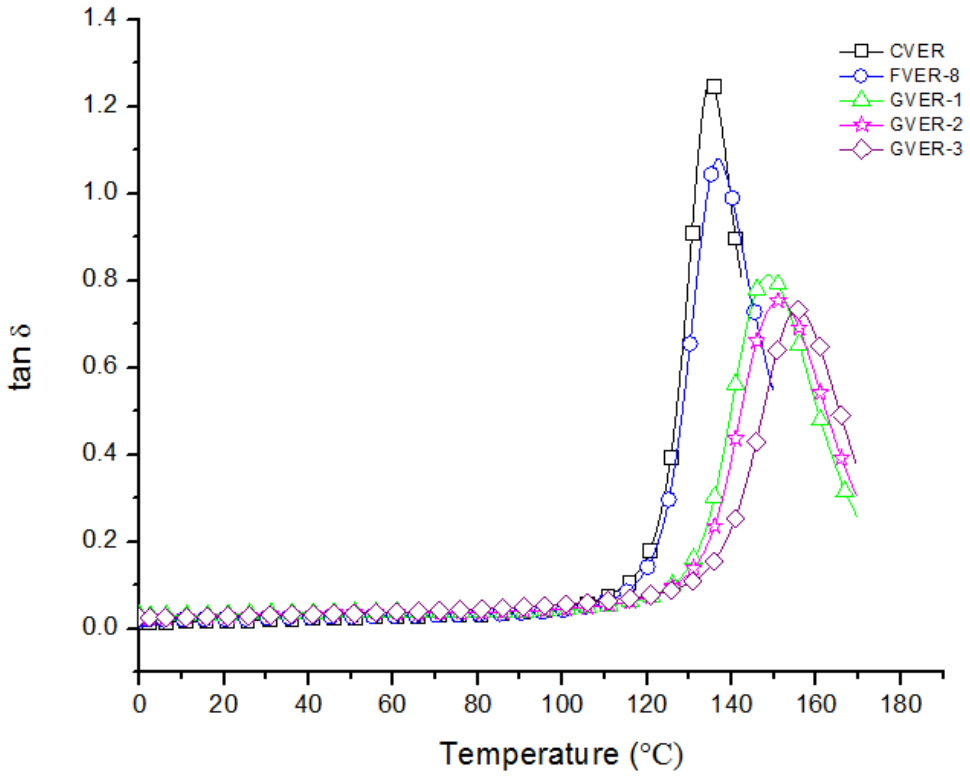

Figure 11. Plot of tan δ as a function of temperature used to determine the T_g for all seven resin compositions

CONCLUSIONS

A scalable method to synthesize flame retardant vinyl ester resin that can accept reactants from products has been demonstrated. The brominated vinyl ester monomer was synthesized by the reaction of tetrabromobisphenol A and glycidyl methacrylate and the product was thereafter purified by column chromatography. The cure behaviour of the novel brominated vinyl ester resin can be described using autocatalytic behaviour and the recommended cure cycle is 6-8 hours at 50°C followed by a 2 hour post cure at 120°C. Rheological studies on resin compositions showed that the Br-GVER has a significantly lower viscosity (34 cPs vs. 542 cPs) and a longer pot life (9 hours vs. 2 hours) than the commercial resin (Derakane 510A-40), thereby eliminating the need for an inhibitor when used for applications such as resin infusion. All the formulations with varying weight fractions of GVER-1 showed increases of thermo-mechanical properties such as storage modulus and glass transition temperature, and can be utilized depending on the desired processing parameters for their eventual end use applications. Future work will investigate further scale-up of the resin synthesis for composite applications as well as extensive flammability testing of composites and water uptake studies for usage in marine environments.

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Appendix M

Environmentally benign synthesis of vinyl ester resin (VER) and its fabrication for anti-flammable VER composites from glycerin bio-waste

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University of Massachusetts Lowell
Lowell, MA

ACS-NERM Meeting
Binghamton, NY
Oct. 7th, 2016

Sustainable "Green" Vinyl Ester Resin (GVER) from Renewable Resources

Performers:

Y. Lee, P. Shah, N.Kim, R. F. Kovar, and A. Kokil

Technology Focus

- *Synthetic protocol for GVER and its processing into VARTM composites, pyrolysis of lignin, extraction of phenol*

Research Objectives

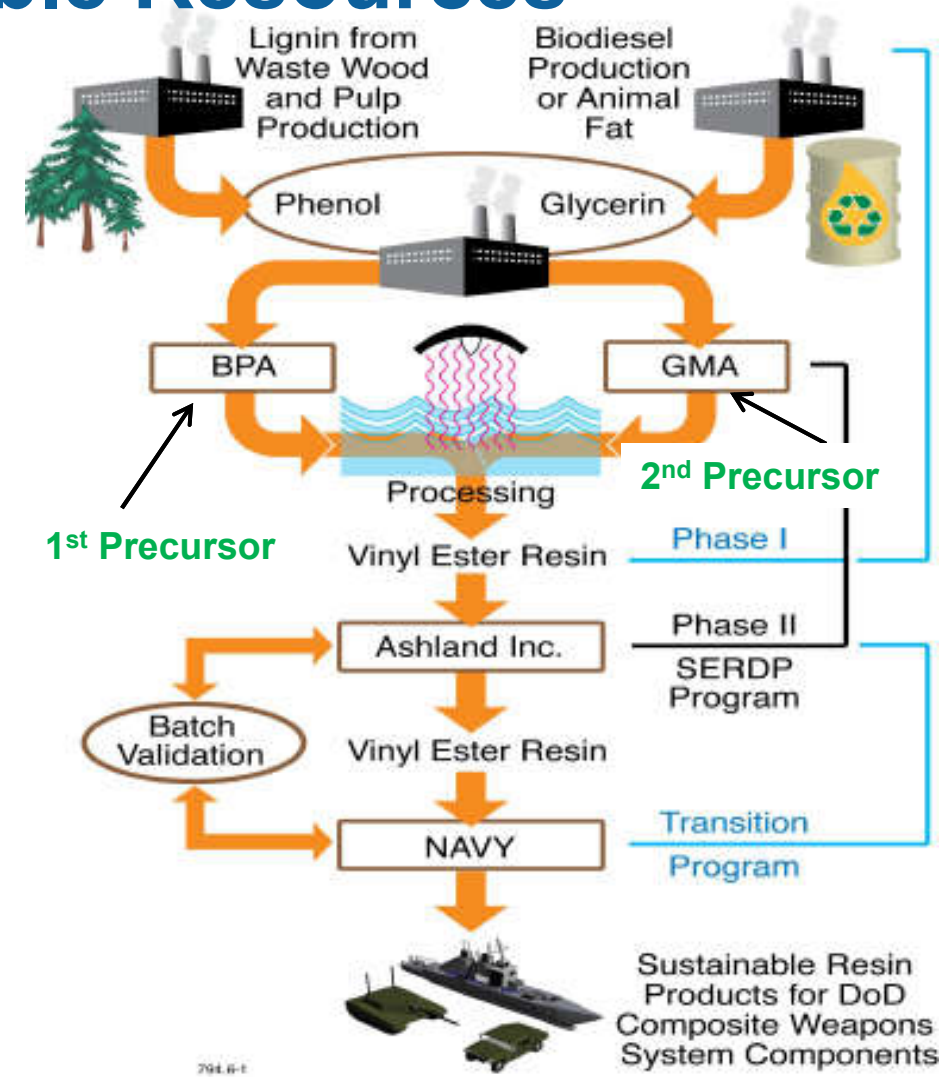
- *Demonstrate synthesis of GMA from glycerin.*
- *Isolation of phenol from lignin to get BPA.*
- *Demonstrate synthesis of GVER and VARTM processing.*

Project Progress and Results

- *Successfully scaled up synthesis of GMA and GVER from biowaste glycerin.*
- *Fabricated neat coupons using GVER*
- *synthesized from bio-waste glycerin .*
- *Synthesized Green BPA using lignin pyrolysate.*
- *Developed alternate lignin depolymerization protocols for selective yield of constituent chemicals.*

Technology Transition

- *Working with Ashland Inc. to understand industrial demands.*
- *Working with paper and biodiesel company for procuring lignin and glycerin.*



Technical Objective

- Refine Phenol from Lignin
- Refine GMA from Glycerin
- Scale up VER resin

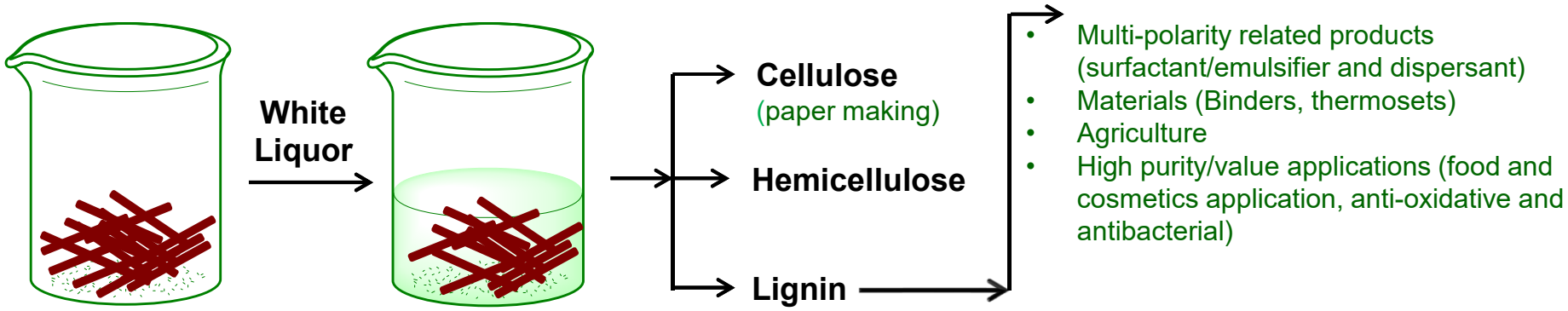
Year I

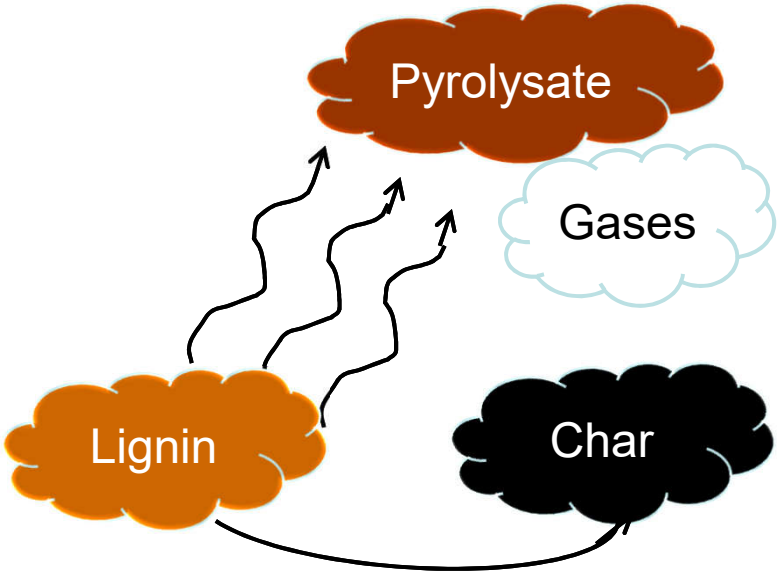
- Formulation with Derakane Vinyl Ester
- Fabricate composites with VARTM
- Conduct structural testing for equivalence

Year II & Year III

Technical Approach-1A

Pyrolysis of Lignin





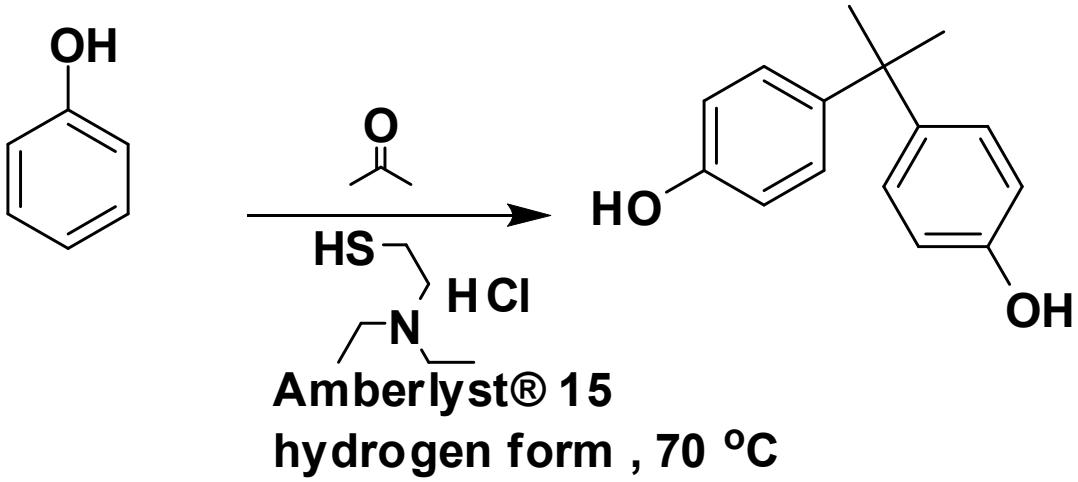
Pyrolysis Concept

Samples of lignin provided by Flambeau River Papers LLC (Park Falls, WI) and Maine Seed Company (Mapleton, ME)

http://www.ili-lignin.com/

Technical Approach-IB

Synthesis of BPA



Technical Approach-2A

Introduction to Glycerin

Vegetable Oil, Animal Fat (Triglycerides)[1] →

- **Water, NaOH (Hydrolysis, Saponification)** → **long-chain carboxylate salts used as soaps**
- **Alcohol, NaOH Transesterification** → **esters of fatty acids used as biodiesel**

+ glycerin

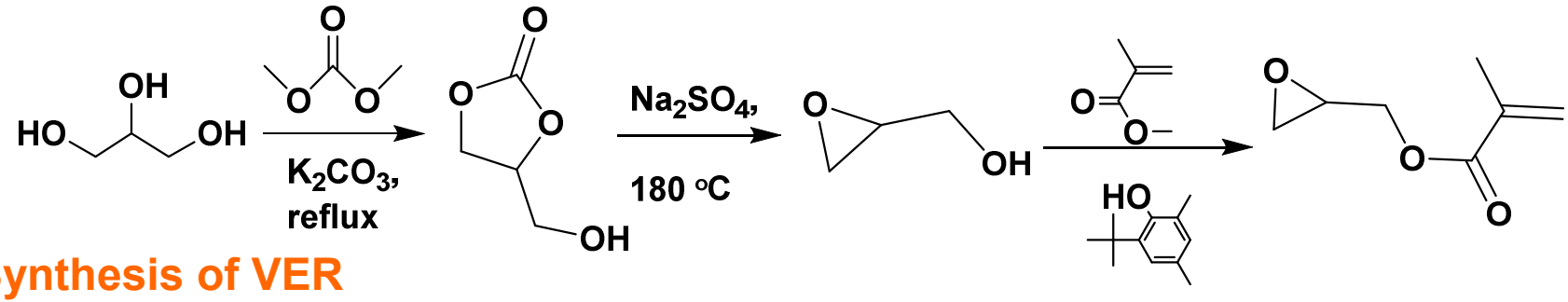
- By 2020, the production of glycerin will be six times higher than its demand. [2]
- Disposal of glycerin in the waste stream would require increasing expenditures for biodiesel industry

We are using crude glycerin from bio-diesel waster stream provided by Maine Standard Biofuels (Portland, Maine)

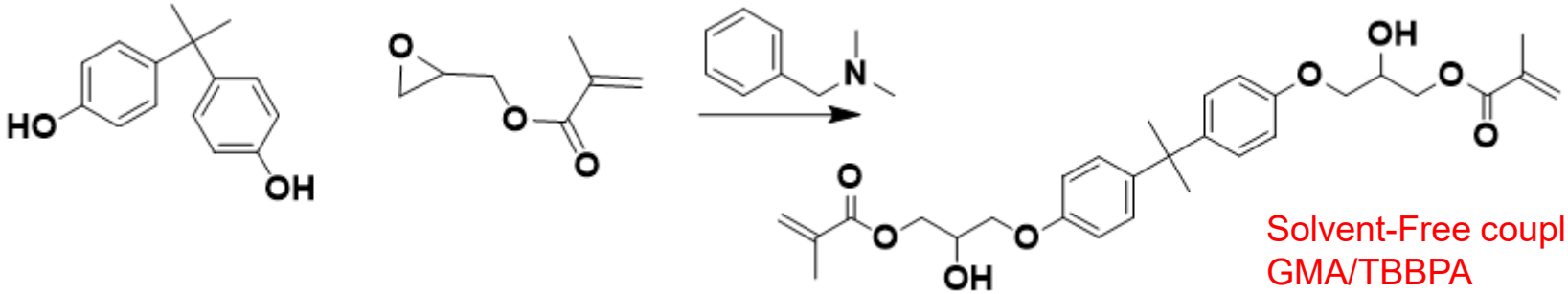
1. Sims, Bryan (2011-10-25). "Clearing the Way for Byproduct Quality: Why quality for glycerin is just as important for biodiesel". Biodiesel Magazine
2. Christoph, Ralf; Schmidt, Bernd; Steinberner, Udo; Dilla, Wolfgang; Karinen, Reetta (2006). "Glycerol". Ullmann's Encyclopedia of Industrial Chemistry. doi:10.1002/14356007.a12_477.pub2. ISBN 3527306730.

Technical Approach-III

Synthesis of GMA

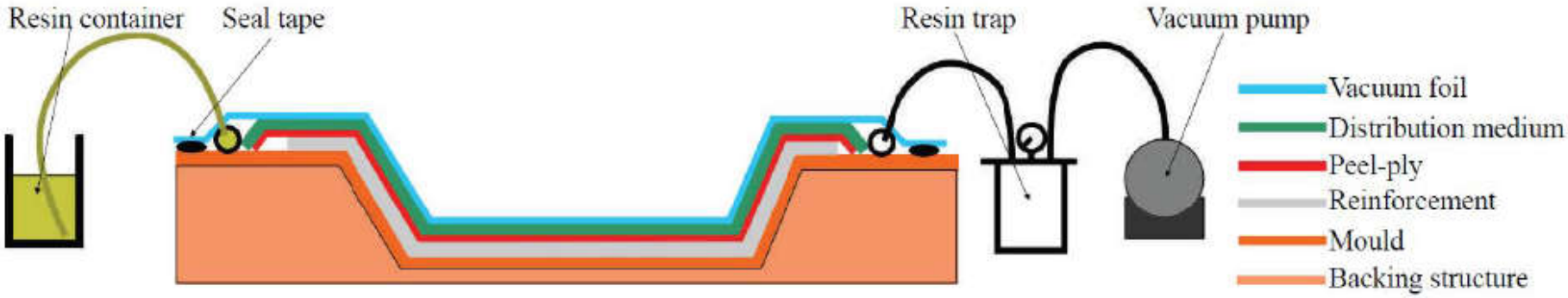


Synthesis of VER



Solvent-Free coupling of GMA/TBBPA

Carbon fabric reinforced panel fabrication by VARTM



Significance

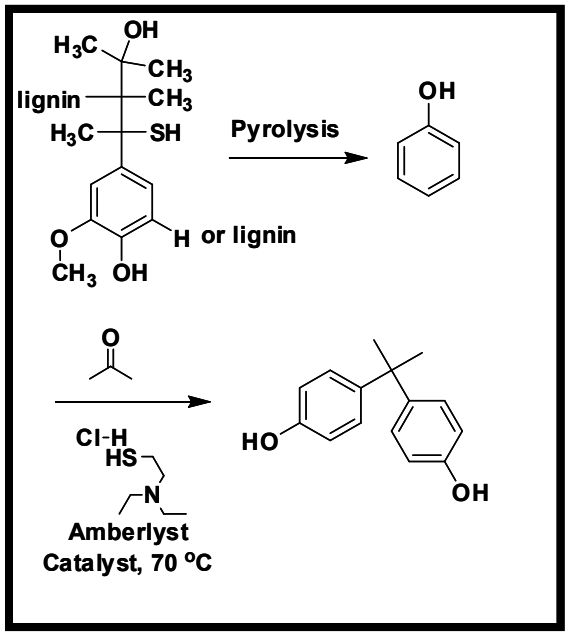
Environmental Advantages

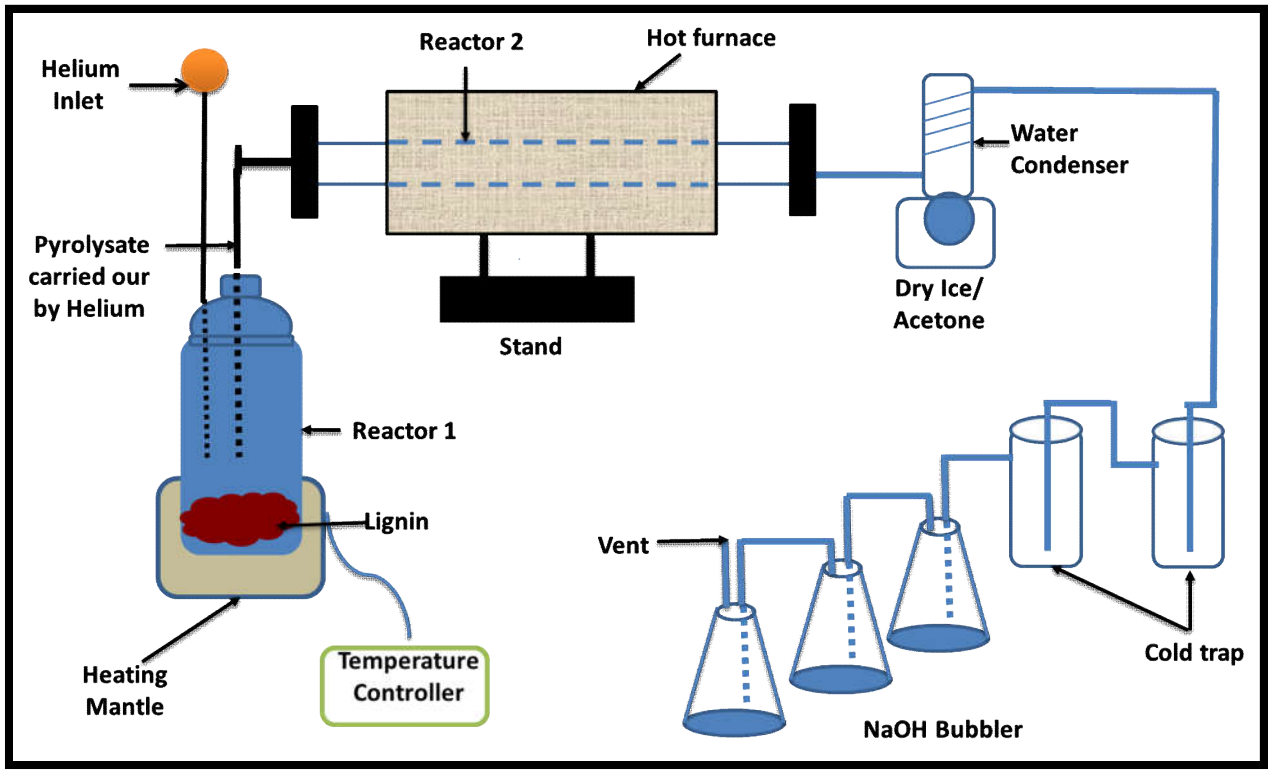
- **Elimination of US dependence upon foreign oil** in manufacturing critical military composites.
- **Replacement of epichlorohydrin** with GMA yields an environmentally benign synthesis.
- Production of green BPA and GMA will provide raw materials **for other high-value chemical products**.
- Finally, the proposed use of biomass waste **will not affect the nation's food supply**.
- Pyrolysis of lignin produces **many other valuable phenolic derivatives**.

Technical Advantages

- **Solvent-free** synthesis of vinyl ester resin monomer.
- GVER from BPA and GMA forms only **pure, low molecular weight product**,
  - Good for VARTM processing
  - Reduces usage of reactive diluent (styrene)
  - Increases wetting of resins and decrease voids/bubbles in composites

Pyrolysis of Lignin





Coal was pyrolyzed to isolate phenol before WW-I and during WW-II in shortage of petroleum

"Advanced Organic Chemistry"; Louis F. Fieser and Mary Fie. e , New York, Reinhold Publishing Corporation, Chapman & Hall, Ltd., London, 1961, pp.640-645.

Elemental Analysis and Pyrolysis Yields

Source of Lignin Material	SA	TCI (alk)	MSC-BL
Elemental Analysis			
C	62.2	48.3	28.7
H	5.74	4.30	2.86
N	0.56	0.12	0.10
O	30.5	34.4	40.7
S	1.26	3.34	4.34
O:C	0.49	0.71	1.42
H:C	0.09	0.09	0.10
Pyrolysis yields			
Char (wt. %)	54.9	62.6	65.7
Liquids (wt. %)	12.6	11.5	14.2
Gases (wt. %)[a]	32.5	25.9	20.1

[a] The amount of gas was calculated by difference.

No	Standard Compounds	Yield (% of Standard Compound in Pyrolysates)		
		SA	TCI (alk)	MSB-BL
S1	Guaiacol	10.3	9.48	6.59
S2	4-Methyl guaiacol	1.95	1.34	0.64
S3	Phenol	9.41	20.2	10.7
S4	4-Ethyl-guaiacol	1.85	0.91	0.71
S5	4-Vinyl guaiacol	0.66	1.44	0.62
S6	2,6-Dimethoxyphenol	0.57	0.25	0.00
S7	Vanillin	0.03	0.92	0.00
S8	4-Acetyl guaiacol	0.55	0.61	0.39
S9	Catechol	11.7	2.27	4.82
S10	Homovanillic acid	0.50	0.43	0.00

Purified product after solvent extraction

Purification Methods for Pyrolysate

Solvent Extraction

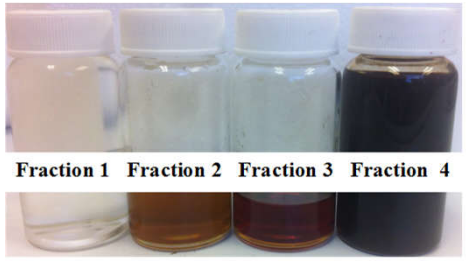
No	Standard Compounds	Yield (% of Standard Compound in Extracted Fractions)	
		Nonpolar	Polar
S1	Guaiacol	6.59	12.3
S2	2-methoxy-4-methylphenol	0.64	2.07
S3	Phenol	10.7	11.8
S4	4-ethyl-2-methoxyphenol	0.71	2.45
S5	2-methoxy-4-vinylphenol	0.62	0.00
S6	2,6-dimethoxyphenol	0.00	12.6
S7	Vanillin	0.00	0.00
S8	4-hydroxy-3-methoxyacetaphenone	0.39	0.00
S9	Catechol	4.82	5.86
S10	Homovanillic acid	0.00	0.00

Pyrolysate were purified by combining:

(a) Solvent extraction
(b) Distillation and
(c) Column chromatograph

Distillation

No.	Standard Compounds	Yield (% of Standard Compound in Distilled Fractions)			
		1st Fraction	2nd Fraction	3rd Fraction	4th Fraction
S1	Guaiacol	29.6	23.3	14.4	0.00
S2	2-methoxy-4-methylphenol	0.00	2.64	4.16	0.00
S3	Phenol	61.6	24.5	10.1	0.00
S4	4-ethyl-2-methoxyphenol	0.00	0.00	4.21	2.62
S5	2-methoxy-4-vinylphenol	0.00	0.00	0.00	0.00
S6	2,6-dimethoxyphenol	0.00	2.78	8.92	25.2
S7	Vanillin	0.00	0.00	0.00	0.00
S8	4-hydroxy-3-methoxyacetaphenone	0.00	0.00	0.00	0.00
S9	Catechol	0.00	0.00	4.28	12.6
S10	Homovanillic acid	0.00	0.00	0.00	0.00
	Yield of Each Fractions				
	% of total	1 %	37 %	26 %	36 %

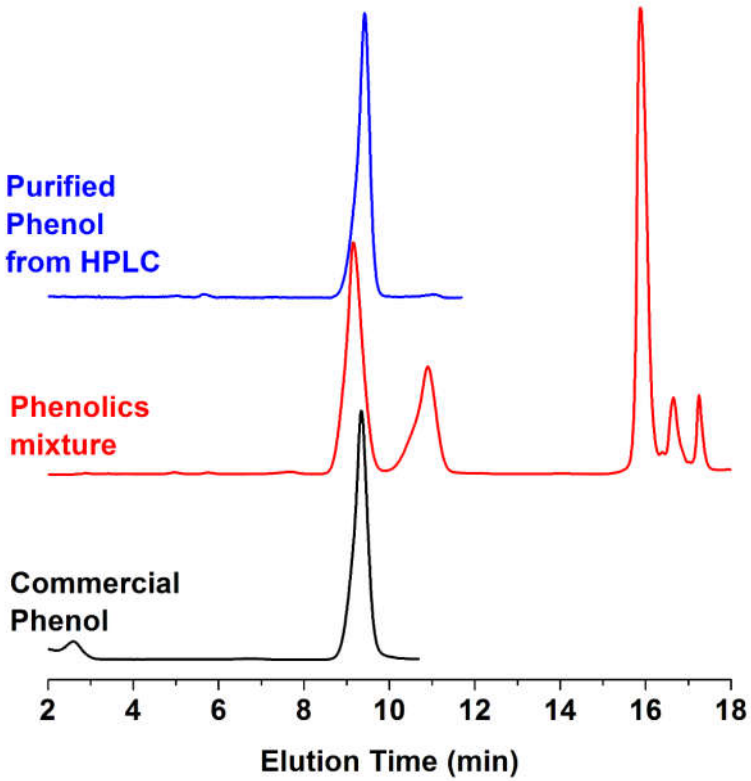


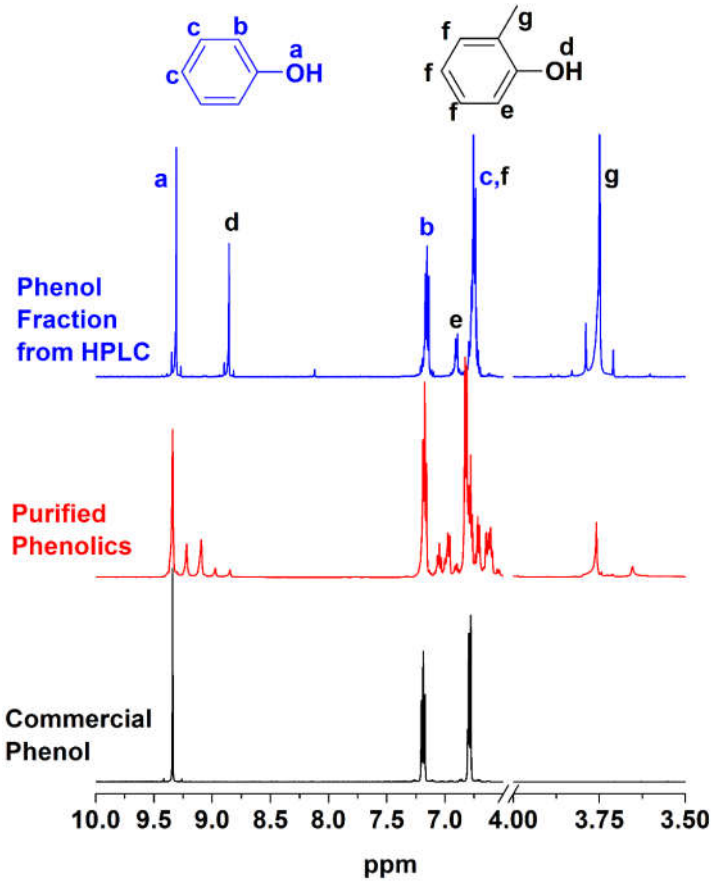
Phenols from lignin pyrolyzed bio-oil

Compound	wt %
phenol	3.90%
1,2-benzenediol	2.60%
2-methyl phenol	1.60%
3-methyl phenol	2.60%
4-methyl phenol	2.60%
3-methylbenzene-1,2-diol	3.20%
4-methylbenzene-1,2-diol	0.00%
2-ethylphenol	0.10%
2,5-dimethylphenol	0.80%
2,4-dimethylphenol	0.50%
3,5-dimethylphenol	0.40%
2,6-dimethylphenol	0.20%
3,4-dimethylphenol	0.40%
4-ethylbenzene-1,2-diol	1.80%
4-ethylphenol	0.90%
,5-trimethyl phenol	0.10%
tal	21.70%

University of Massachusetts UMASS Lowell

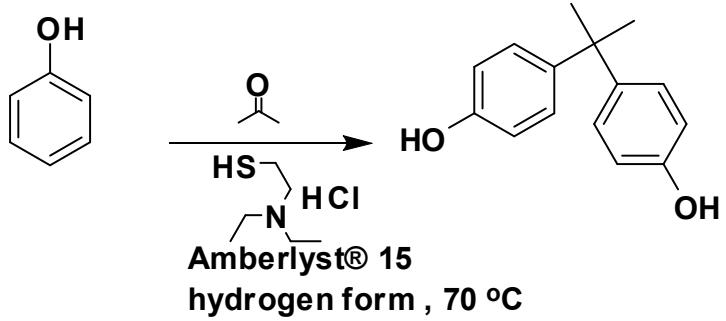
HPLC and ^{1}H NMR of Phenol

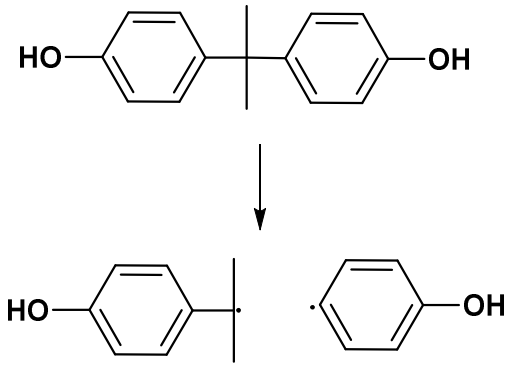




Synthesis of BPA

- In stoichiometry high amount of phenol and very low amount of acetone is required.
- Higher the purity of the phenol, better will be conversion.

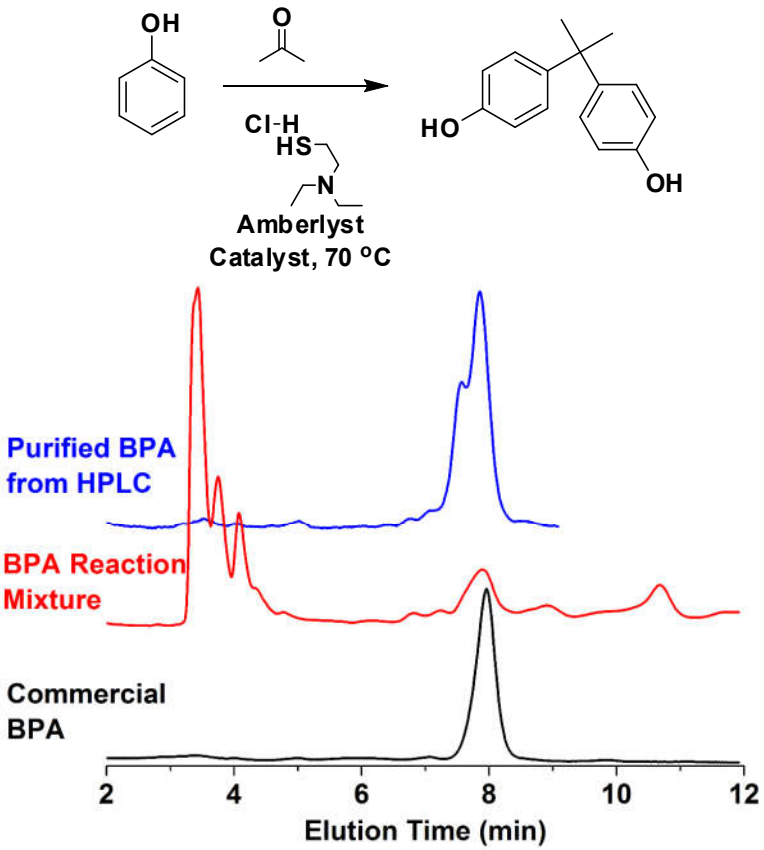


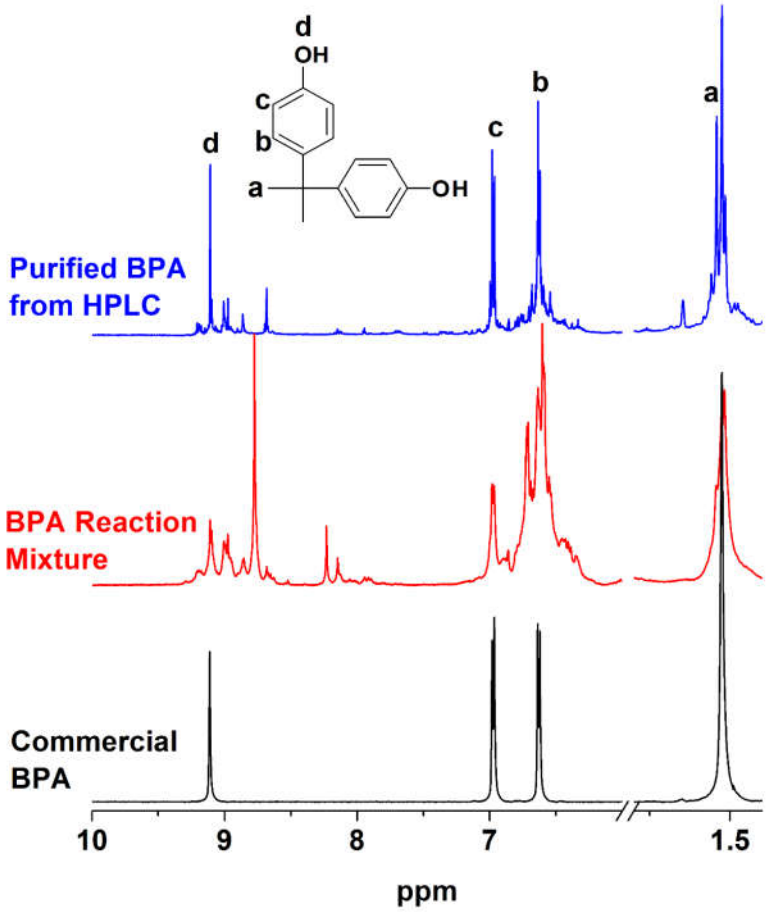


Exact Mass: 135.08 Exact Mass: 93.03

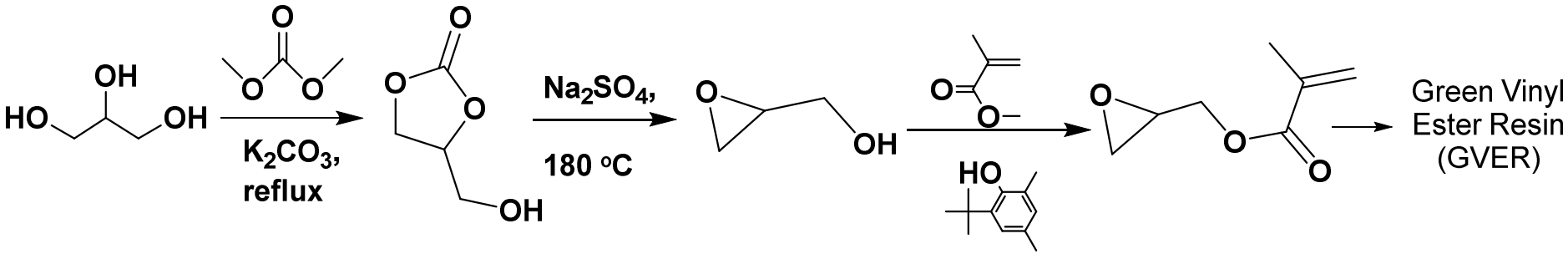
- The mass spectra of peak at 7.885 and 10.663 confirmed presence of phenol and p-isopropyl phenol respectively.
- The GC-data confirmed that we have successfully synthesized BPA starting from lignin.

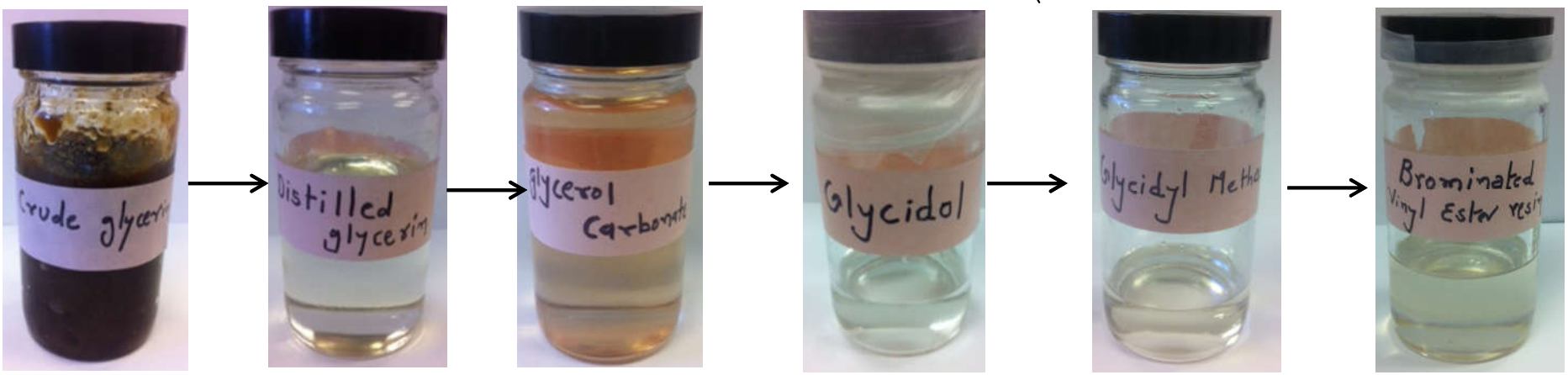
HPLC and ^{1}H NMR of BPA





Green Vinyl Ester Resin from Biodiesel Glycerin





Crude Glycerin → *Distilled Glycerin* → *Glycerol Carbonate* → *Glycidol* → *Glycidyl Methacrylate* → *Green Vinyl Ester Resin*

Applications of Greener Phenolics

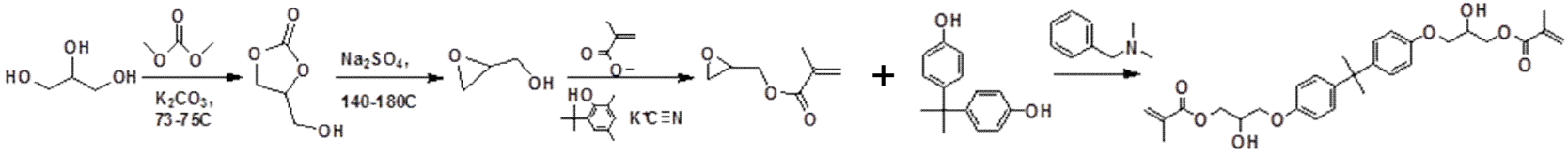
- **Various Resin Materials**. The isolated phenolic can be used as a building block for synthesis of different types of resin materials, which can be used for defense purposes. Such as benzoxazine resin can be made from vanillin, and other resins can be made from bisphenol A.

- **Food Flavoring Agents**. Several phenolics have large number of applications as food flavoring agents; such as, vanillin, syringol, syringadehyde, 2-methoxy-4-vinylphenol, etc.

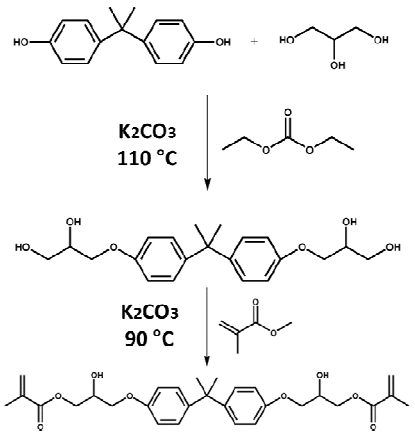
- **Precursor for Pharma Industries**. Many phenolics can be used as an important precursor in many pharma industry. Such as, Guaifenesin (Robitussin®) from guaiacol and many more. So, by several simple organic reactions one pyrolyzed material can be easily converted to more economical products.

C. F. H. Allen and G. W. Leubner, "Syringic aldehyde", *Org. Synth.; Coll.* 4: 866 **(1963)**

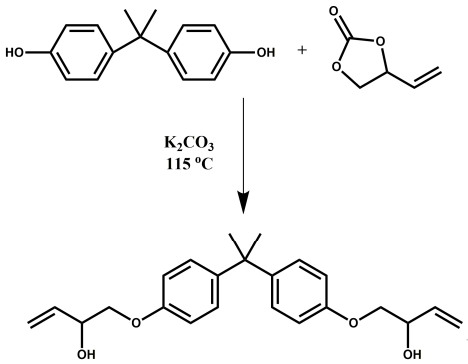
Results-IP



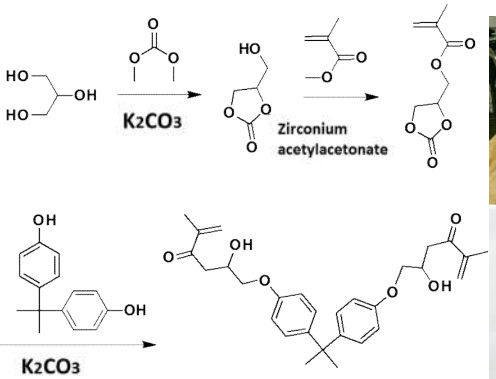
Y. Lee, Vinyl Ester Resin (VER) from Renewable Resources, FMI ID 2076, Nov. 2012
Shah and Lee "Environmentally benign synthesis of VER from biowaste glycerin" RSC AdvancesMay 2015



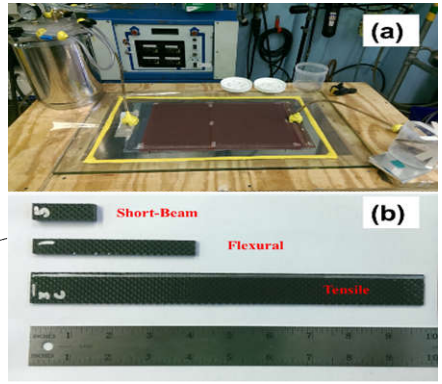
Y. Lee , Methods of making BHDE & VER UML 2015-038-01 (atty.Ref.no.4724.005PRV), US Application no.62/387,443



Y. Lee, Resins of VHER,UML # 2015-041(atty.Ref.no.4724.007PRV) US Application no.62/303,724



Y. Lee and P. N. Shah, GVER from GCMA and Bisphenol A, UML # 2016-020.



Y.Lee, P.N.Shah, C.Hensen, S.Dev Green Composites UML # 2016-008

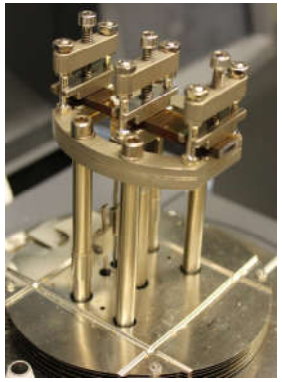
Characterization tests were conducted on neat resin specimens

- Resin synthesis was scaled-up and coupons were fabricated by mixing green resin with Ashland's commercial resin in different compositions.

Rheology

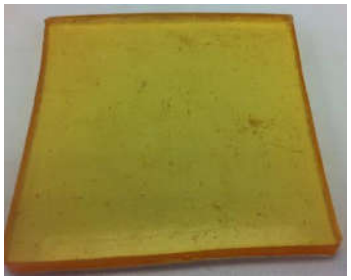
1) Gel Time
2) Zero Shear Viscosity

Dynamic Mechanical Analysis



1) Storage Modulus
2) Glass Transition temperature (T_g)

Flammability



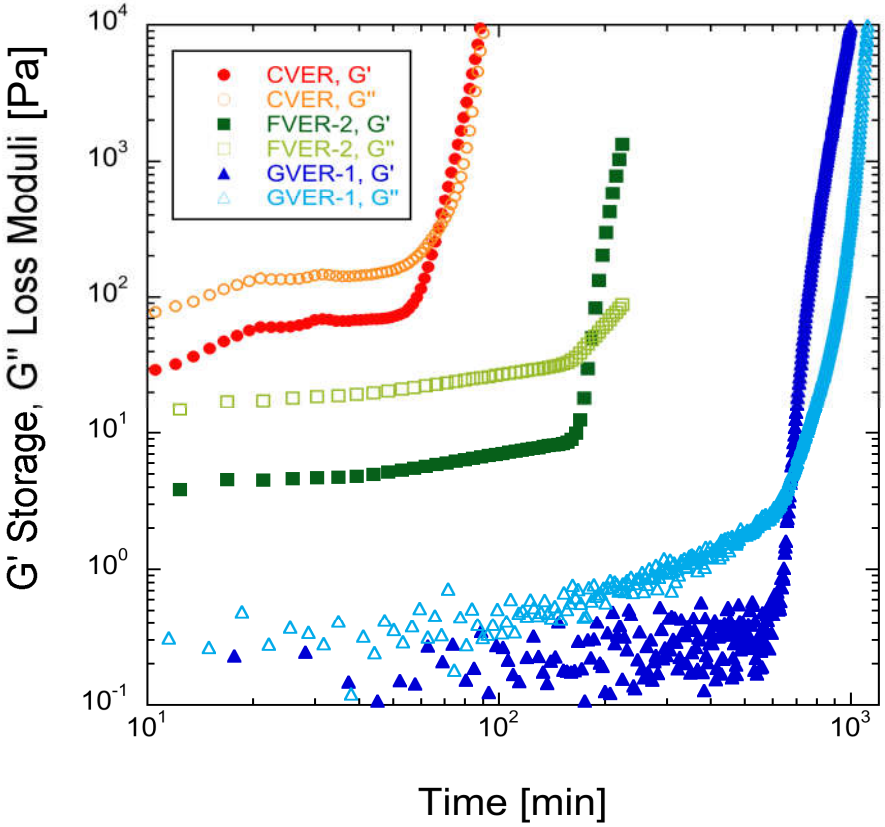
1) Heat Release Rate
2) Smoke Density

Rheology Image Source: www.sheffield.ac.uk

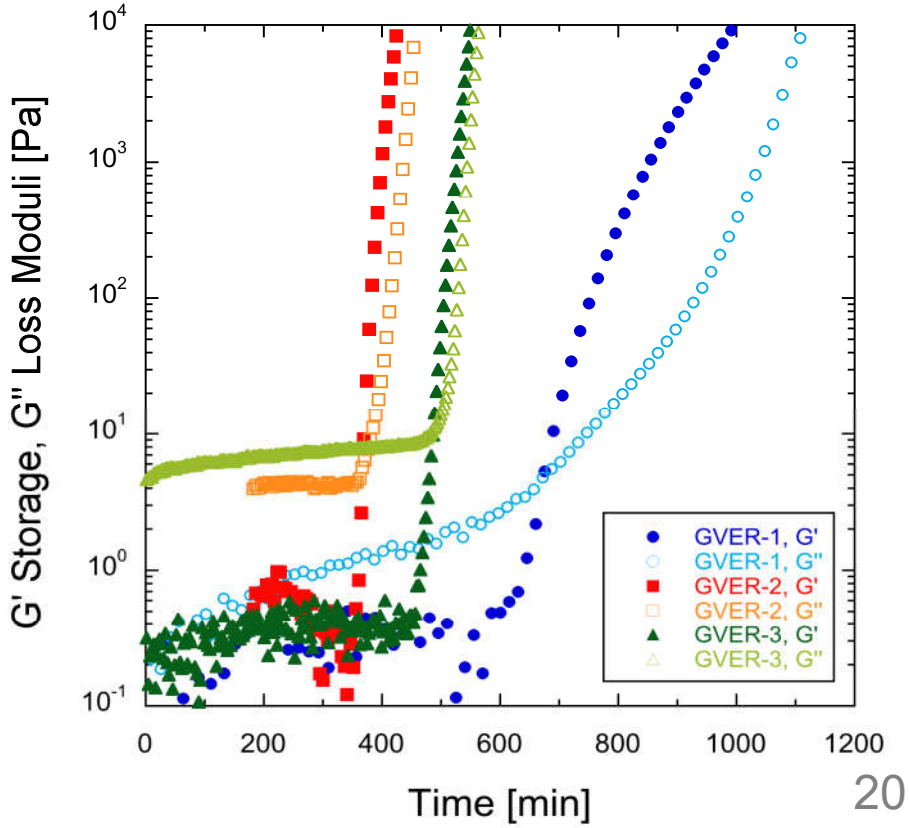
Chemo-Rheological Studies

- Gel time is defined as the crossover point between the storage and loss moduli
- Longer gel time leads to improved permeability of resin through fabric preform and a higher fiber volume fraction which in turn improves mechanical properties
- 3 resins(CVER,FVER-2 & GVER-1) were characterized for their processing time before gelation
- Zero shear viscosities: CVER → 458 cP, FVER-2 → 245 cP, GVER-1 → 65 cP

Impact of varying GVER content



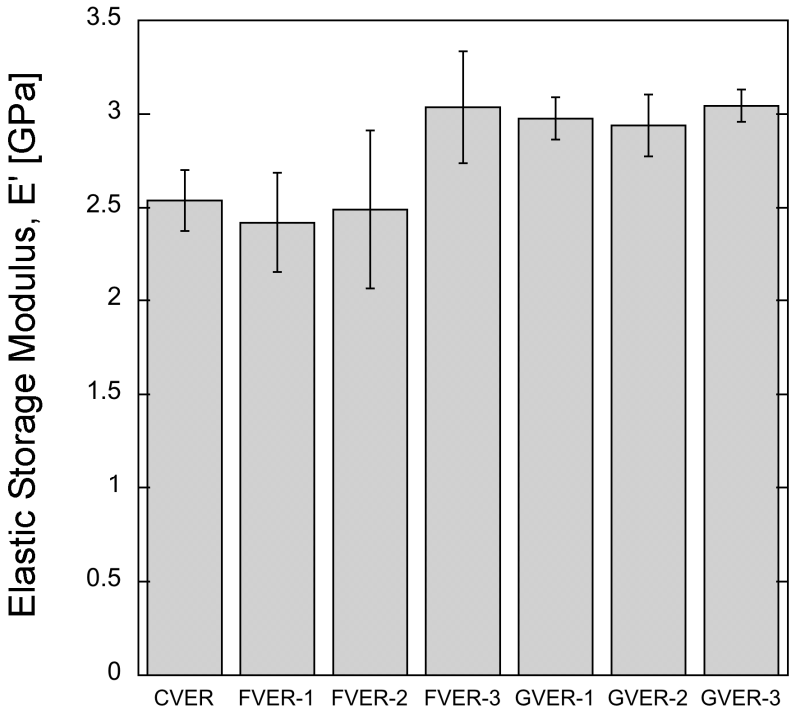
Impact of varying styrene content in GVER formulations



DMA

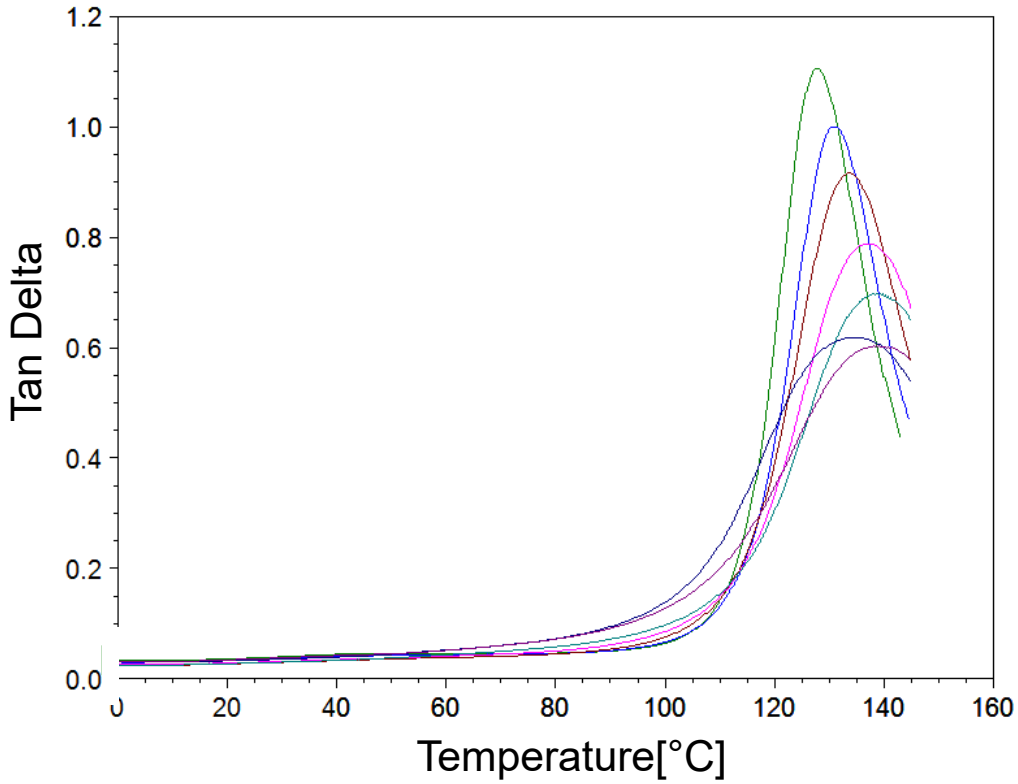
- Two key parameters of interest
  - **Storage Modulus –** Higher value indicates better resistance to deformation
  - **Glass Transition Temperature (T_g)** – Indicates higher cross link density

Storage modulus at room temperature



Increasing the content of bio-derived GVER leads to a higher storage modulus

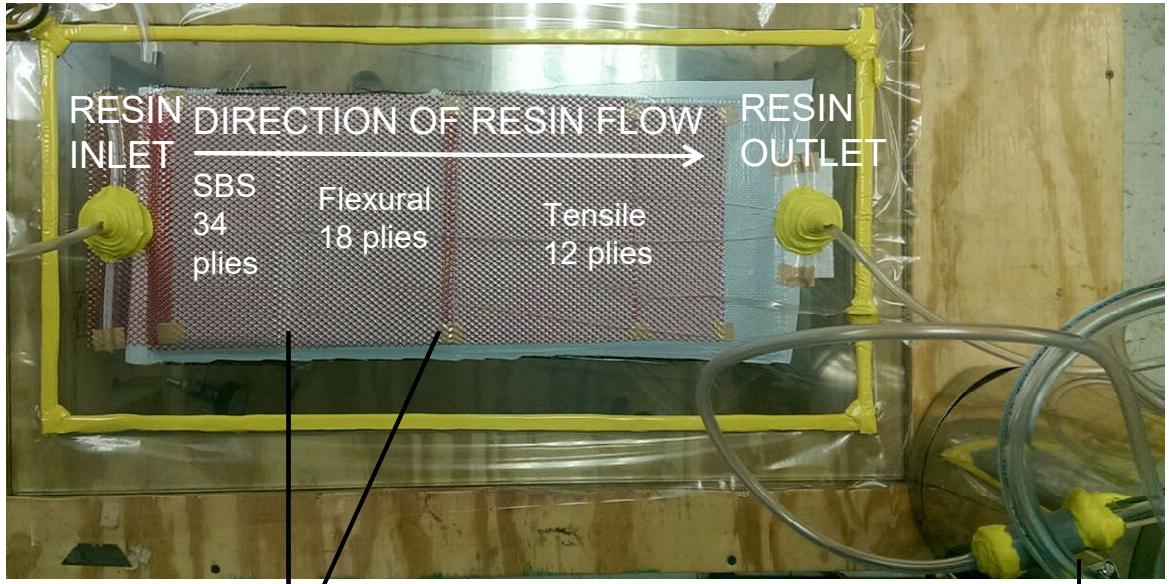
Tan delta peaks representative of [T_g]



Increasing the content of bio-derived GVER increases the T_g

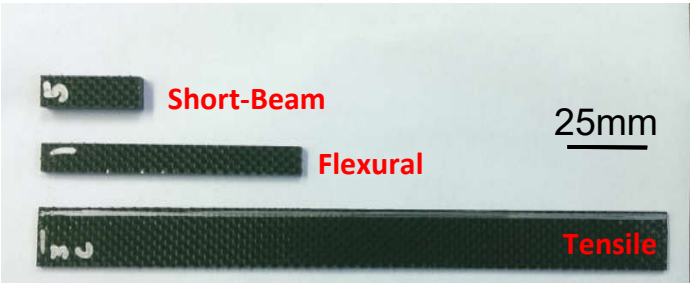
Fabrication of composite specimens

- Composites manufactured using 7 GVER compositions
- Samples manufactured to ASTM standards (D3039, D7264, D2344) for tensile, flexural and short beam shear strength, respectively

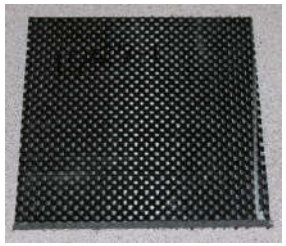
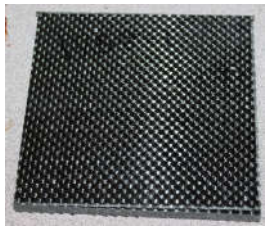


Ply drops

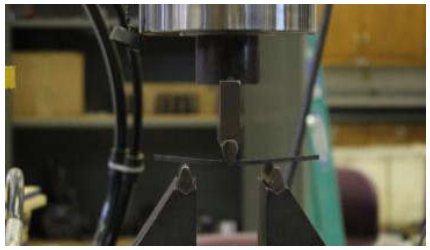
Resin Catch pot



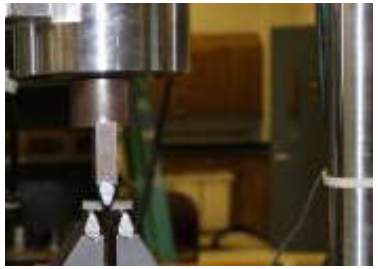
Mechanical and Flammability Testing

Material ID Material Description	UMass Lowell				NAVAIR	
	1742 VER	1750 VER	1757 'C' Fabric Reinforced / VER	1758 'C' Fabric Reinforced VER	1760 'C' Fabric Reinforced VER	1763 'C' Fabric Reinforced VER
Photo						

Setup for tensile testing of GVER composite.

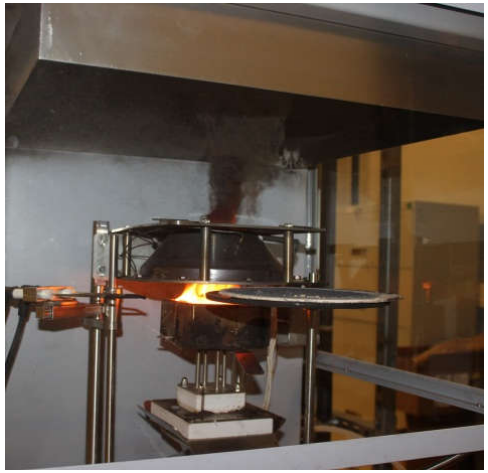


Setup for flexure testing of VER specimens.



Short Beam Strength Testing

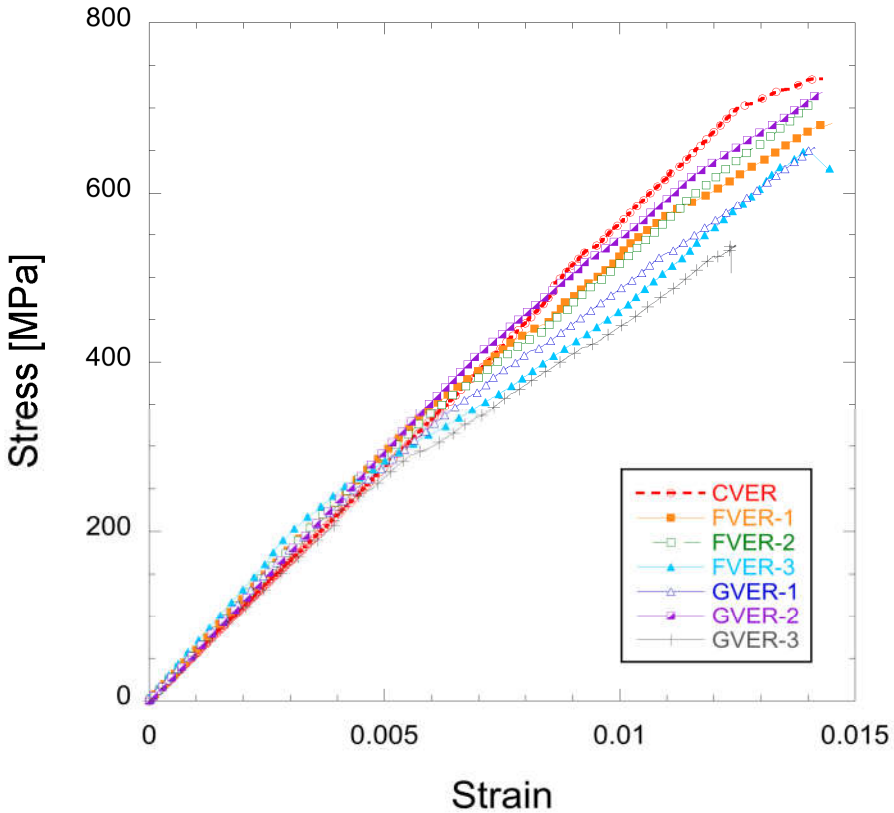
Maximum burning of the sample during cone calorimetry testing



Maximum generation of smoke during cone calorimetry testing

Tensile Testing

- Tensile strength and Modulus are fiber dominated properties

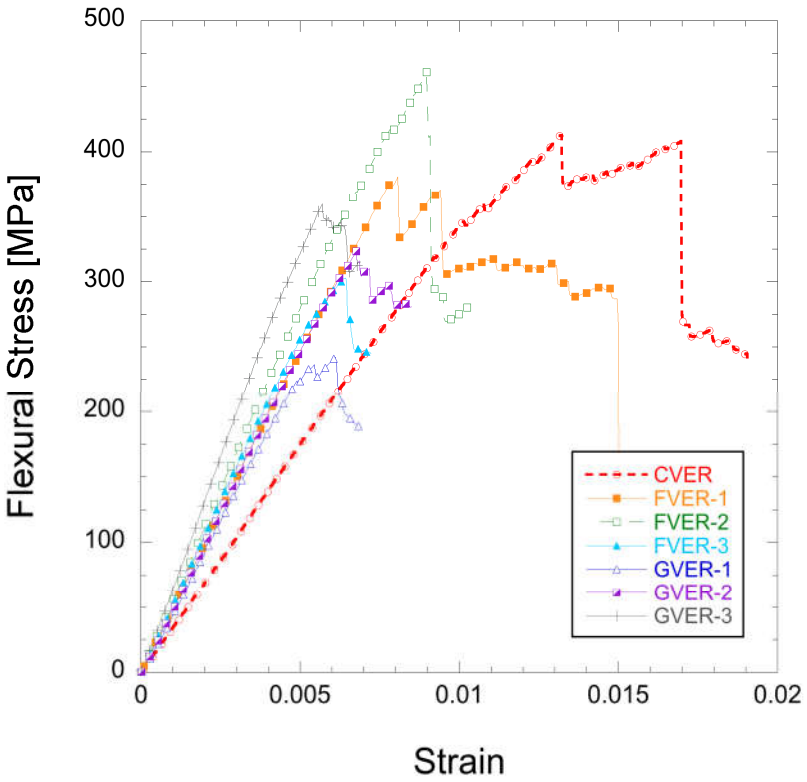


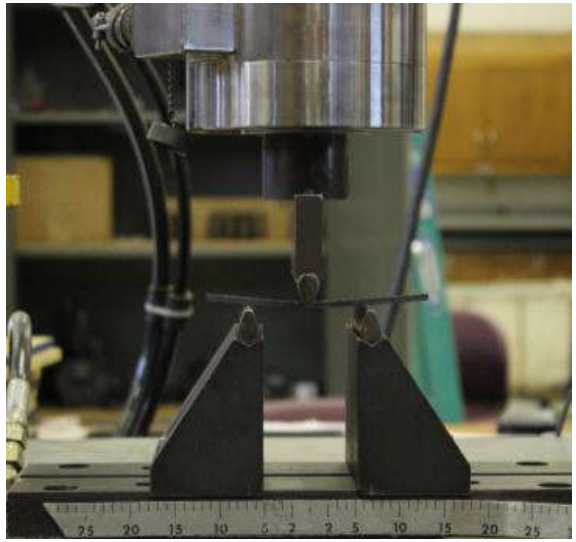
Specimen (sample size)	Fiber Volume Fraction	Tensile modulus (GPa)	Ultimate tensile strength (MPa)
CVER (n = 4)	0.41	53.0 ± 1.2	691 ± 41
FVER-1 (n = 3)	0.56	61.4 ± 2.9	669 ± 14
FVER-2 (n = 3)	0.59	60.5 ± 1.4	683 ± 22
FVER-3 (n = 3)	0.55	59.7 ± 2.8	684 ± 26
GVER-1 (n = 3)	0.55	59.0 ± 1.2	681 ± 35
GVER-2 (n = 3)	0.50	57.9 ± 1.4	692 ± 19
GVER-3 (n = 3)	0.48	52.3 ± 1.8	558 ± 14

All resins show good performance in this orientation. Low fiber volume fraction and shorter pot life explain low modulus for CVER

Flexural Testing

- Flexural Strength and modulus are mixed mode dependent





Specimen (sample size)	Fiber Volume Fraction	Flexural strength (MPa)	Flexural modulus (GPa)
CVER (n = 5)	0.42	422 ± 8	34.1 ± 1.3
FVER-1 (n = 3)	0.54	398 ± 15	49.7 ± 0.5
FVER-2 (n = 3)	0.56	446 ± 18	49.5 ± 2.5
FVER-3 (n = 3)	0.56	263 ± 9	46.4 ± 0.9
GVER-1 (n = 3)	0.56	190 ± 9	44.6 ± 2.0
GVER-2 (n = 3)	0.57	363 ± 34	49.8 ± 2.0
GVER-3 (n = 3)	0.59	373 ± 17	63.3 ± 1.9

All 6 of the bio-derived resins show excellent modulus. 4 of the 6 FVER/GVERs show excellent flexural strength. Low fiber volume fraction explains low modulus for CVER

Short Beam Strength Testing

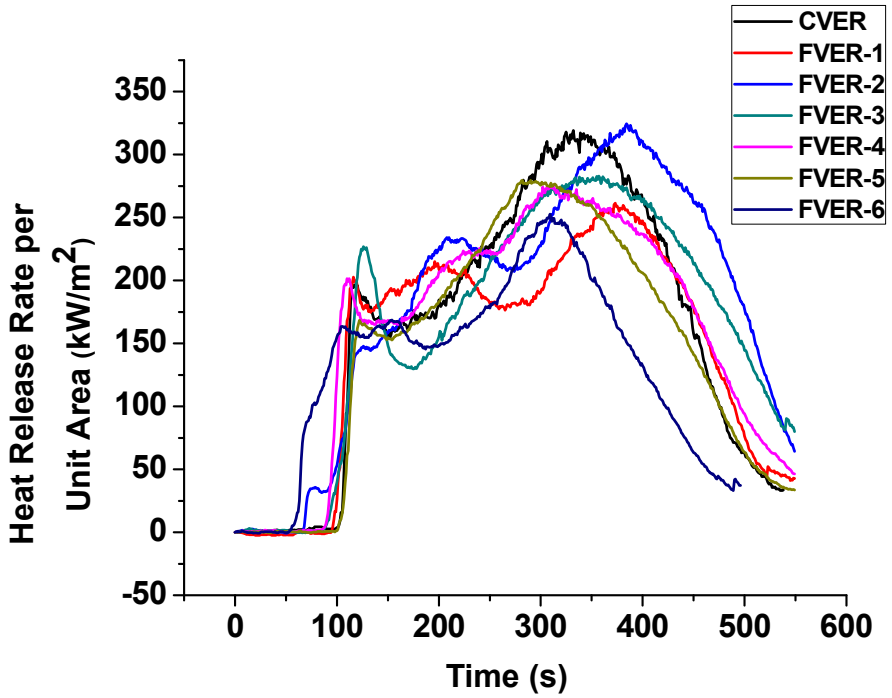
- Short beam strength is resin dominated

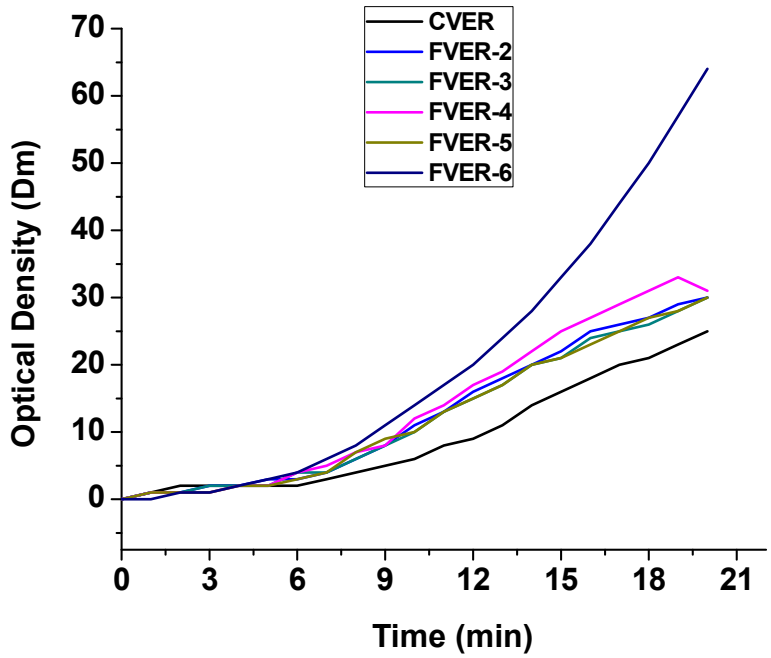
Specimen (sample size)	Short beam strength (MPa)
CVER (n = 5)	32 ± 3.0
FVER-1 (n = 5)	31.6 ± 2.0
FVER-2 (n = 3)	35 ± 0.6
FVER-3 (n = 3)	23.7 ± 1.5
GVER-1 (n = 3)	18.5 ± 0.4
GVER-2 (n = 3)	30.8 ± 2.1
GVER-3 (n = 3)	31.4 ± 0.9

Short beam strength values are consistent with the flexural strength values

Flammability Testing

- ASTM E1354
- 2 key parameters are typically of most interest
  - Avg. Heat Release Rate
  - Smoke Density

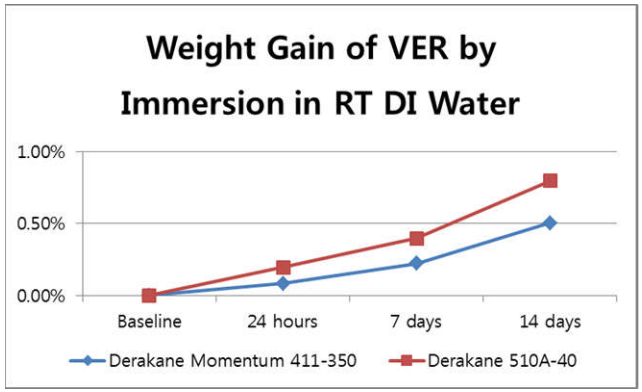


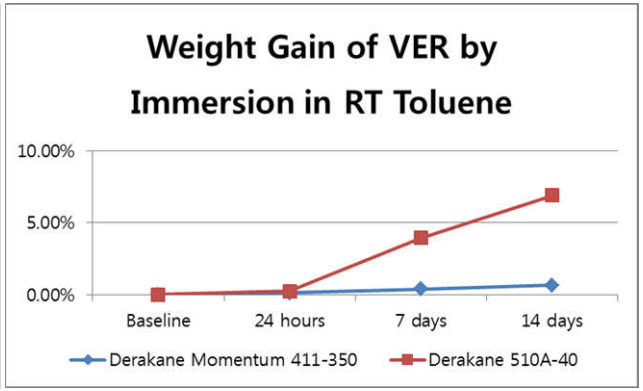


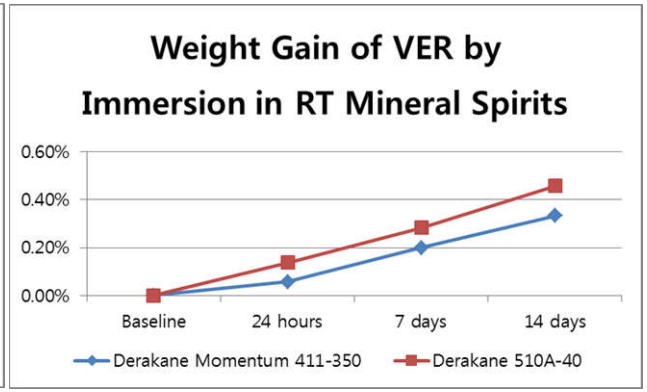
Peak HRR and Avg. eff. heat of combustion is lower for all bio-derived resins indicating better flammability performance. All 6 samples have comparable time to ignition values except FVER-6.

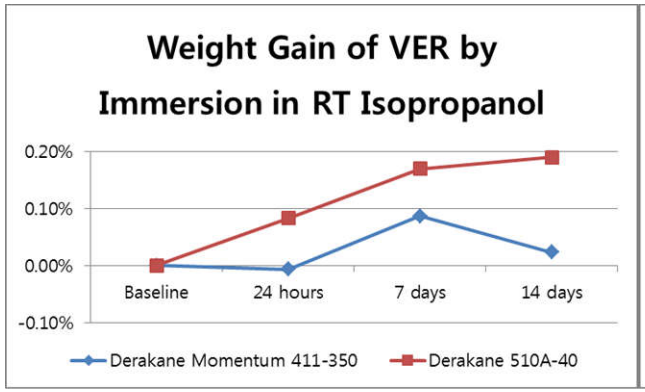
Fluid Uptake Studies

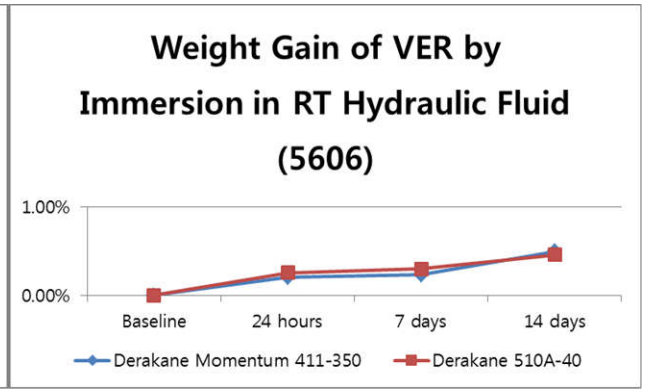
Uptake of water, hydraulic fluids, or hydrocarbon fuels by Green Vinyl Ester Resins

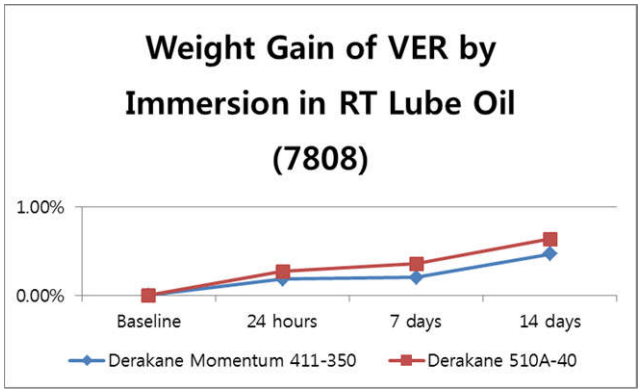




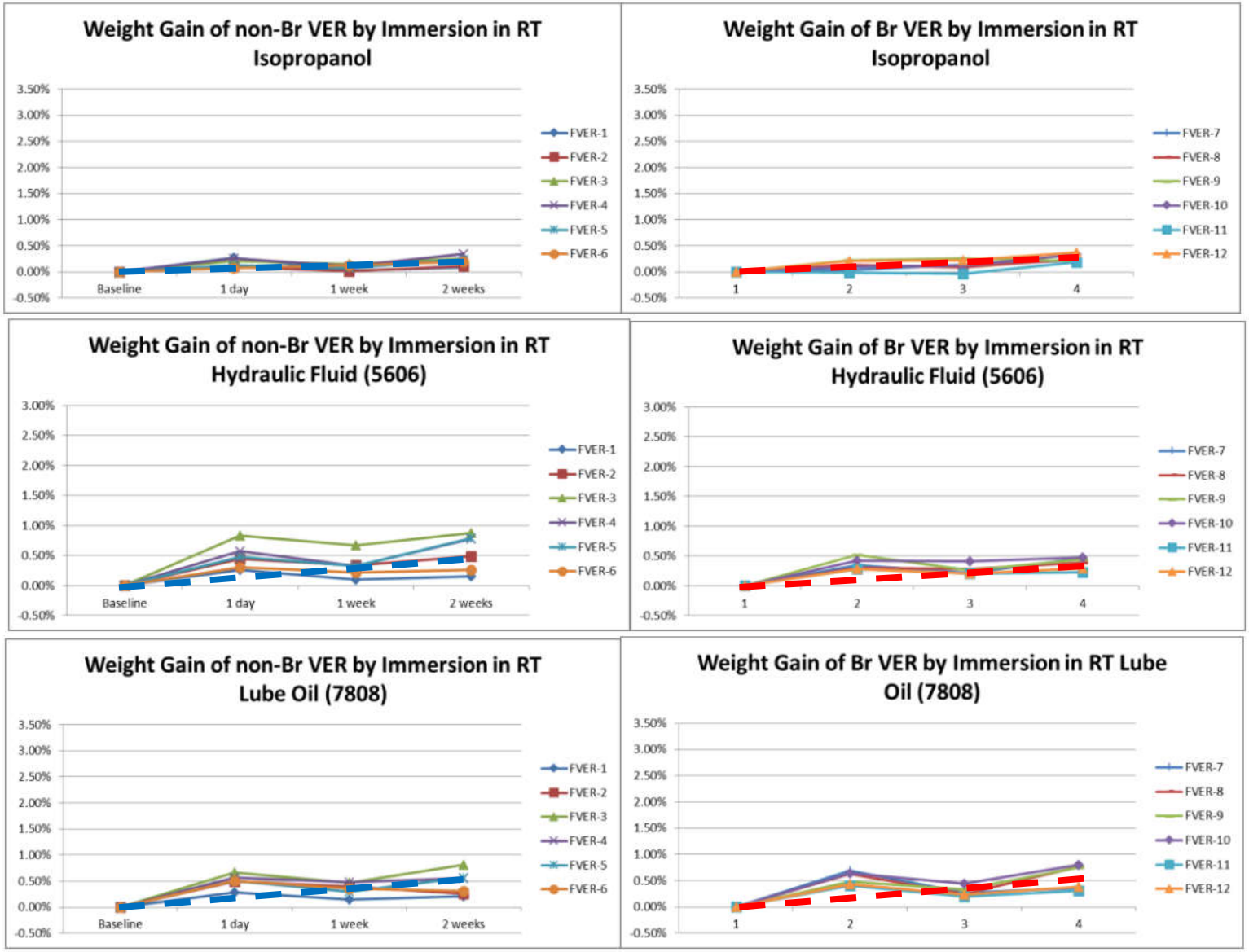








Fluid Uptake Studies (UML)



Conclusions

- Most of the bio-derived resins show similar if not better mechanical properties than the commercially available resin
- All bio-derived resins have a significantly longer pot life than the commercial resin (CVER)
- Ease of processing for manufacturing composites using VARTM becomes easier as the GVER content increases.
- Most of the bio-derived resins show improved flammability properties in comparison with the commerical resin
- Order of Resin Performance→ FVER 2 > FVER 1 > GVER 2 > GVER 3 (This is only one perspective as there are multiple determining factors)

Specimen (sample size)	Flexural modulus (GPa)	Flexural strength (MPa)
CVER (n = 5)	34.1 ± 1.3	422 ± 8
FVER-2 (n = 3)	49.5 ± 2.5	446 ± 18

FVER-2 shows a 6% increase in flexural strength over CVER

Specimen (sample size)	Short beam strength (MPa)
CVER (n = 5)	32 ± 3.0
FVER-2 (n = 3)	35 ± 0.6

FVER-2 shows a 9% increase in short beam shear strength over CVER

Sample ID	Average Effective Heat of Combustion (MJ/kg)	Peak HRR (kW/m^2)
CVER (n = 3)	30	317
FVER-2 (n=3)	27	333

FVER-2 shows a lower heat of combustion and a similar peak HRR

Teaming Partners

Team	Person In-Charge (Point of Contact)	Role
UMass Lowell	Dr. Yongwoo Lee (PI) Dr. Priyank Shah (Co-PI) Dr. Namjoon Kim Dr. Akshay Kokil	Developing GVER from biowaste and coordinating research teams
UMass Lowell	Prof. Hansen/Mr. Sid Dev	Developing GVER composites using VARTM
UMass Lowell	Prof. David Ryan	Developing analytical technique for characterization of pyrolysates
UMaine Orono	Prof. W. DeSisto	Fluidized fast pyrolysis to generate bio-oils: New Partnership
UMass Lowell	Prof. H. Wong	GC-MS analysis prior to LC-MS analyses for separation
Bentley University	Prof. Ryan Bouldin	Business development
NAVAIR	Dr. John Brennan	Developing composites with flame retardant ability
NAVSEA	Mr. Usman Sorathia	Examine flame retardant properties of the composites
R.F. Kovar & Associates	Dr. Robert F. Kovar	Provide technical expertise to UML team.
Ashland Inc.	Dr. Stevens, Dr. Joe Fox	Industrial teaming partner
Maine Standard Biofuels	Mr. Jarmin Kaltsas	Provide unrefined glycerin obtained during biodiesel manufacturing
Flambeau River Paper LLC	Mr. Bill Tomczak	Provide lignin from paper industry waste stream
Maine Seed Company	Mr. Tate McPherson	Provide lignin from different plant source
Dixie Chemical Co.	Mr. Alexander T. Grous (Dr. John La Scala-ARL)	MFAs as Styrene replacements-New Partnership
TPI Composite, Inc.	Mr. Stephen C.Nolet	New Partnership

Acknowledgement

- Dr. Robin Nissan (SERDP)
- Financial support through SERDP

  Contract # W912HQ-13-C-0067

Appendix N

Properties of Bio-derived Vinyl Ester Resin based Composites

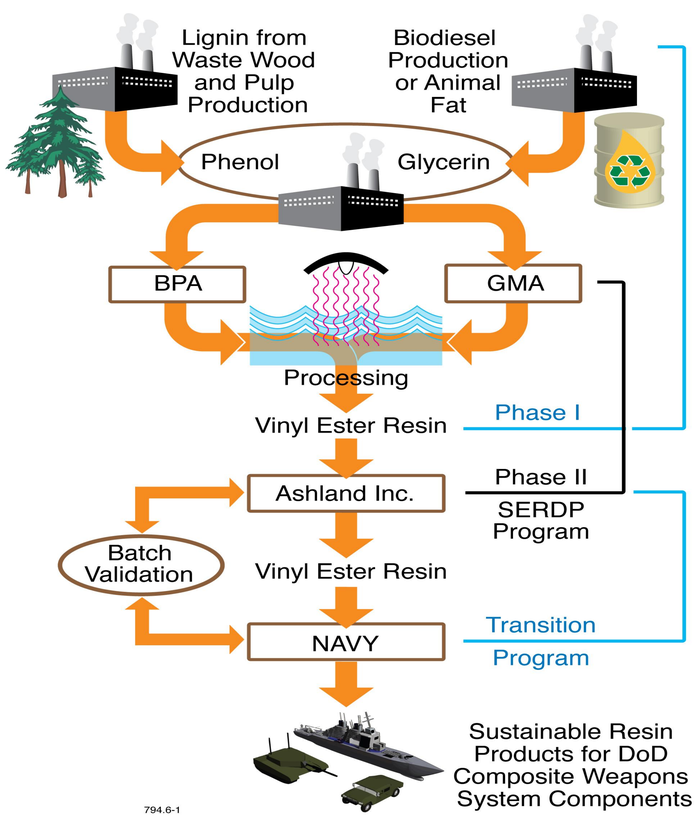
Siddharth Dev[2], Priyank Shah[1], Akshay Kokil[1], Namjoon Kim[1], Christopher Hansen[2], and Yongwoo Lee[1]
U-Mass Lowell, Depts. of Chemistry[1] and Mechanical Engineering[2], Lowell, MA

Abstract

A green vinyl ester resin (GVER) was formulated using a monodisperse vinyl ester created via a novel synthetic route capable of using bio-waste materials from biodiesel industries. The GVER was used as a neat resin or as blended as FVER (1-20%, 2-50 %, and 3-80%) with a commercial vinyl ester resin. The formulated GVER (FVER) as blended reaches a similar viscosity as the commercial resin with only half the styrene monomer content thereby reducing the volatile organic compounds associated with manufacturing. The mechanical performance of carbon reinforced GVER compared favorably with commercial resin and provide a route for composites manufacturing from sustainably sourced vinyl ester matrix. (S. Dev et al., **J. Appl. Polym. Sci**., Nov. **2016**)

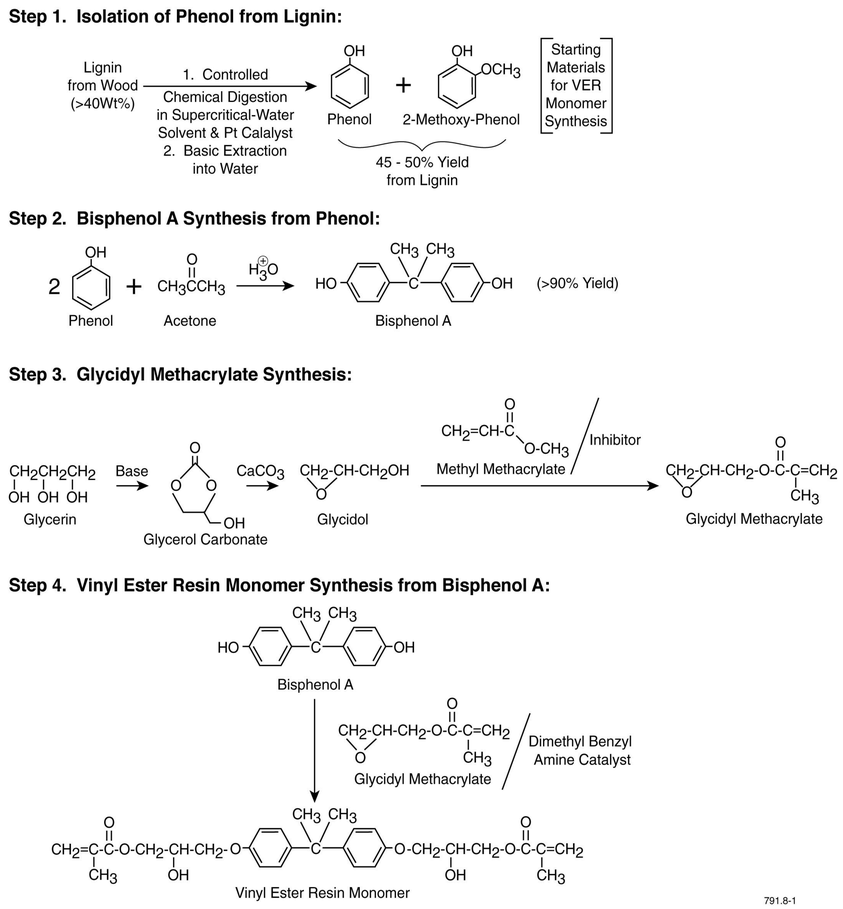
VER based Green Composites

A. Green Approach



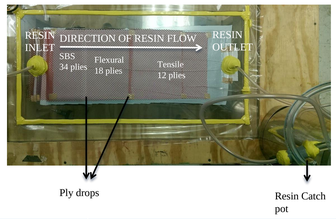
Phase I and II: Sustainable Green Vinyl Ester Resin rom Renewable Resources (WP-1755, WP-2317); 2011, 2013

B. Green VER



*P. N. Shah, et al. Environmentally Benign Synthesis of Vinyl Ester Resin from Biowaste Glycerin, **RSC Advances**, 2015, 6, 38673*

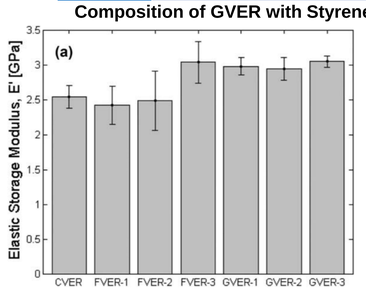
C. Green VER Composites



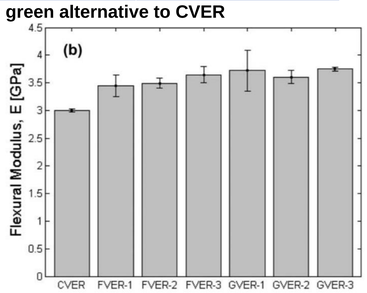
Samples manufactured to ASTM standards (D3039, D7264, D2344) for tensile, flexural and short beam shear strength.

Name[a]	Formulated GVER (wt. %)	Derakane Momentum 411 350 (wt. %)	Styrene Fraction (wt. %)
CVER	-	100.0	40.0
FVER-1	20.0	80.0	40.0
FVER-2	50.0	50.0	40.0
FVER-3	80.0	20.0	40.0
GVER-1	100.0	-	40.0
GVER-2	100.0	-	30.0
GVER-3	100.0	-	20.0

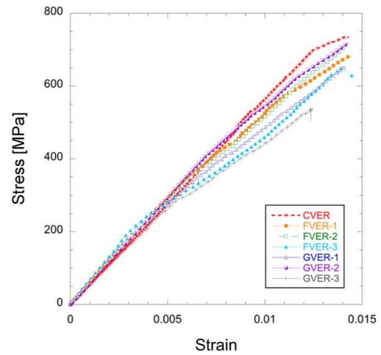
Composition of GVER with Styrene Content as green alternative to CVER



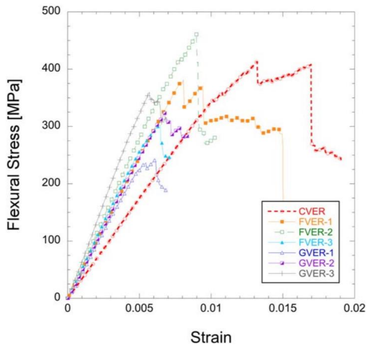
Elastic storage modulus (E') at RT in VER compositions.



Flexural modulus (E) at RT in VER compositions.



Stress vs. strain plot for representative tensile curves for carbon fiber-reinforced composites infused with CVER and GVER formulations



Flexural stress vs. strain plot for representative curves for carbon fiber-reinforced composites infused with CVER and GVER resin formulations.

Acknowledgments

Dr. Robin Nissan and SERDP for their funding (Contract # W912HQ-13-C-0067)
Drs. Patel and Kovar for their technical guidance
Prof. David Ryan for analytical expertise

Status

-Epichlorohydrin-free one-pot synthesis-Kokil. Prov. Pat. 16
-Similar or comparable mechanical strength to State of the Art
-Potential for scale-up industrial processes

Appendix O

Flame-Retardant Surfaces from Green Vinyl Ester Resin

Priyank Shah, Akshay Kokil, Robert F. Kovar, Yongwoo Lee (PI)
UMass Lowell, Dept. of Chemistry, Lowell, MA

Abstract

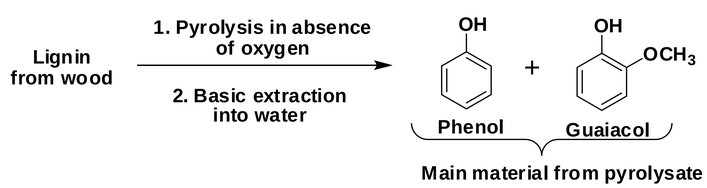
Use of composite materials for construction of DoD weapons platforms will approach 200 million pounds per year. VER is a low-cost resin that can be processed at ambient temperature using vacuum-assisted resin transfer molding (VARTM) into massive carbon-fiber-reinforced composite structures such as ship hulls and transportation vehicles. The objective of this work is to make flame retardant surfaces by developing an environmentally safe "green" vinyl ester resin (GVER) from renewable biomass wastes. Lignin was obtained from waste of wood and pulp production, while glycerin was obtained from waste stream of biodiesel production unit.

Environmentally Compliant Vinyl Ester Resin (VER) Composite Matrix Resin Derived from Renewable Resources (WP-1755), SERDP, 2011

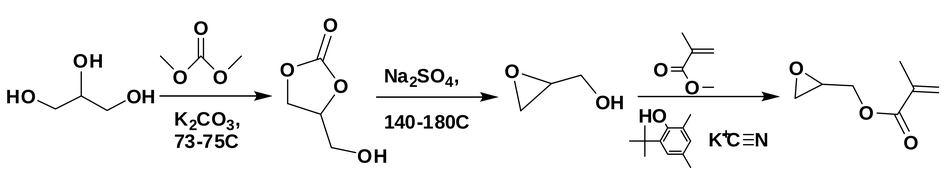
Synthesis and Process Experimentation

A. Chemical Synthesis Procedures

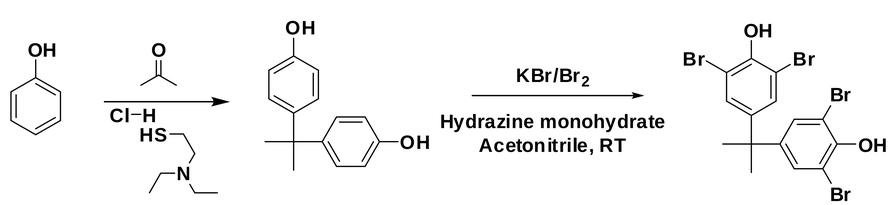
Step 1. Isolation of Phenol from Lignin



Step 2. Synthesis of glycidyl methacrylate from glycerin

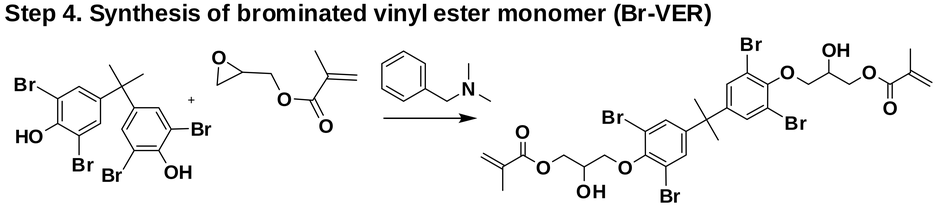


Step 3. Synthesis of tetrabromobisphenolA from phenol



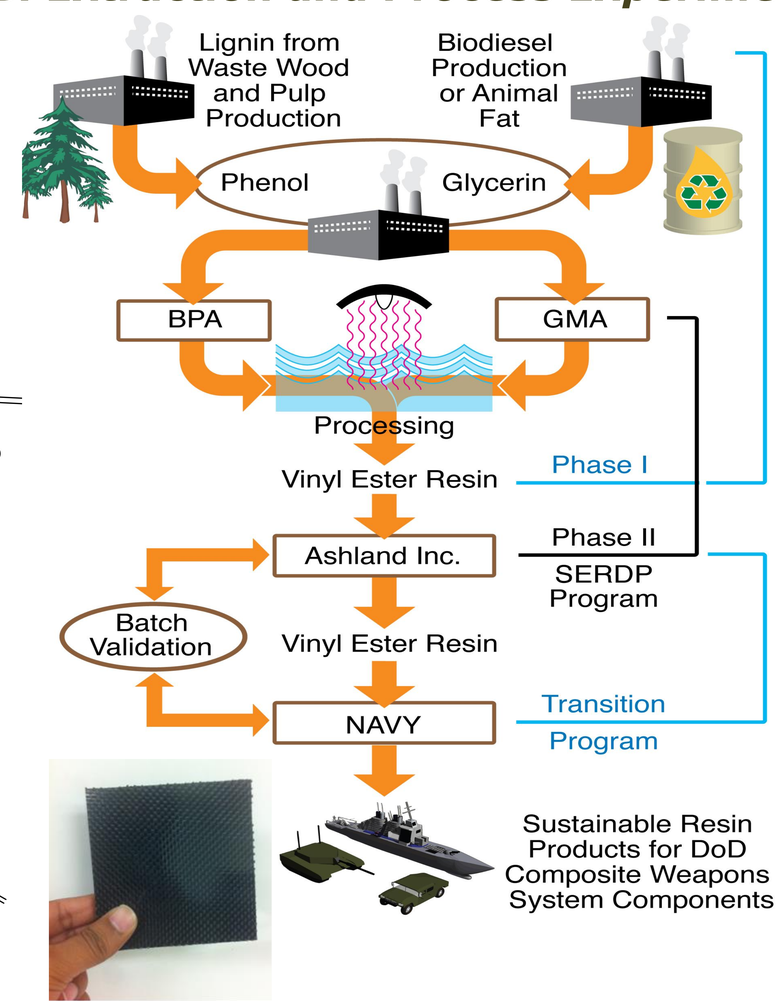
Munehisa Okutsu, T. K. United States, 2002; Vol. 6,495,703 B1.
John David Malkemus, e. a. United States, 1958; Vol. 2,856,413.

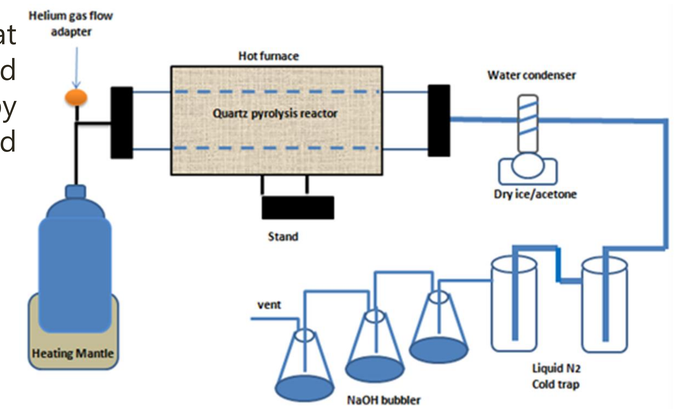
Step 4. Synthesis of brominated vinyl ester monomer (Br-VER)



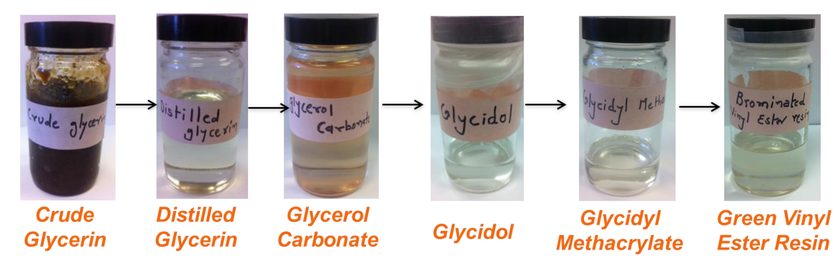
R.L. Bowen et al., US Provisional Patent 3,179,623, Apr. 1965.

B. Extraction and Process Experimentation





Laboratory Scale Fast Flow Pyrolysis Set-up



Brominated Green Vinyl Ester Resin from Biowaste Glycerin

Conclusions

- Demonstrated feasibility of producing environmentally compliant vinyl ester from renewable biowaste lignin and glycerin
- Eliminated the use of toxic epichlorhydrin and dependence on petroleum products
- Showed potential for scale-up industrial processes

Acknowledgments

We would like to thank Dr. Robin Nissan and SERDP for their support and funding (Contract # W912HQ-13-C-0067) and Dr. Navin Patel for his significant contribution to phase I.

250th American Chemical Society National Meeting, August 16-20, Boston

Appendix P

Green Vinyl Ester Resin from Renewable Biowaste Glycerin

Priyank Shah, Akshay Kokil, Robert Kovar, Mahesh Jayamanna, David Ryan and Yongwoo Lee

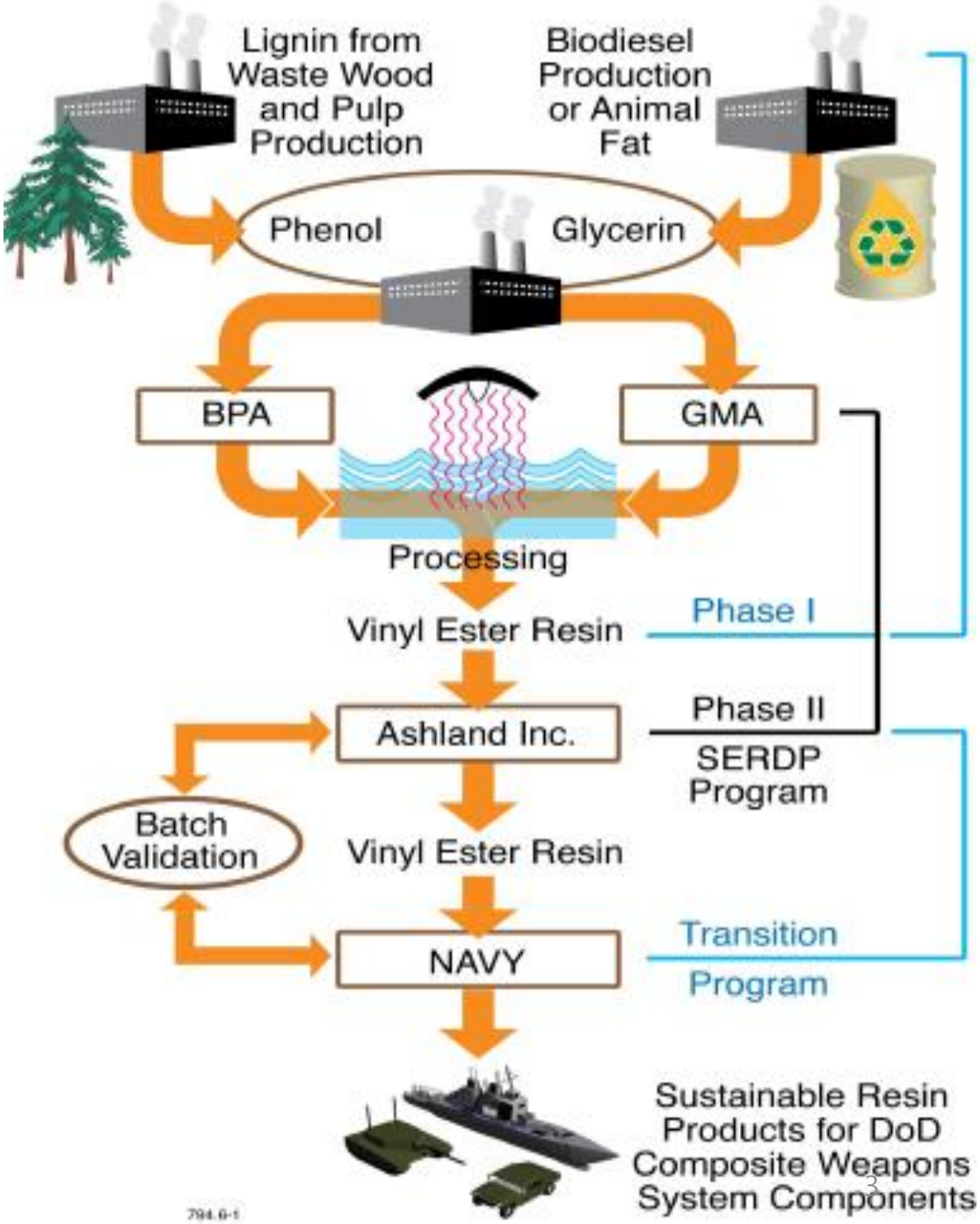
June 11, 2015

University of Massachusetts Lowell
UMASS

Content

- **Introduction**
  - ✓ Objective
  - ✓ Biowaste material and their supplier.
  - ✓ Benefits
  - ✓ Technical Approach
- **Pyrolysis Setup and Phenol Isolation**
- **Synthesis of Bisphenol A (BPA)**
- **Synthesis of Glycidyl Methacrylate (GMA) from Waste Glycerin**
- **Synthesis and Characterization GVERs**

Objective


Lignin from Waste Wood and Pulp Production
Biodiesel Production or Animal Fat
Phenol
Glycerin
BPA
GMA
Processing
Vinyl Ester Resin
Phase I
Ashland Inc.
Phase II
SERDP Program
Batch Validation
Vinyl Ester Resin
NAVY
Transition Program
Sustainable Resin Products for DoD Composite Weapons System Components

Bio-waste Supplier

Lignin:

Two samples of lignin will be provided by Flambeau River Papers LLC. (Park Falls, WI) and Maine Seed Company (Mapleton, ME)

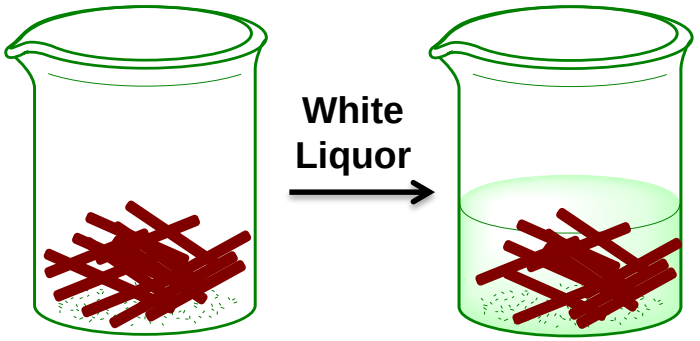
(a) Sugared lignosulfonate
(b) desugared lignosulfonate
(c) Black liquor.

Glycerin:

Two samples may be provided by Maine Standard Biofuels (Portland, ME)

(a) Crude glycerin
(b) Refined glycerin

Pyrolysis of Lignin

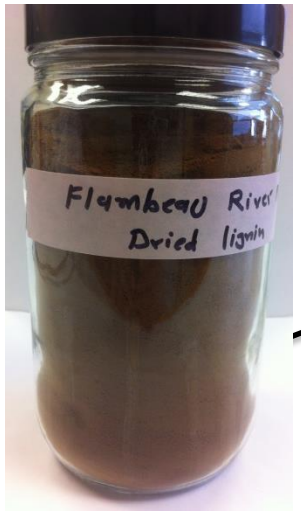


Cellulose
(paper making)

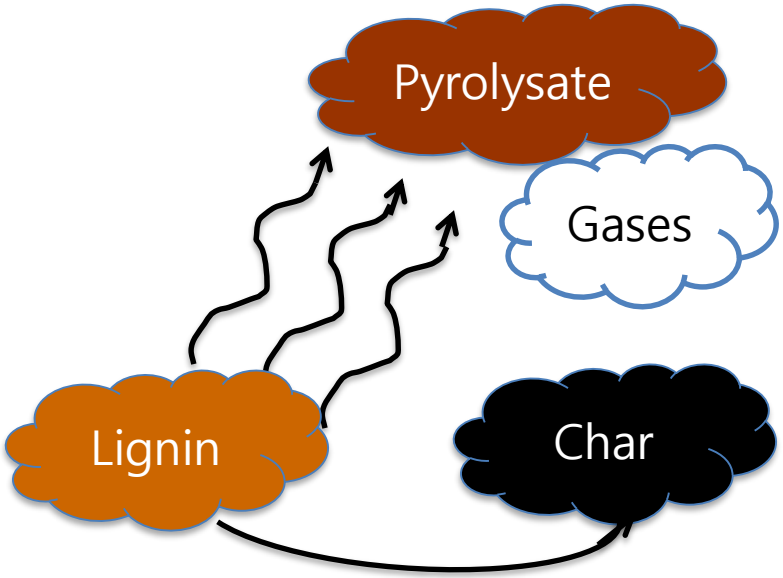
Hemicellulose

Lignin

- Multi-polarity related products (surfactant/emulsifier and dispersant)
- Materials (Binders, thermosets)
- Agriculture
- High purity/value applications (food and cosmetics application, anti-oxidative and antibacterial)



Samples of lignin provided by Flambeau River Papers LLC (Park Falls, WI) and Maine Seed Company (Mapleton, ME)

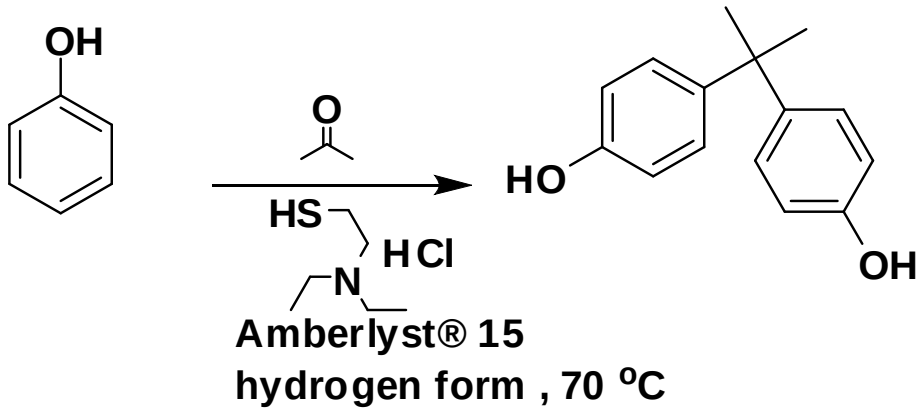


Pyrolysis Concept

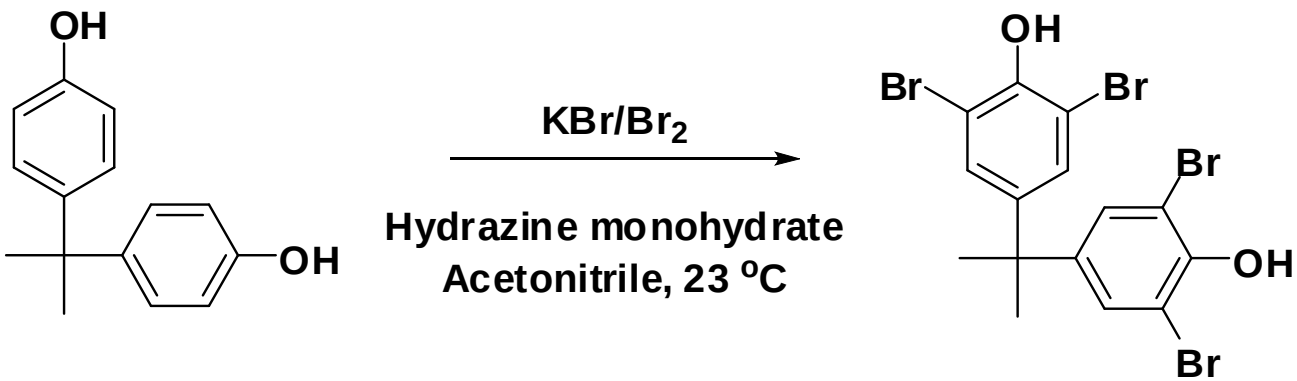
http://www.ili-lignin.com/

BPA and Brominated-BPA

Synthesis of BPA



Synthesis of TBBPA



Purification by precipitation in water

Introduction to Glycerin

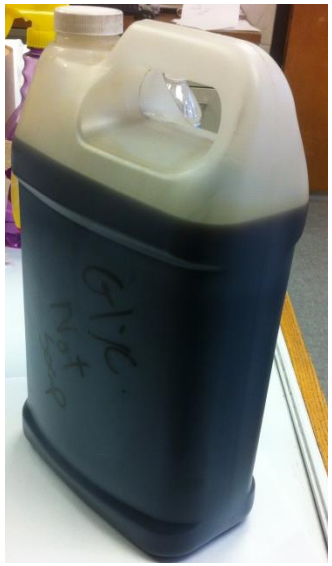
Vegetable Oil, Animal Fat (Triglycerides)[1] →

- **Water, NaOH (Hydrolysis, Saponification)** → **long-chain carboxylate salts used as soaps**
- **Alcohol, NaOH Transesterification** → **esters of fatty acids used as biodiesel**

+ glycerin

- By 2020, the production of glycerin will be six times higher than its demand.[2]
- Disposal of glycerin in the waste stream would require increasing expenditures for biodiesel industry

We are using crude glycerin from bio-diesel waster stream provided by Maine Standard Biofuels (Portland, Maine)



)."Clearing the Way for Byproduct Quality: Why quality for glycerin is just as
Biodiesel Magazine
Bernd; Steinberner, Udo; Dilla, Wolfgang; Karinen, Reetta (2006). "Glycerol".
of Industrial Chemistry. doi:10.1002/14356007.a12_477.pub2. ISBN 3527306730.

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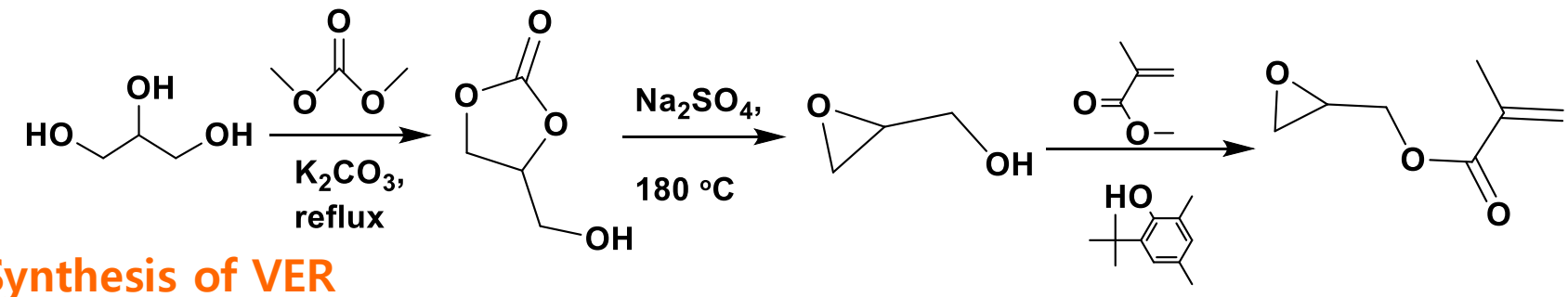
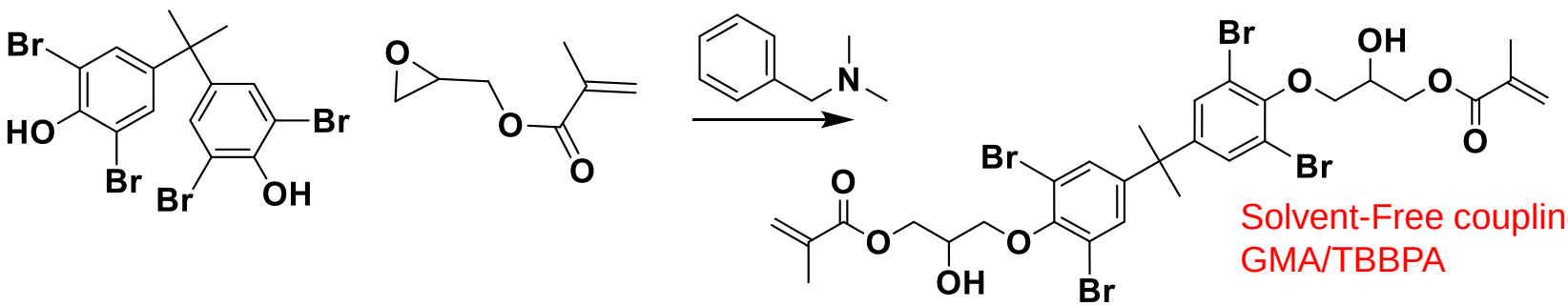
Synthesis of GVER

Synthesis of GMA

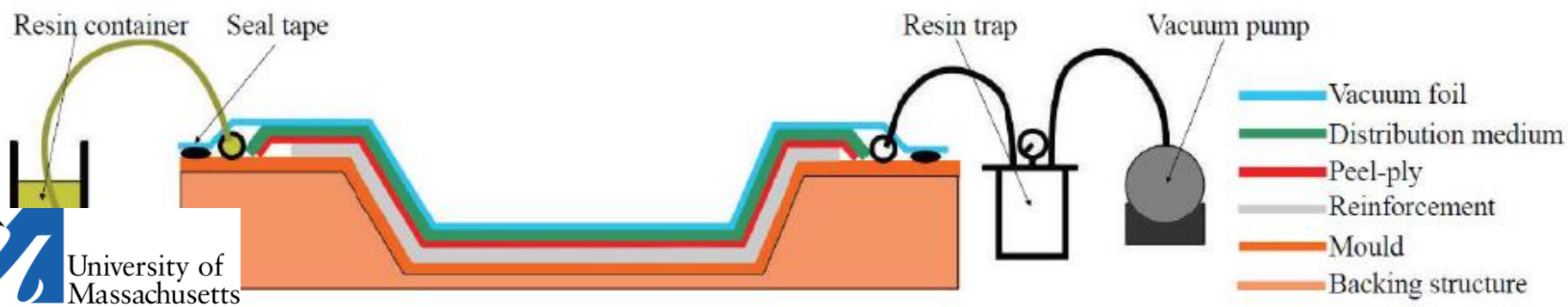


Synthesis of VER



Solvent-Free coupling of GMA/TBBPA

Carbon fabric reinforced panel fabrication by VARTM



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Technical Approach

1) Recovery of phenol from lignin and/or wood wastes.

2) Conversion of the recovered phenol into bisphenol A.

3) Synthesis of glycidyl methacrylate (GMA) from waste glycerin.

4) Synthesis of GVER from BPA or TBBPA and GMA.

Environmental and Economical Benefits

- **Elimination of US dependence upon foreign oil** for manufacturer of critical military and commercial composites.
- **Replacement of epichlorohydrin** with GMA yields an environmentally benign synthesis.
- Production of BPA and GMA from nonpetroleum bio-wastes will provide sustainable raw materials **for production of other high-value chemical products.**
- Finally, the proposed use of biomass waste **will not affect the nation's food supply**.
- Pyrolysis of phenol produces **many valuable phenolic derivatives**, which will expand new markets and makes the process more economical.

Technical Benefits

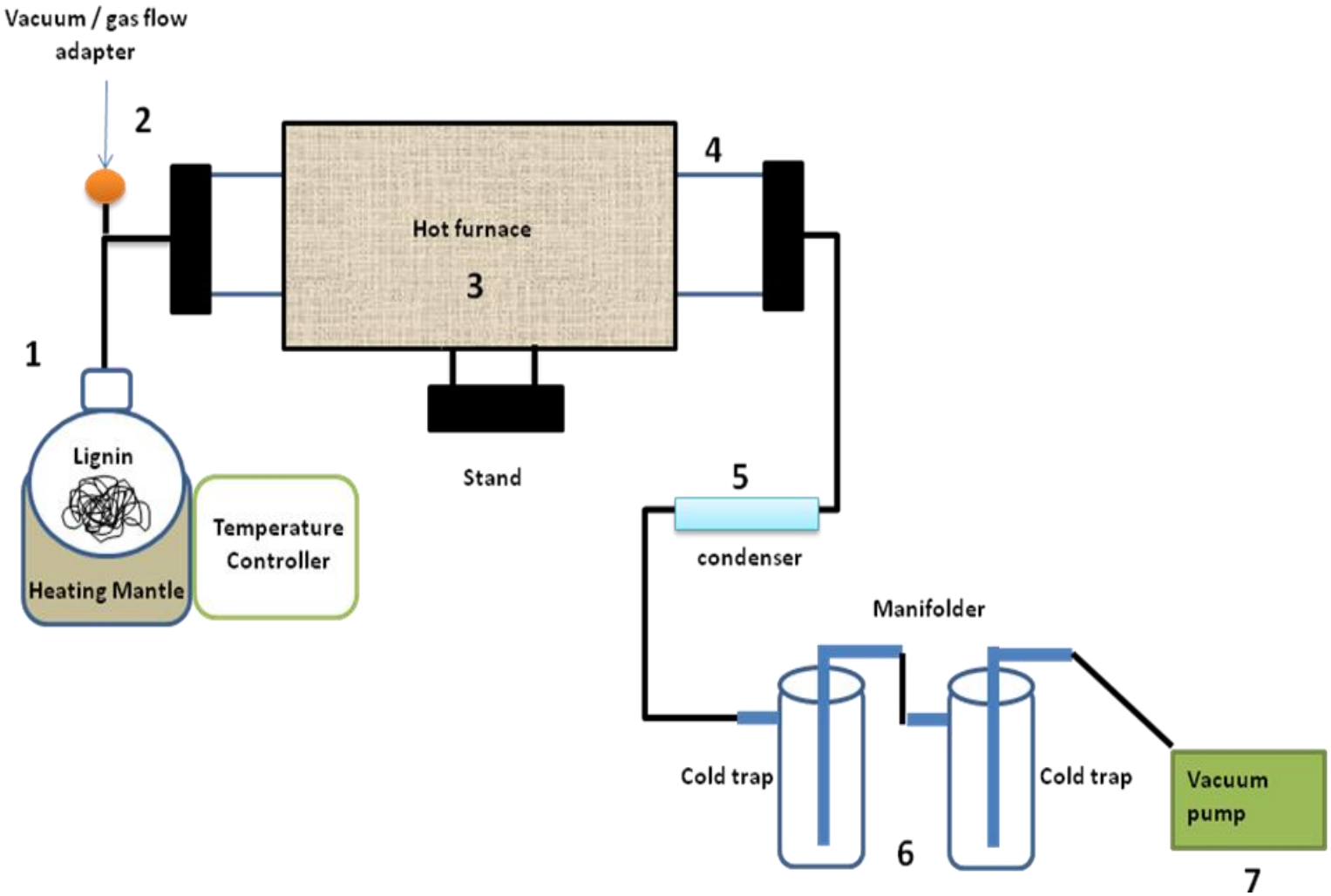
- **Solvent-free** synthesis of brominated vinyl ester resin monomer.

- GVER from TBBPA and GMA forms only **pure, low molecular weight product**,
  - Good for VARTM processing
  - Reduces usage of reactive diluent (styrene)
  - Increases wetting of resins.
  - Decrease voids/bubbles in composites

- For VARTEM, longer chain of oligomer is not suitable, so our GVER can be added to longer chained VER in different amount. **This will improve its strength and ease for VARTM processing**.

- Low MW GVER can be mixed in different ratios with high MW GVER to improve properties of the composites.

Pyrolysis Setup



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Phenol Purification

Crude mixture (50ml)

↓ Diethyl Ether (200ml)
Filtration

Diethyl Ether Layer

↓ 0.1N NaOH

Diethyl Ether Layer ► discard

Basic Aqueous Soln.

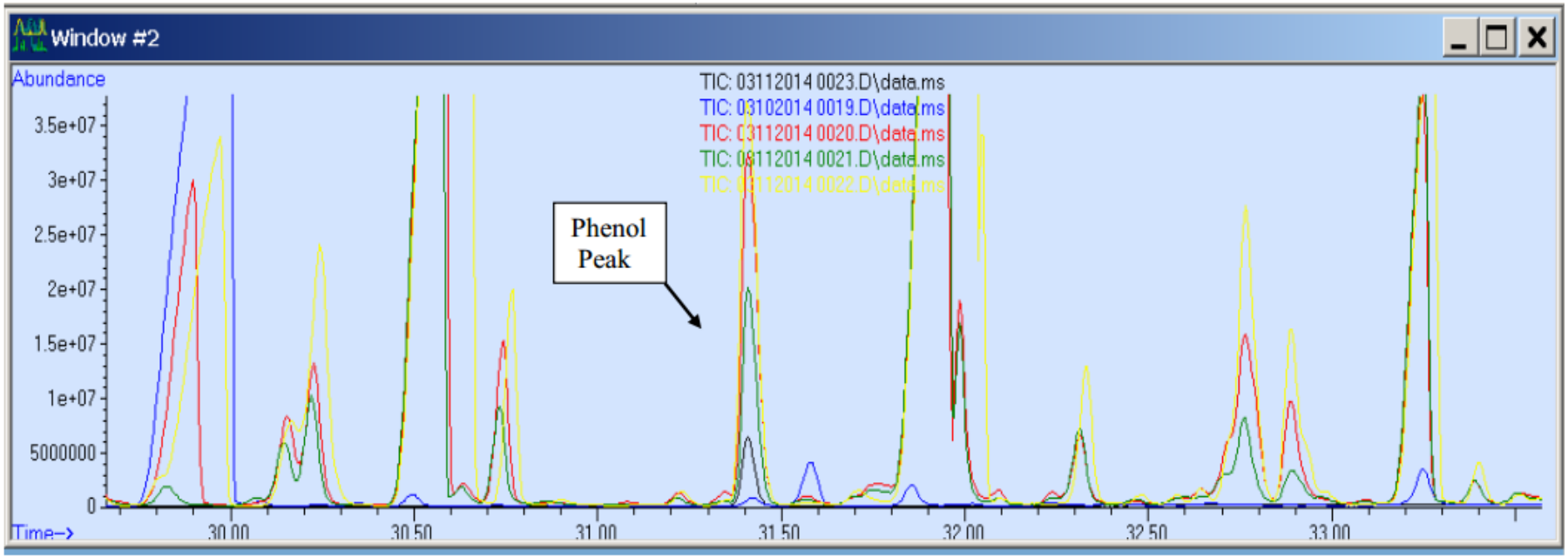
↓ 0.1N HCl

Acidic Aqueous Soln.

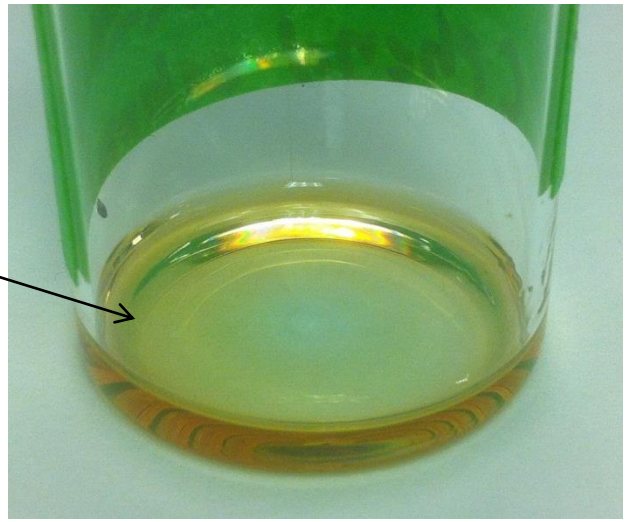
↓ 3 x Diethyl Ether(200ml)
extraction

Diethyl Ether Layer

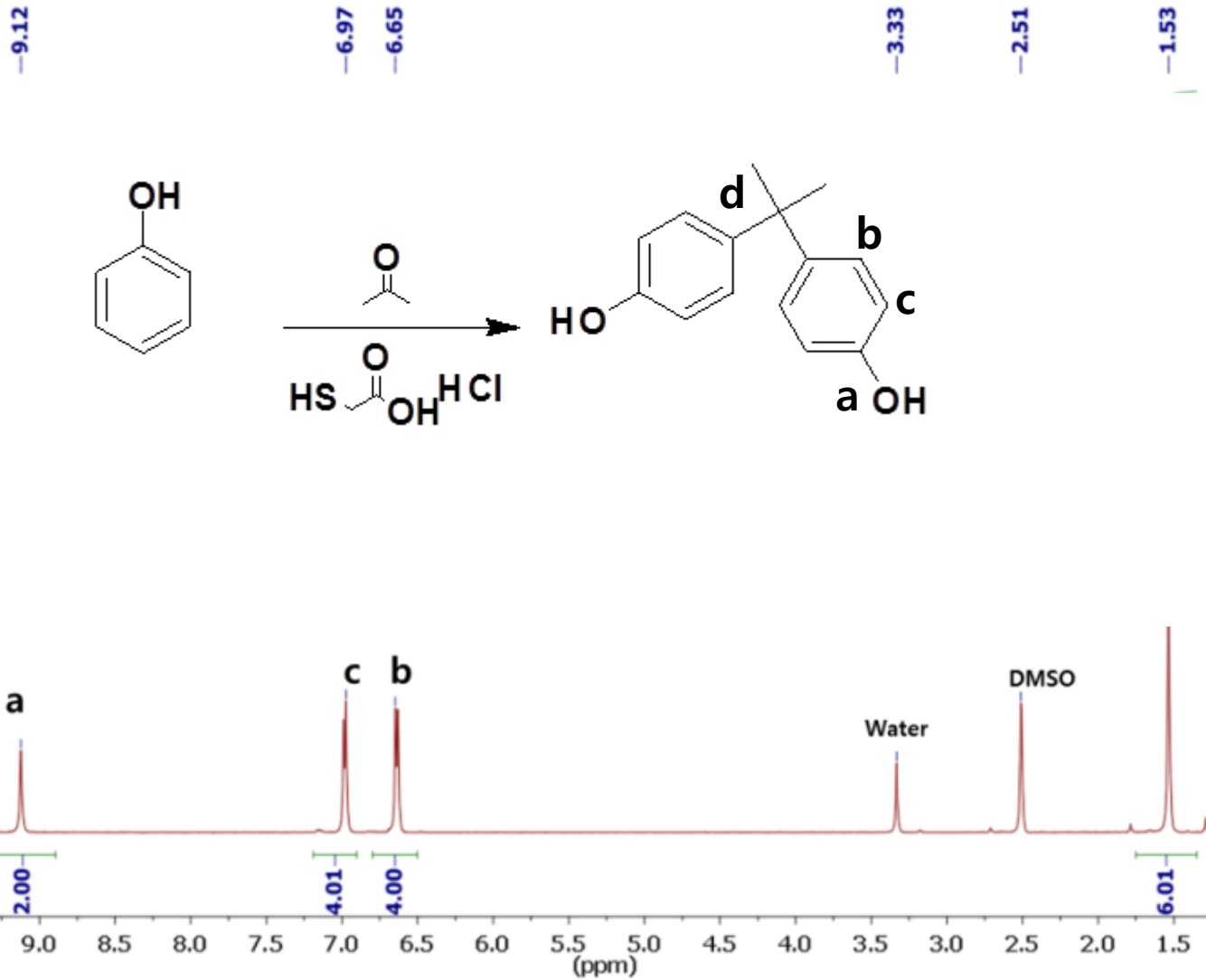
GC Chromatogram of Pyrolyzed Material



Isolated phenolic



Synthesis and ^{1}H NMR of BPA



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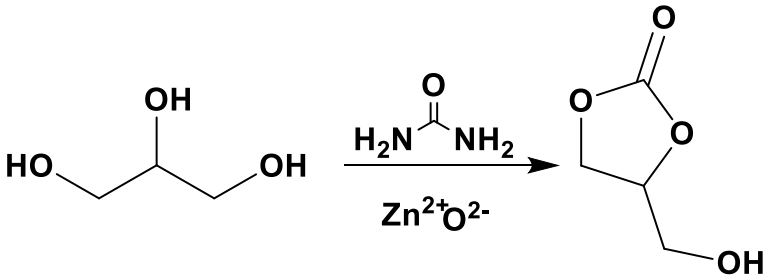
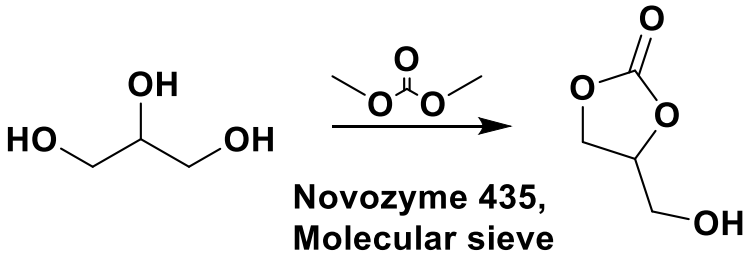
Synthesis of Glycerol Carbonate

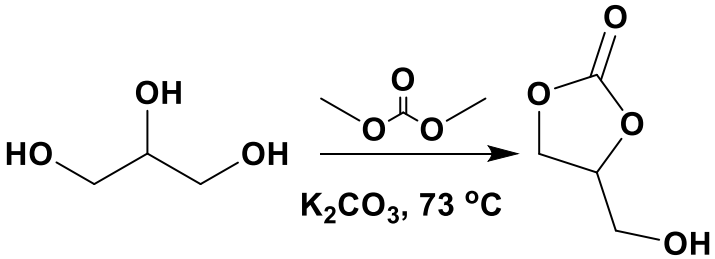
1. **In a flask with under inert condition and high pressure**



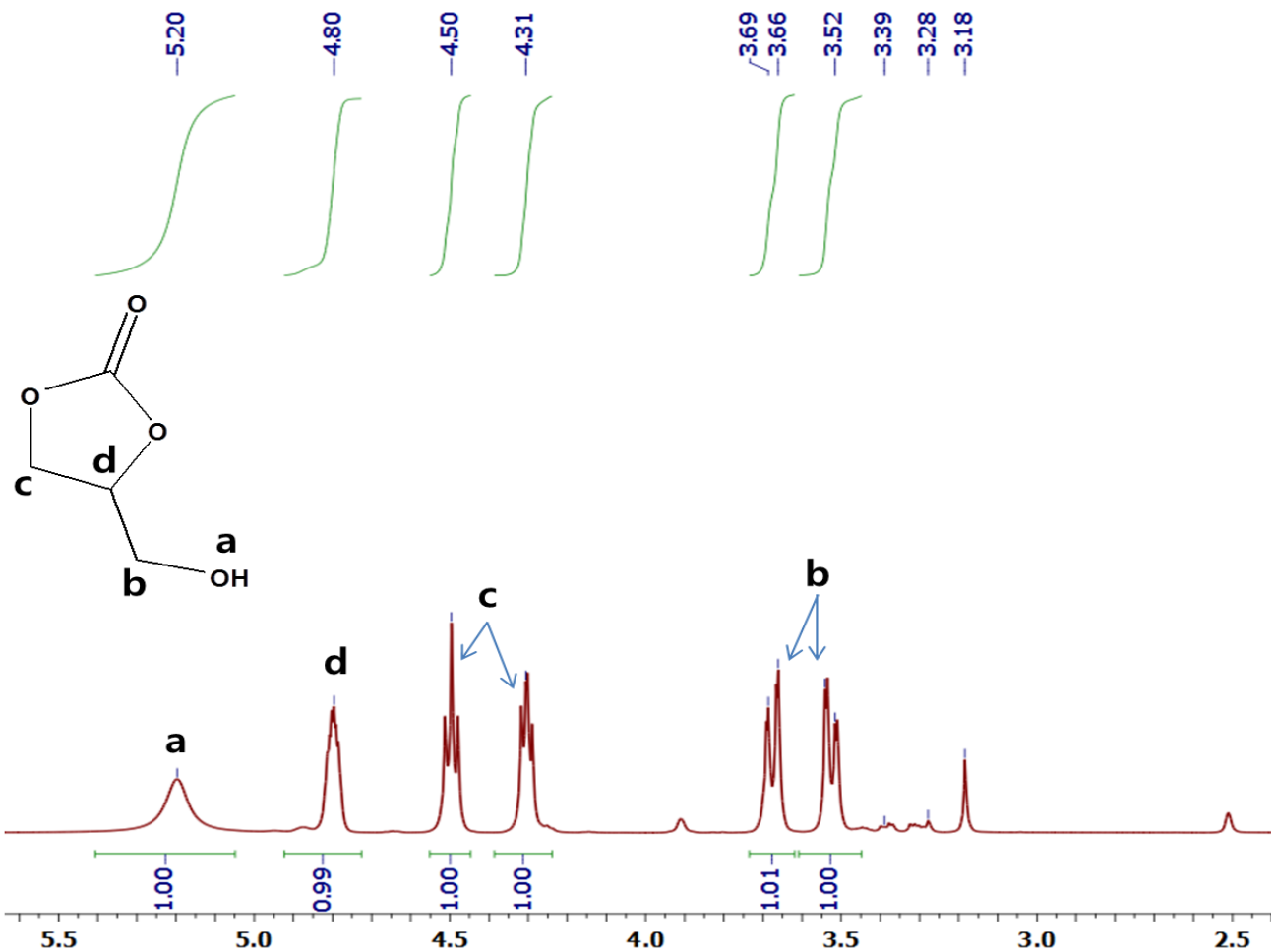
2. **Using Novozyme 435**



3. **Using DMC and K_2CO_3**

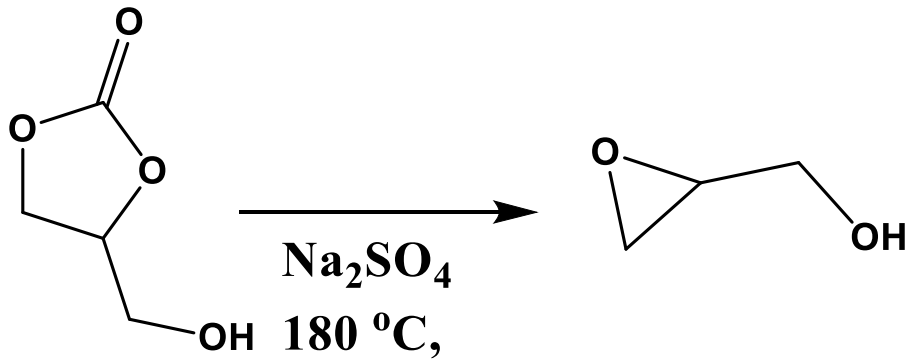


^{1}H NMR of Glycerol Carbonate

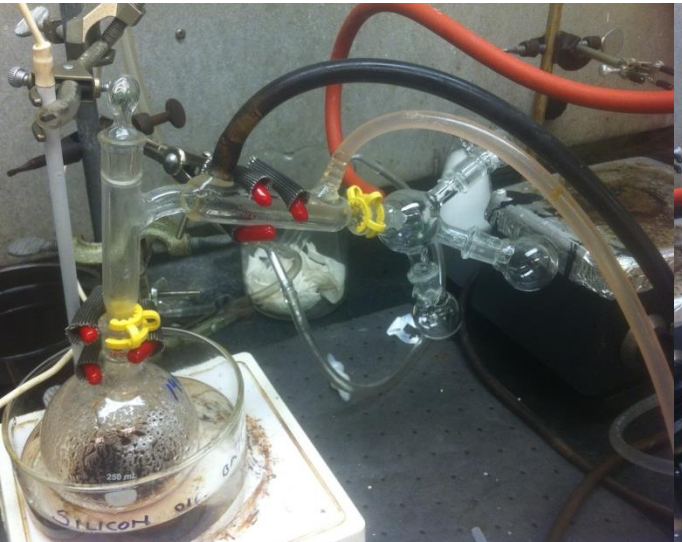


Neutralization using Ambelite IR 120-acidic resins

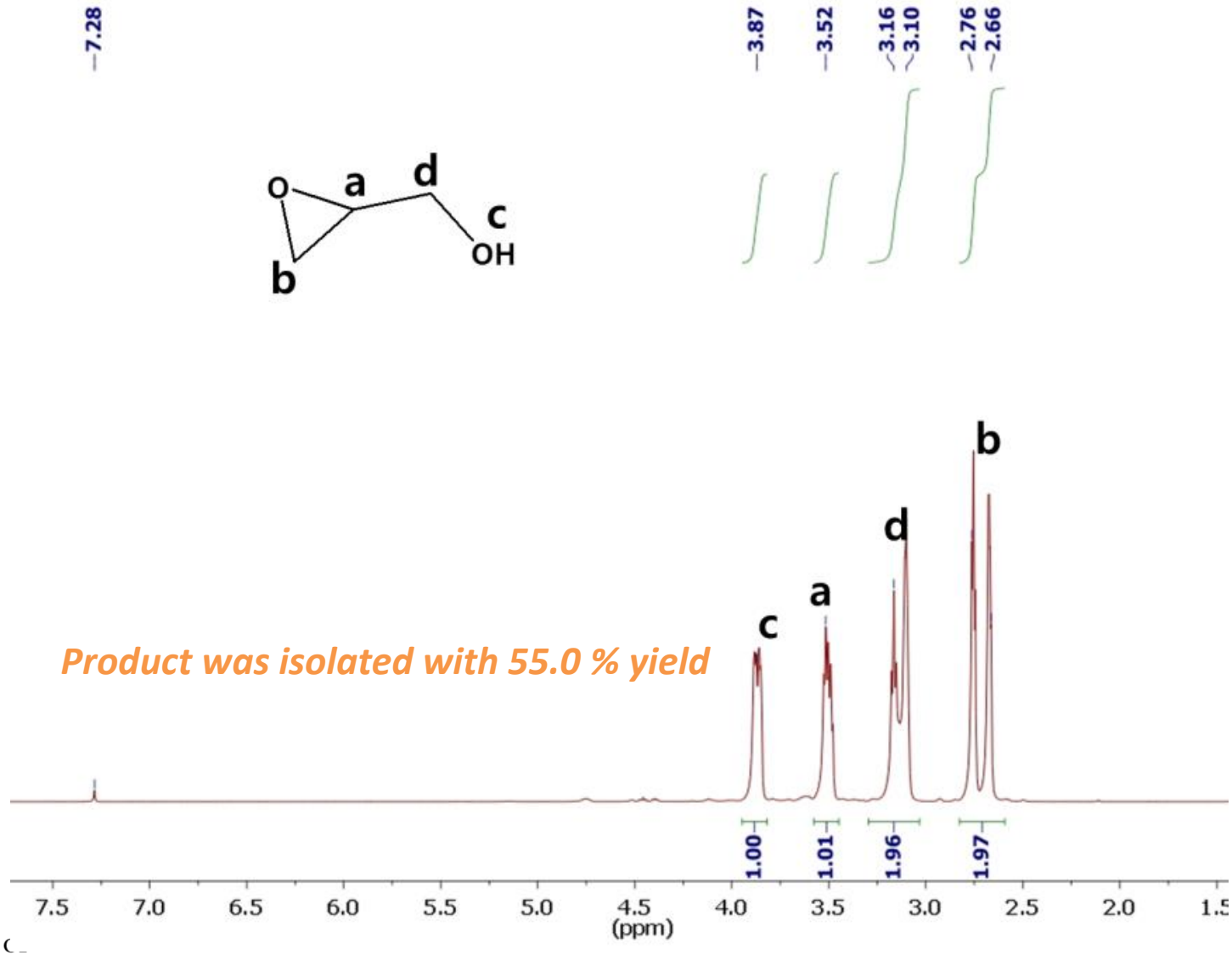
Synthesis of Glycidol



Glycerol carbonate was heated with sodium sulfate at 180C for 2 h and glycidol was distilled-off.

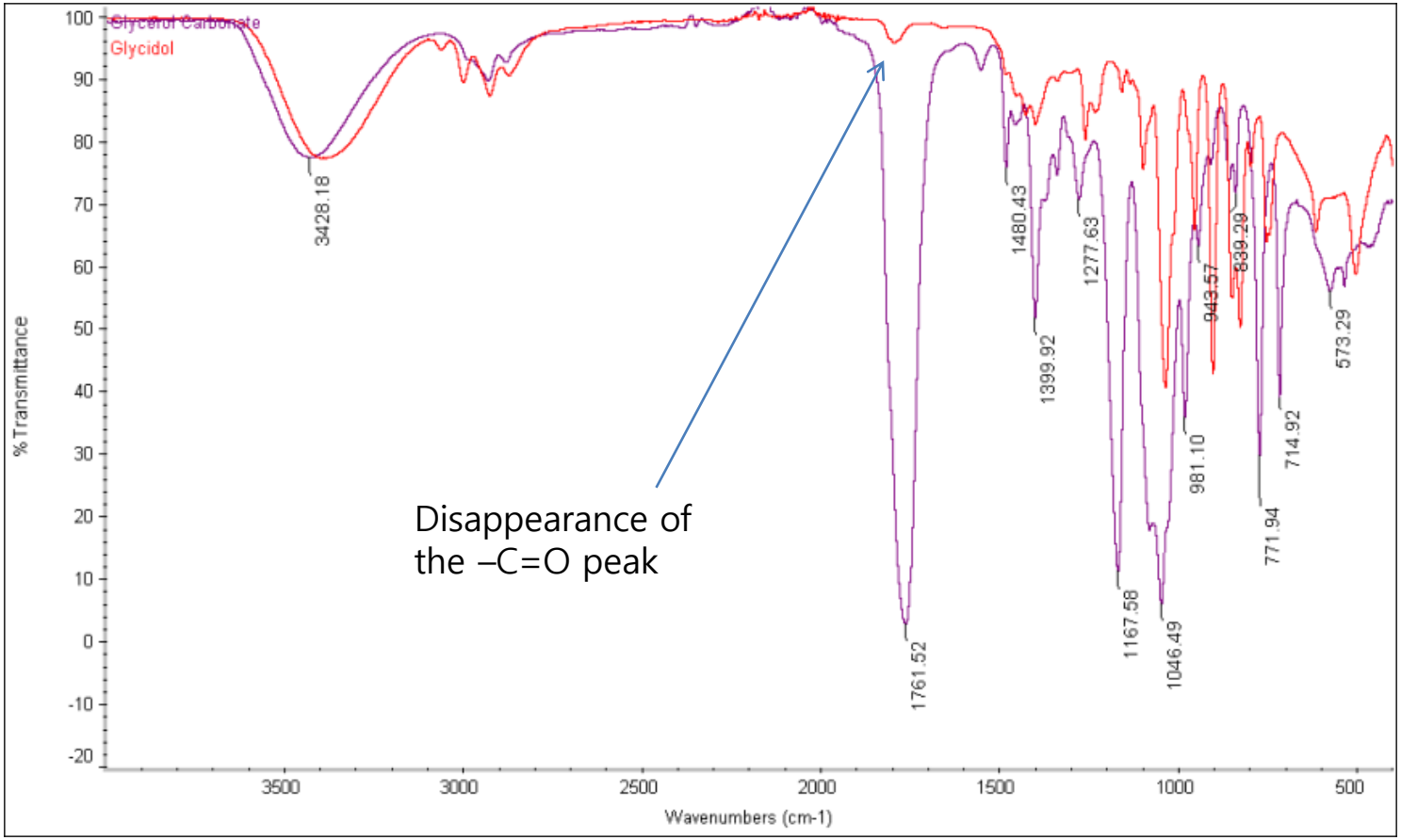


^{1}H NMR of Glycidol

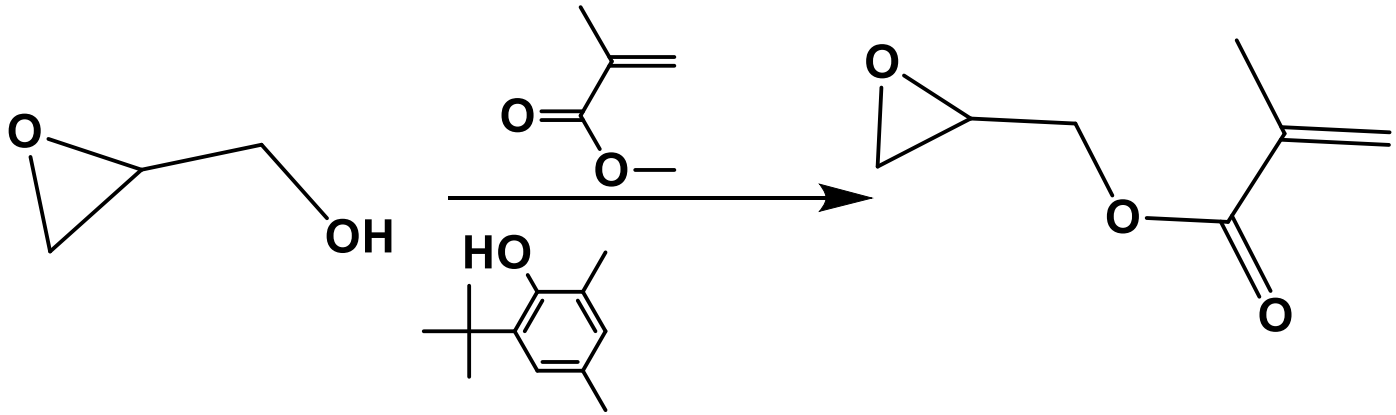


Product was isolated with 55.0 % yield

IR of Glycidol



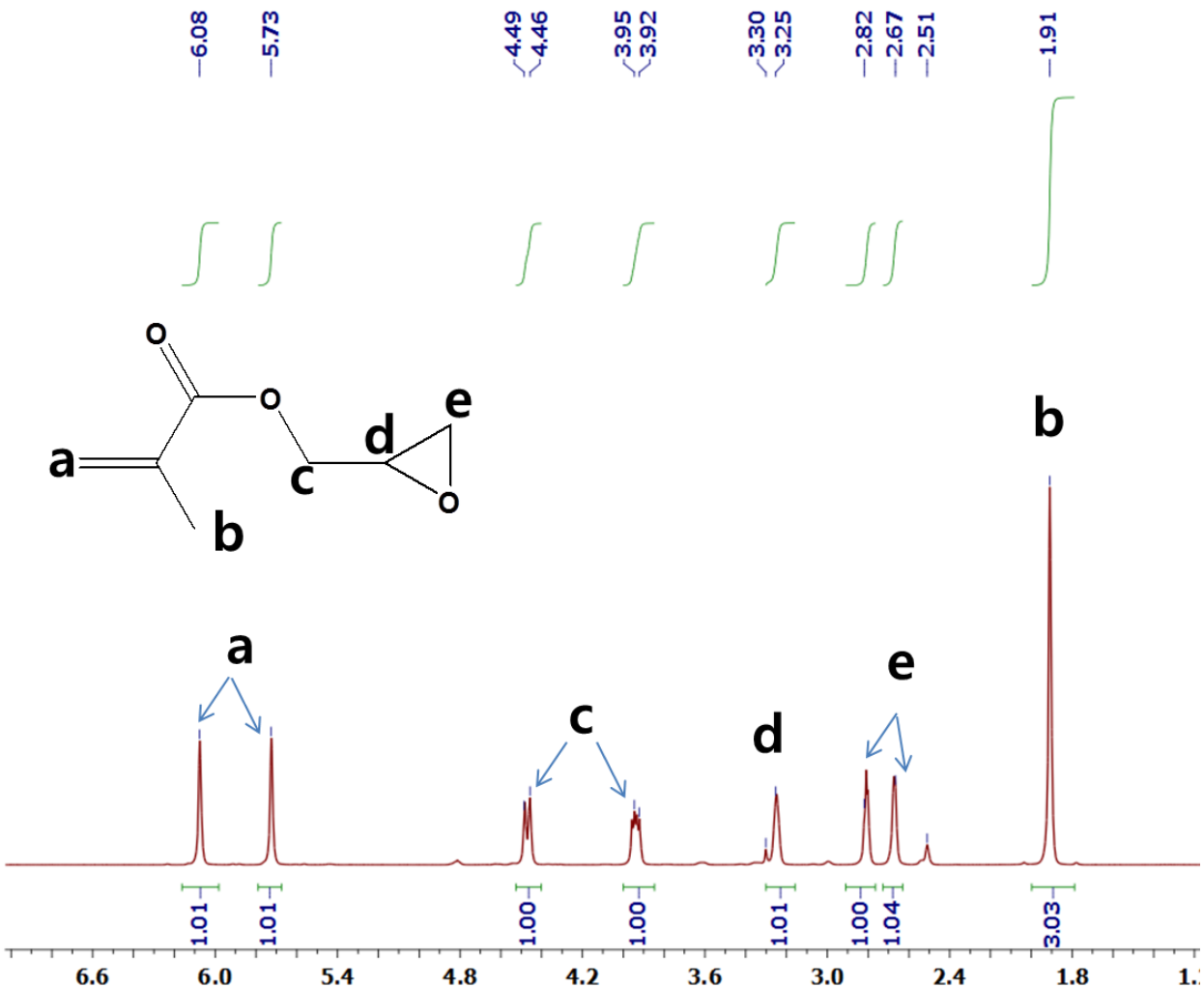
Synthesis of Glycidyl Methacrylate



The reaction was performed at 70 ˚C under reduced pressure for 2 h

^{1}H NMR of Glycidyl Methacrylate

GMA was obtained with 25.3 % yield



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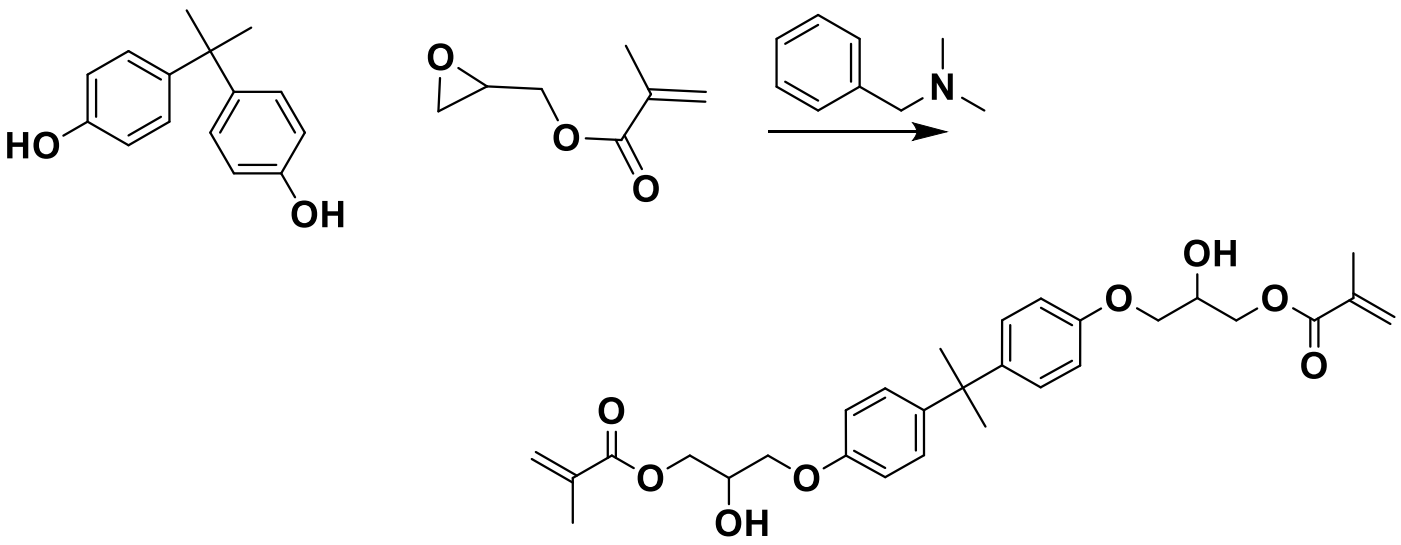
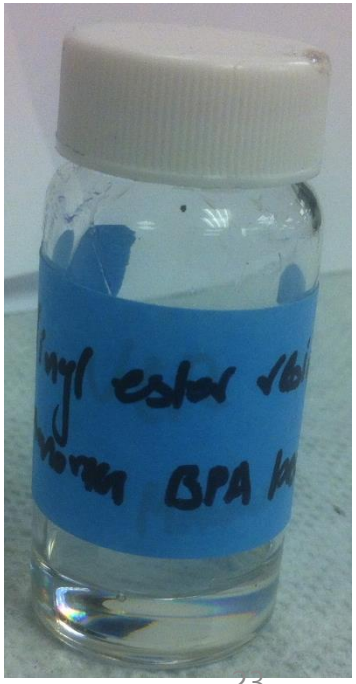
Synthesis of VER Monomer





The reaction was performed at 70 ℃ under inert condition for 2 h

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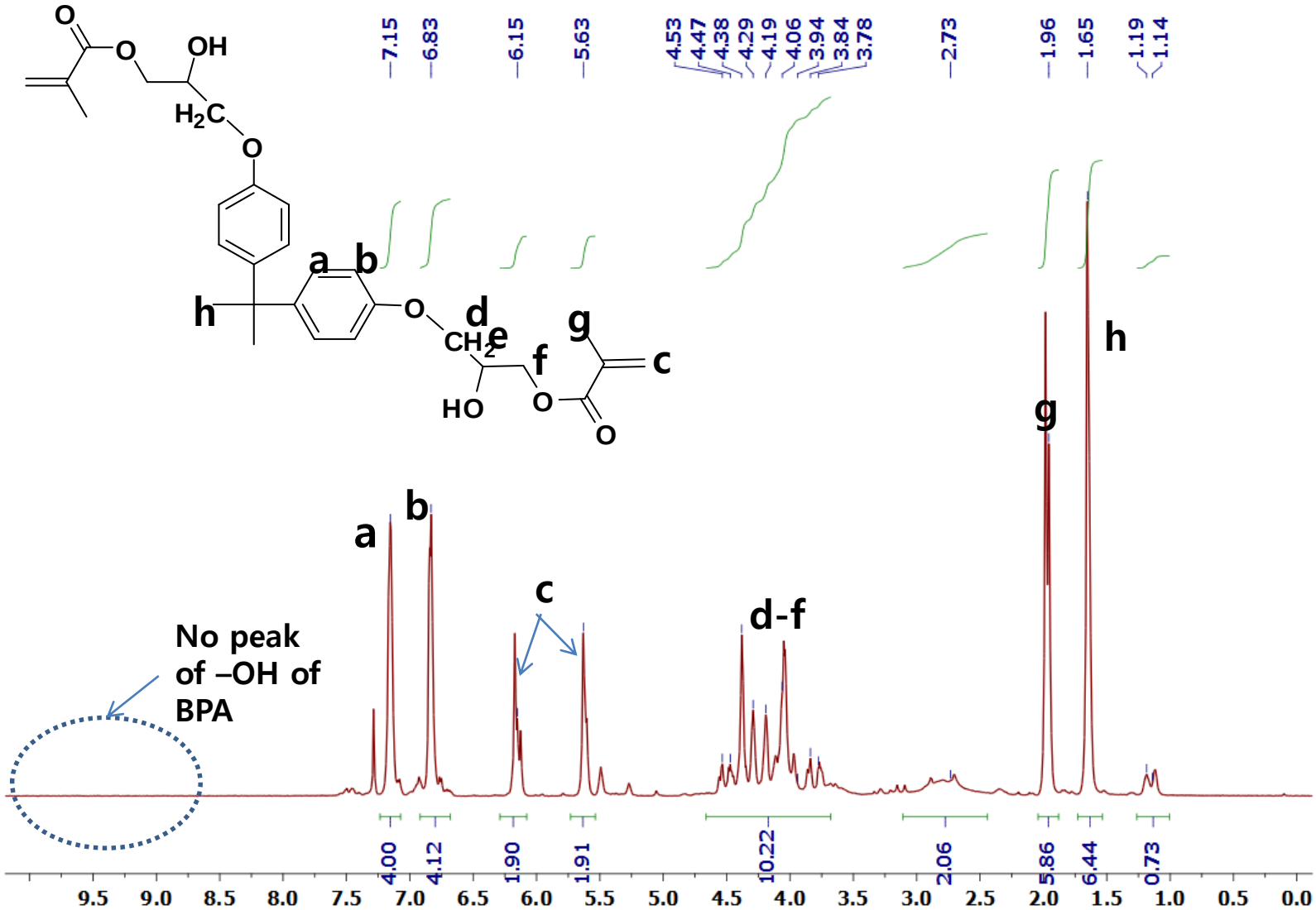
^{1}H NMR of VER Monomer



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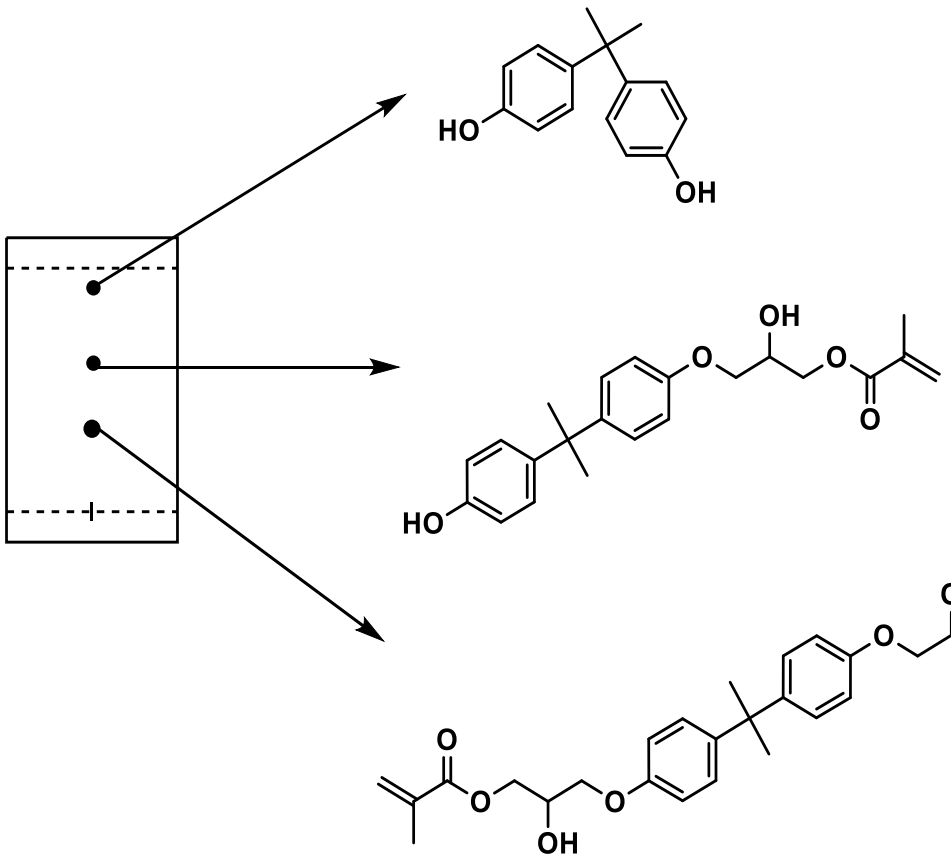
Synthesis and Purification of VER

Column Separation of VER proved presence of three main products

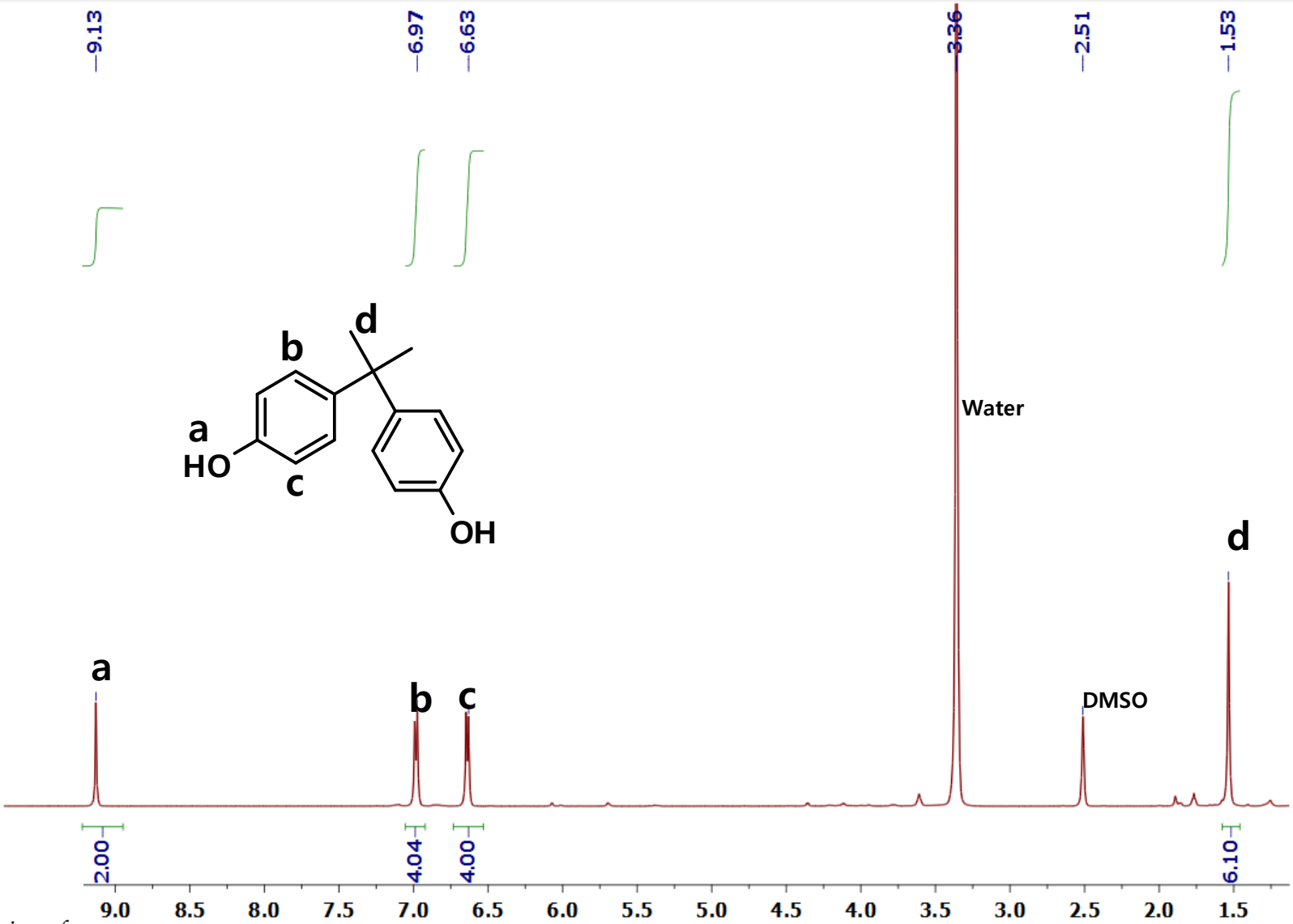


Nonfunctional BPA

Mononfunctional BPA

Difunctional BPA

^{1}H NMR of First Fraction



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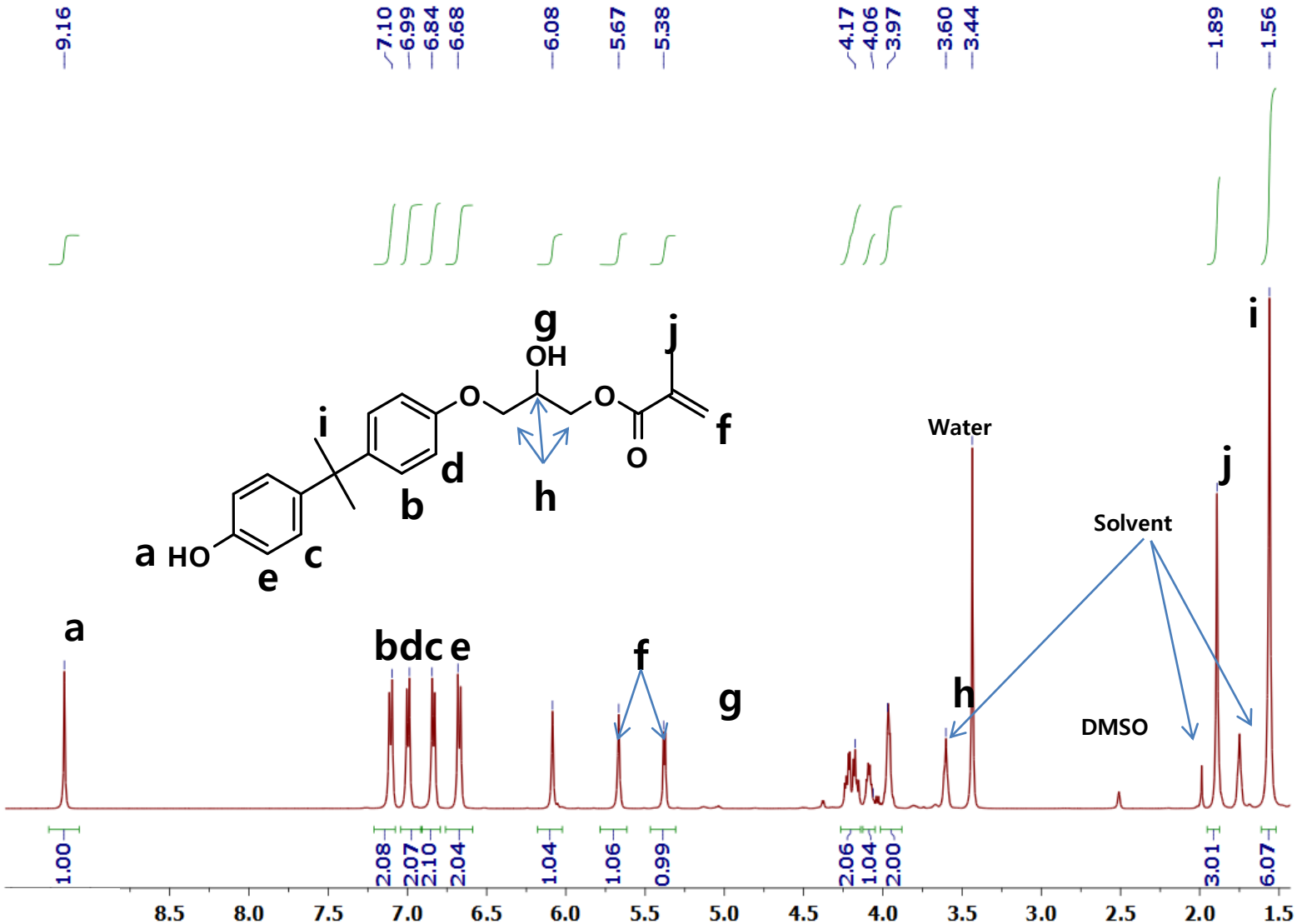
^{1}H NMR of Second Fraction



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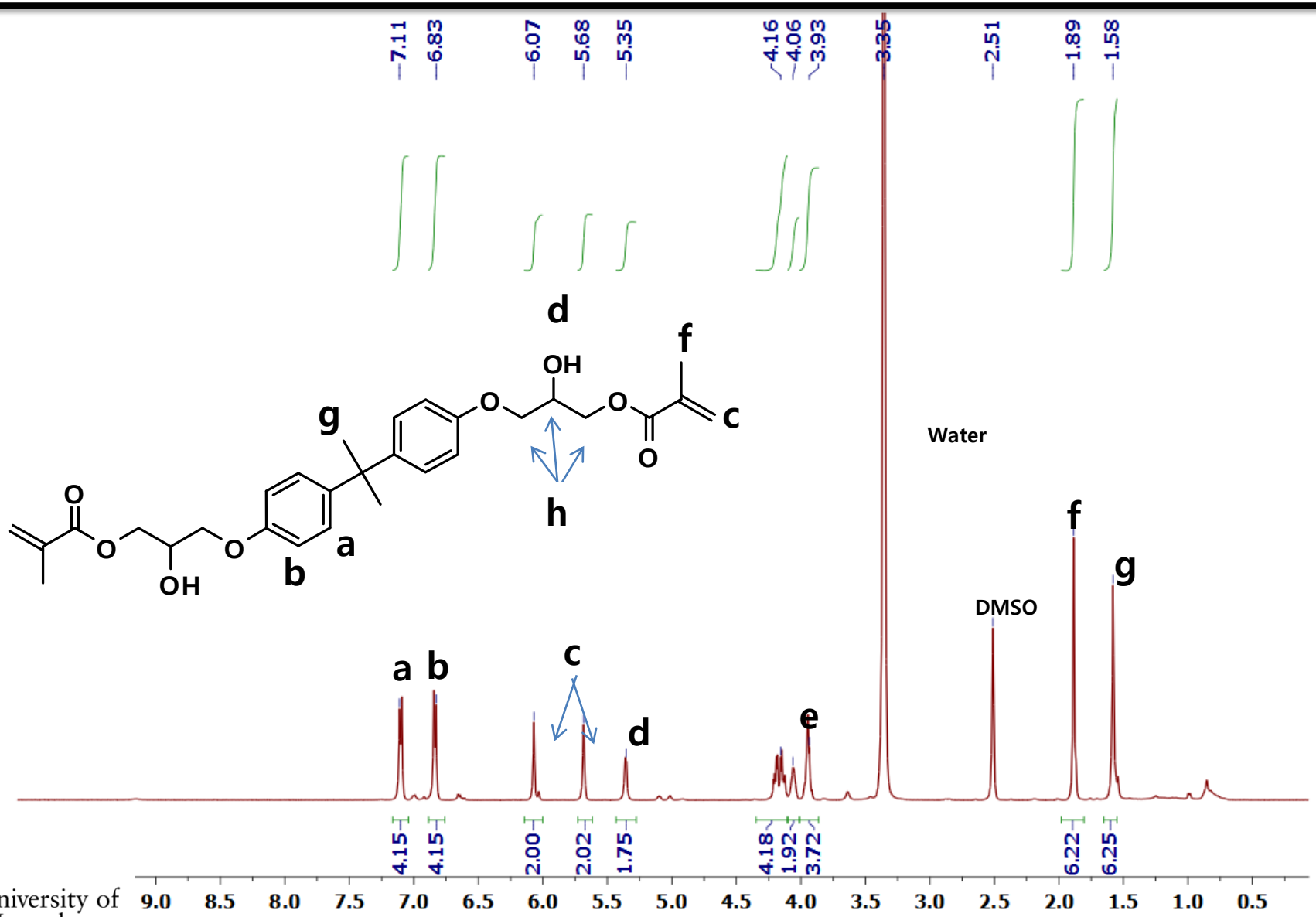
^{1}H NMR of Third Fraction



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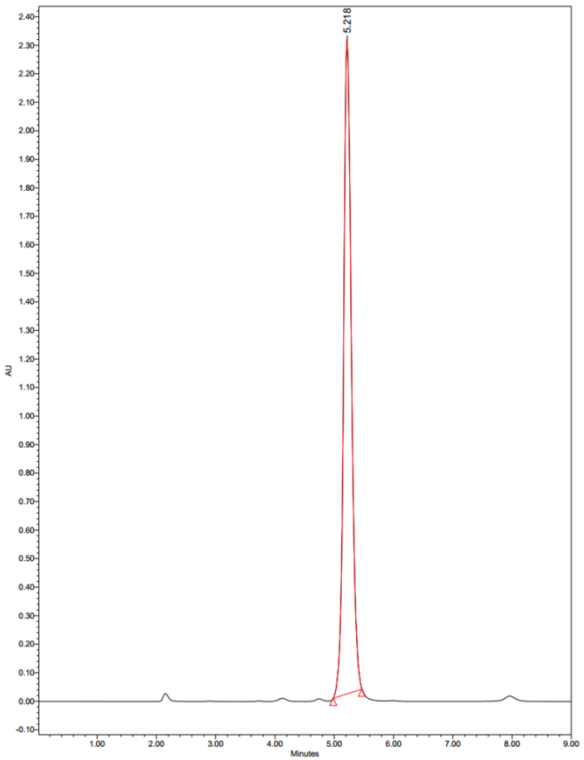
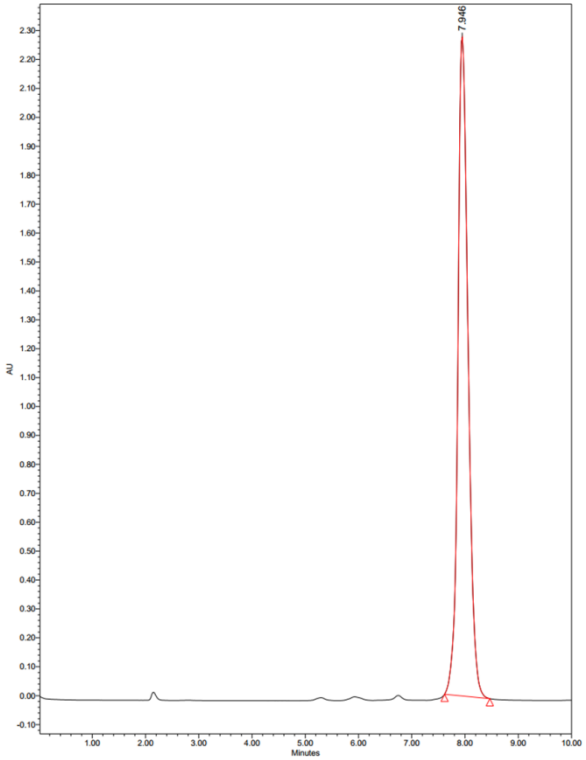
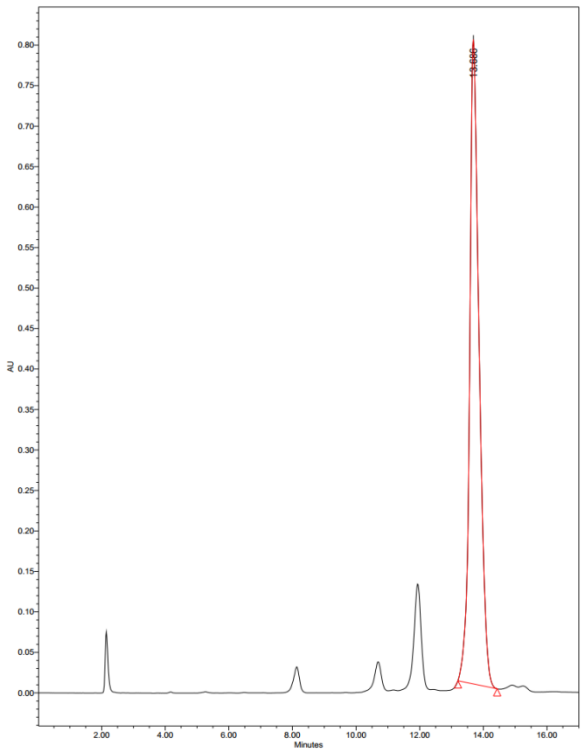
Chromatogram of Each Fraction Isolated During Column Separation



1st Fraction (BPA)



2nd Fraction (GMA-BPA)



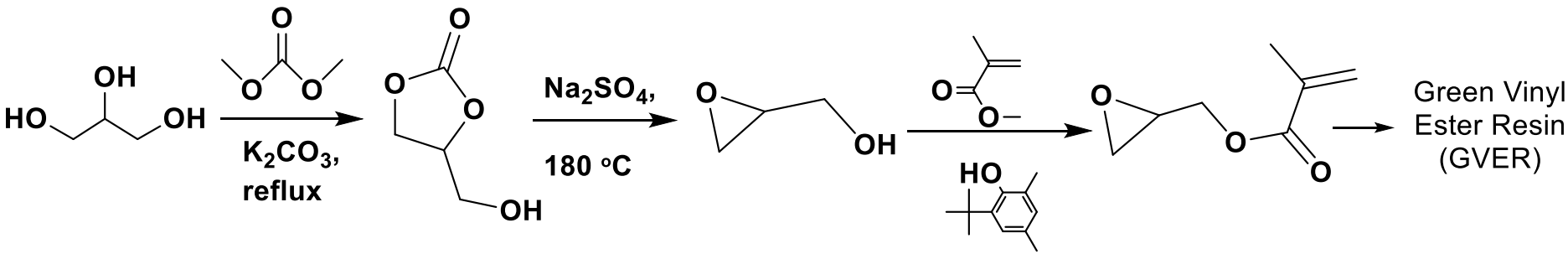
3rd Fraction (GMA-BPA-GMA)

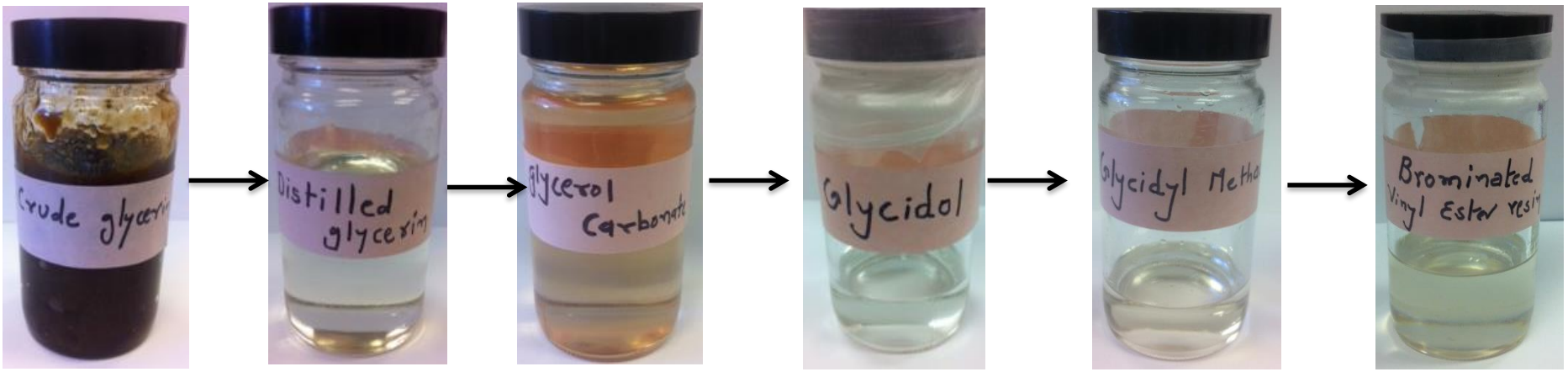
- **System. Water's Alliance system equipped with a photodiode array (PDA) detector monitored at 277 nm and a 4.6 mm × 15 cm column that contains 3-µm packing (Polar - Diol).**
- **The system was run isocratic with a 70:30 mixture of hexane and ethyl acetate. Samples were prepared in ethyl acetate.**

Percentage of Each Fraction at Different Time Interval During VER (GMA:BPA 4:1)

Reaction time (h)	Different functional BPA		
	Non	Mono	Di
2h	32.00	49.24	18.76
3h	20.79	46.28	32.93
4h	14.13	40.63	45.23
5h	13.38	28.27	58.34
6h	12.70	18.05	69.26

Green Vinyl Ester Resin from Biodiesel Glycerin





Crude Glycerin → *Distilled Glycerin* → *Glycerol Carbonate* → *Glycidol* → *Glycidyl Methacrylate* → *Green Vinyl Ester Resin*

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Summary

- Phenol was obtained as one of the product during pyrolysis of lignin. A successful protocol for purification of the phenolic was developed.

- The glycidyl methacrylate was successfully synthesized from vegetable glycerine
  - ✓ A first intermediate, glycerol carbonate, was synthesized with 97.0 % conversion.
  - ✓ A second intermediate, glycidol, was isolated with ~55.0 % yield
  - ✓ Glycidyl methacrylate was synthesized with ~25.3 % yield.

- The second precursor, bisphenol A was synthesised by the reaction of phenol and acetone.

- The vinyl ester oligomer was synthesized by reaction of either BPA with GMA and the product was identified by various characterization techniques.
  - ✓ A new method to monitor the kinetics of the VER was developed using HPLC.

Acknowledgement

Team	Person In-Charge (Point of Contact)	Role
UMass Lowell	Dr. Yongwoo Lee (PI) Dr. Priyank Shah (Co-PI) Dr. Akshay Kokil	Developing GVER from biowaste and coordinating all research team
UMass Lowell	Prof. Chris Hansen	Developing GVER composites using VARTM
UMass Lowell	Prof. David Ryan	Developing analytical technique for characterization of pyrolyzed material.
Bentley University	Prof. Ryan Bouldin	Business development
NAVAIR	Dr. John Brennan Ms. Emily Dumm	Developing composites with flame retardant ability and deliver coupons to NAVSEA
NAVSEA	Mr. Usman Sorathia	Examine flame retardant properties of the composites received from NAVAIR
R.F. Kovar & Associates	Dr. Robert F. Kovar	Provide technical expertise to UML team.
Ashland Inc.	Dr. Michael Stevens, Dr. Joe Fox, Dr. Charlie Lewis	Industrial teaming partner
Maine Standard Biofuels	Mr. Jarmin Kaltsas, Mr. Alex Pine	Provide unrefined glycerin obtained during biodiesel manufacturing
Flamebeau River Paper LLC	Mr. Bill Tomczak	Provide lignin from paper industry waste stream
Maine Seed Company	Mr. Tate McPherson	Provide lignin from different plant source

Strategic Environmental Research and Development Program (SERDP WP-1755; WP-2317)

Appendix Q

Sustainable "Green" Vinyl Ester Resin (GVER) from Renewable Resources

WP 2317

Yongwoo Lee
University of Massachusetts Lowell

In-Progress Review Meeting
October 28, 2014

SERDP
DOD ▪ EPA ▪ DOE

Content

Introduction

- Project overview
- Project team
- Technological objective

Technical Approach

- Pyrolysis of lignin and synthesis of BPA and TBBPA
- Synthesis of GMA from biodiesel glycerin
- Environmental and technical advantages

Overview of Prior Work

- A brief overview of phase-I work

Results

- Pyrolysis of lignin, purification of pyrolysate
- Synthesis of BPA and TBBPA
- Synthesis of GMA from biodiesel glycerin
- Fabrication of neat resin and carbon fabric reinforced panels using commercial VER
- Flammability testing results (NAVSEA)
- Mechanical testing results (UML-NAVAIR)
- Cost analysis

Technology Transition

WP-2317: Sustainable "Green" Vinyl Ester Resin (GVER) from Renewable Resources

Performers:

Dr. Y. Lee, Dr. R. F. Kovar, Dr. P. Shah, Dr. N. Kim, and Dr. A. Kokil

Technology Focus

- *Synthetic protocol for GVER and its processing into VARTM composites, pyrolysis of lignin, extraction of phenol*

Research Objectives

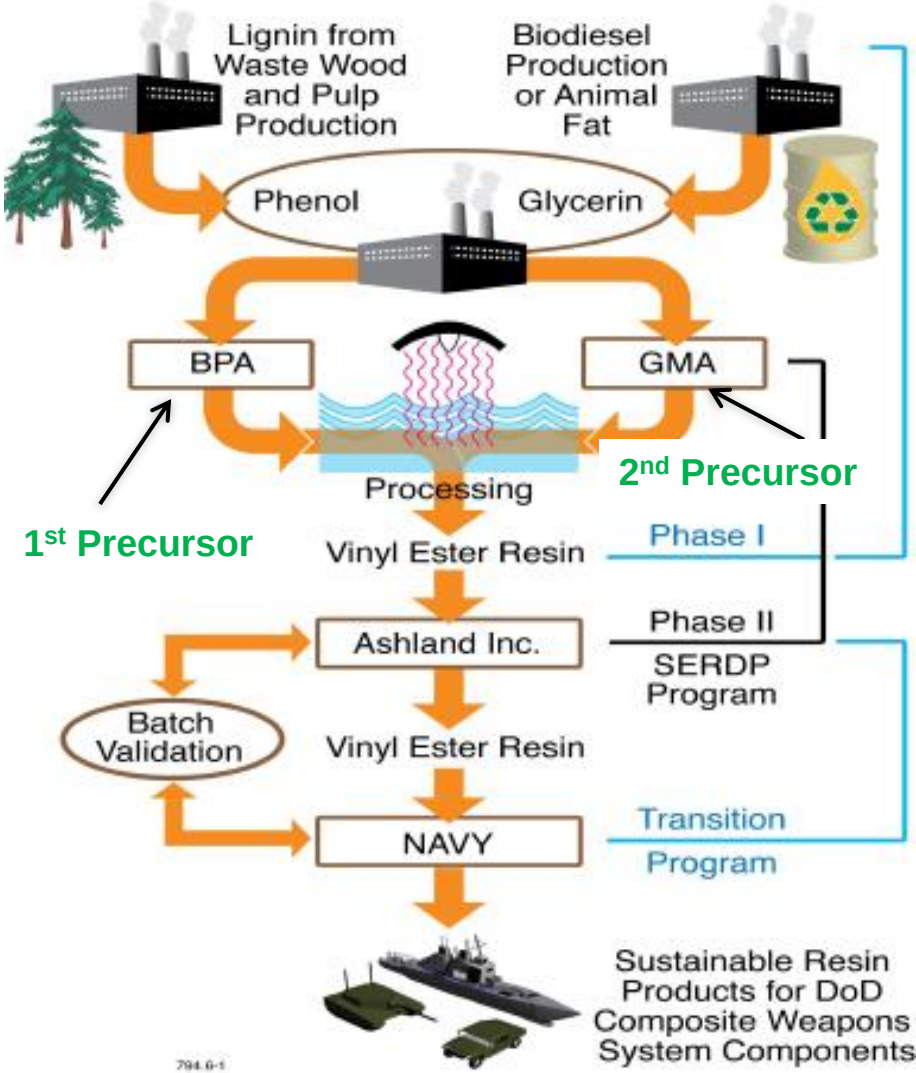
- *Demonstrate synthesis of GMA from glycerin.*
- *Isolation of phenol from lignin to get BPA and TBBPA.*
- *Demonstrate synthesis of GVER and VARTM processing.*

Project Progress and Results

- *Successfully synthesized GMA from biowaste glycerin.*
- *Developed efficient method of pyrolysis .*
- *Synthesized BPA and TBBPA from phenol.*
- *Synthesized 50g GVER starting from waste glycerin.*

Technology Transition

- *Working with Ashland Inc. to understand industrial demands.*
- *Working with paper and biodiesel company for procuring lignin and glycerin.*



Project Team

Team	Person In-Charge (Point of Contact)	Role
UMass Lowell	Dr. Yongwoo Lee Dr. Namjoon Kim (Prof. Yoon-Chem. Eng.) Dr. Priyank Shah (Prof. Manohar-Chem. Eng)	Developing GVER from biowaste and coordinating all research team
UMass Lowell	Prof. Chris Hansen Sid, Andrew, and Dean	Developing GVER composites using VARTM
UMass Lowell	Prof. David Ryan	Developing analytical technique for characterization of pyrolyzed material.
Bentley University	Prof. Ryan Mouldin	Business development
NAVAIR	Dr. John Brennan Ms. Emily Dunn	Developing composites with flame retardant ability and deliver coupons to NAVSEA
NAVSEA	Mr. Usman Sorathia	Examine flame retardant properties of the composites received from NAVAIR
R.F. Kovar & Associates	Dr. Robert F. Kovar	Provide technical expertise to UML team.
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Maine Standard Biofuels	Jarmin Kaltsas, Alex Pine	Provide unrefined glycerin obtained during biodiesel manufacturing
Flamebeau River Paper LLC	Bill Tomczak	Provide lignin
Maine Seed Company	Tate McPherson	Provide different kinds of lignin

Technical Objective

- Refine Phenol from Lignin
- Refine GMA from Glycerin
- Scale up VER resin

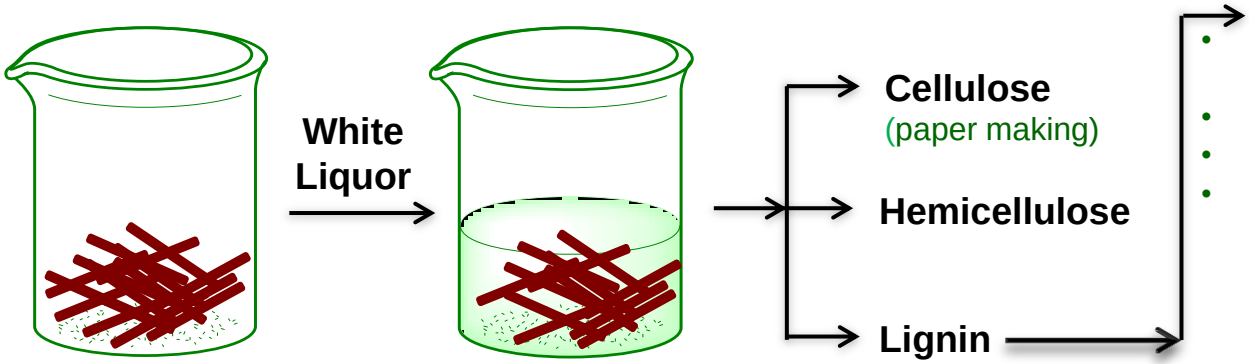
Year I

- Formulation with Derakane Vinyl Ester
- Fabricate composites with VARTM
- Conduct structural testing for equivalence

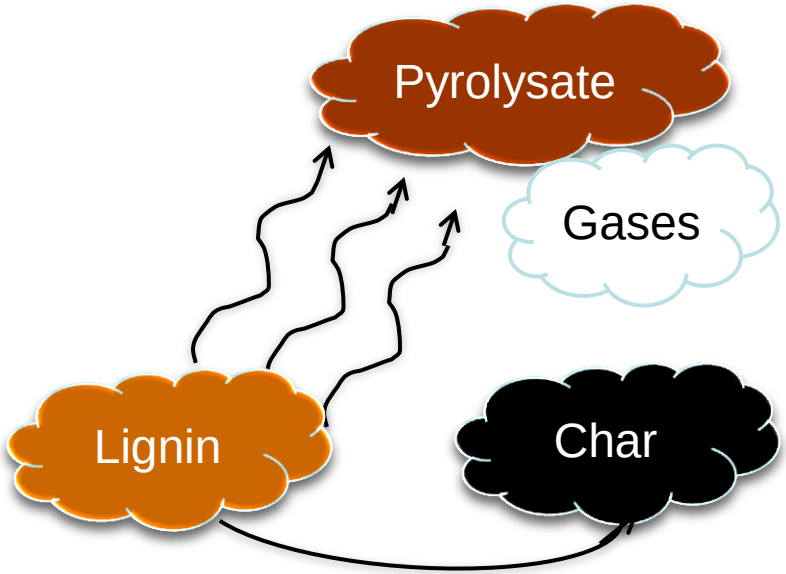
Year II & Year III

Technical Approach

Pyrolysis of Lignin



- Multi-polarity related products (emulsion and dispersant)
- Materials (Binders, thermoset)
- Agriculture (animal nutrition)
- High purity/value applications (food and cosmetics application, anti-oxidative and antibacterial)



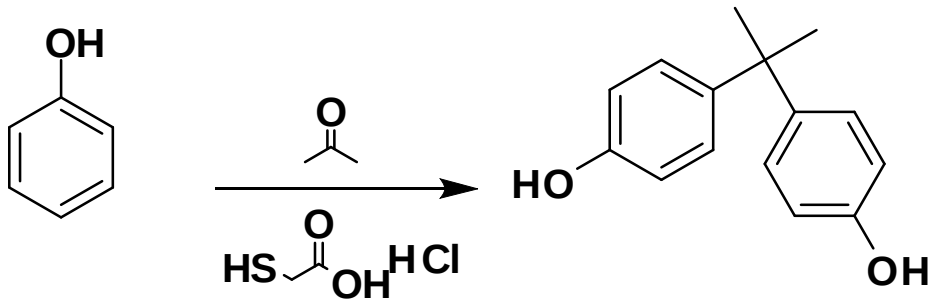
Pyrolysis Concept

Samples of lignin provided by Flambeau River Papers LLC. (Park Falls, WI).

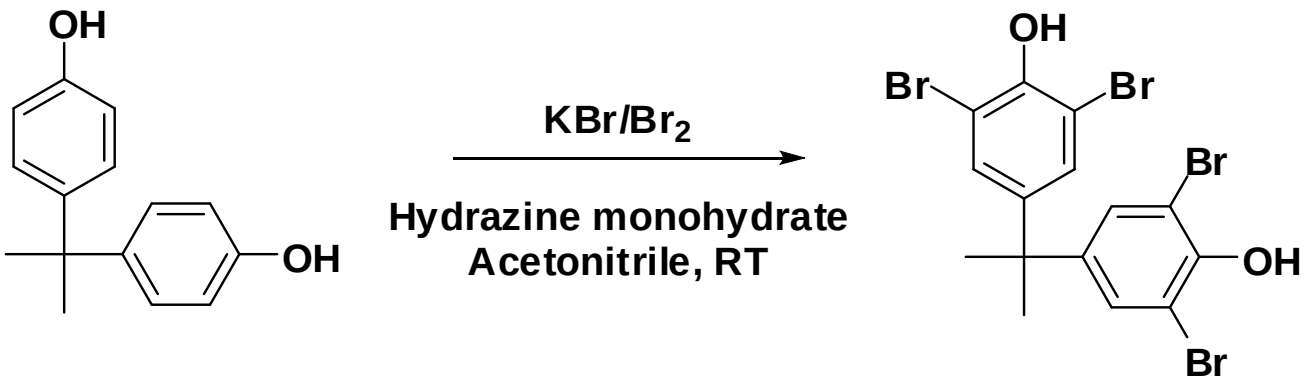
http://www.ili-lignin.com/

Technical Approach

Synthesis of BPA



Synthesis of TBBPA



Purification by precipitation in water

Technical Approach

Introduction to Glycerin

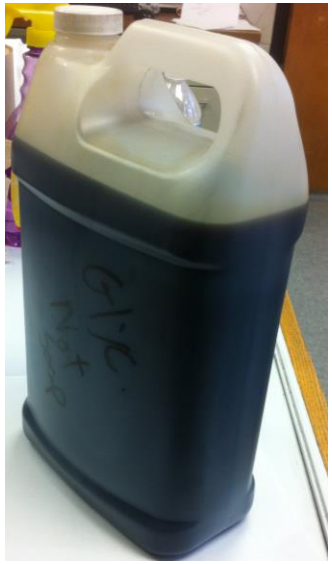
Vegetable Oil, Animal Fat (Triglycerides)[1] →

- **Water, NaOH (Hydrolysis, Saponification)** → **long-chain carboxylate salts used as soaps**
- **Alcohol, NaOH Transesterification** → **esters of fatty acids used as biodiesel**

+ glycerin

- By 2020, the production of glycerin will be six times higher than its demand. [2]
- Its disposal is a problem for biodiesel industry

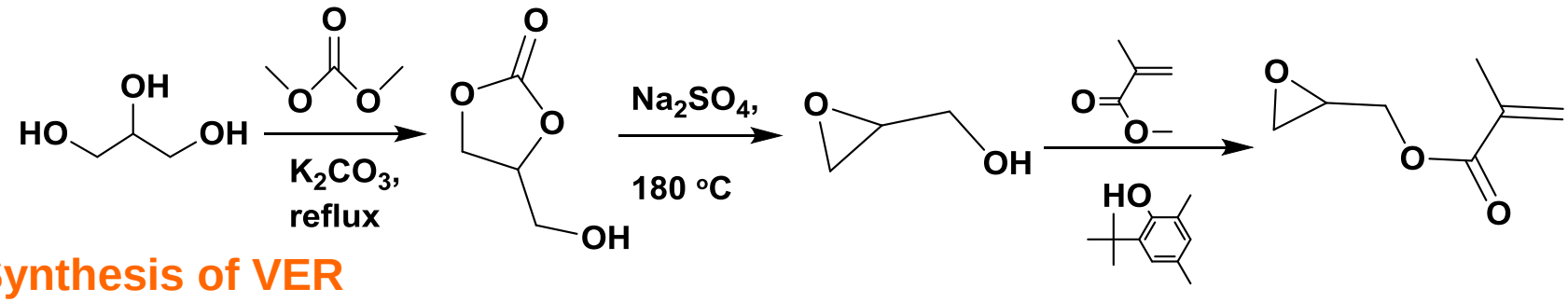
We are using crude glycerin from Maine Standard Biofuels (Portland, Maine)



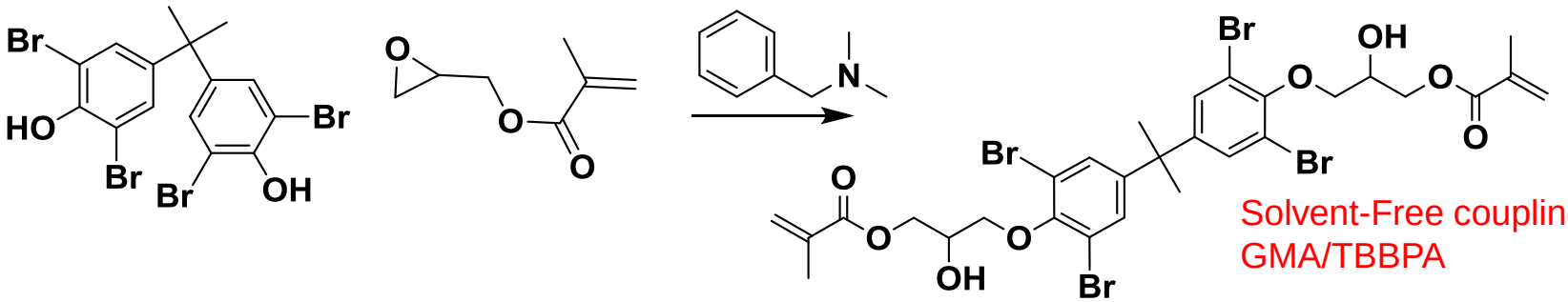
1. Sims, Bryan (2011-10-25). "Clearing the Way for Byproduct Quality: Why quality for glycerin is just as important for biodiesel". Biodiesel Magazine
2. Christoph, Ralf; Schmidt, Bernd; Steinberner, Udo; Dilla, Wolfgang; Karinen, Reetta (2006). "Glycerol". Ullmann's Encyclopedia of Industrial Chemistry. doi:10.1002/14356007.a12_477.pub2. ISBN 3527306730.

Technical Approach

Synthesis of GMA

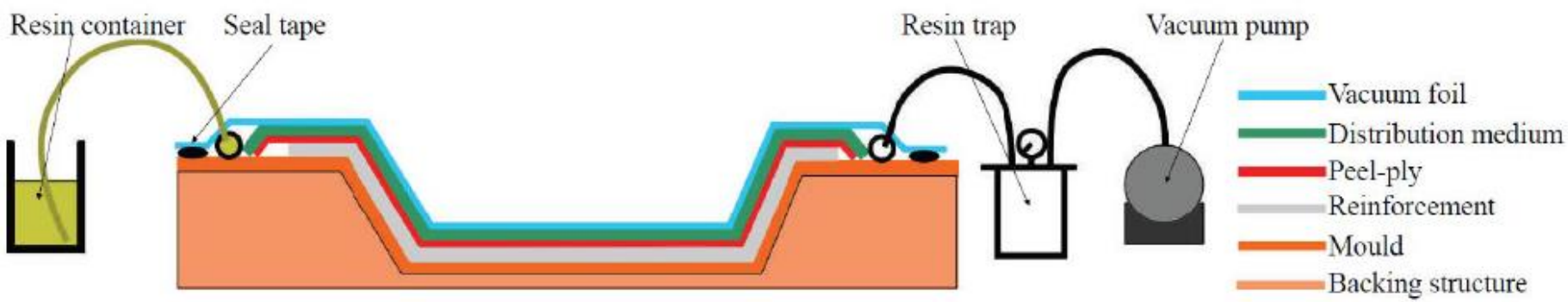


Synthesis of VER



Solvent-Free coupling of GMA/TBBPA

Carbon fabric reinforced panel fabrication by VARTM

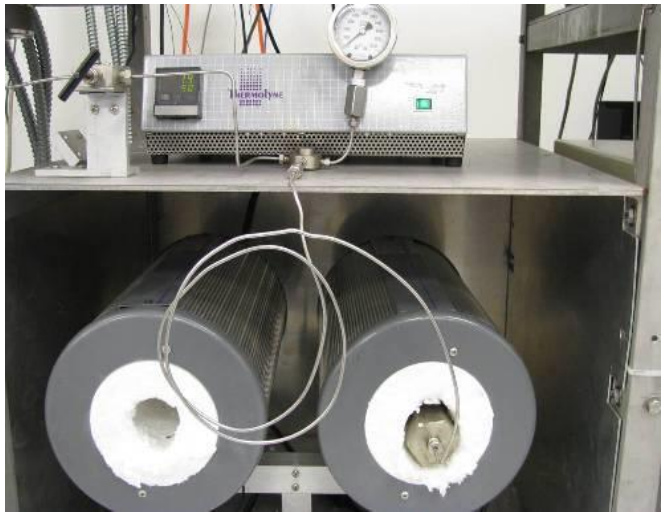


Significance

Advantages

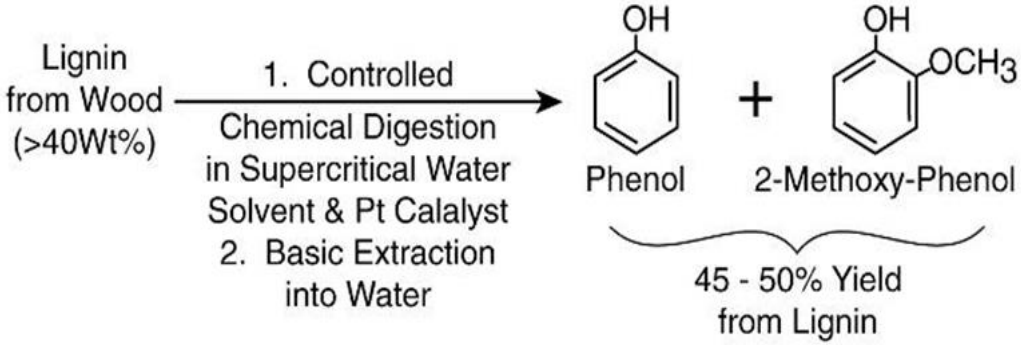
- **Elimination of US dependence upon foreign oil** in manufacturing critical military composites.
- **Replacement of epichlorohydrin** with GMA yields an environmentally benign synthesis.
- Production of green BPA and GMA will provide raw materials **for other high-value chemical products**.
- Finally, the proposed use of biomass waste **will not affect the nation's food supply**.
- Pyrolysis of lignin produces **many valuable phenolic derivatives**.
- **Solvent-free** synthesis of brominated vinyl ester resin monomer.
- GVER from TBBPA and GMA forms only **pure, low molecular weight product**,
  - Good for VARTM processing
  - Reduces usage of reactive diluent (styrene)
  - Increases wetting of resins and decrease voids/bubbles in composites

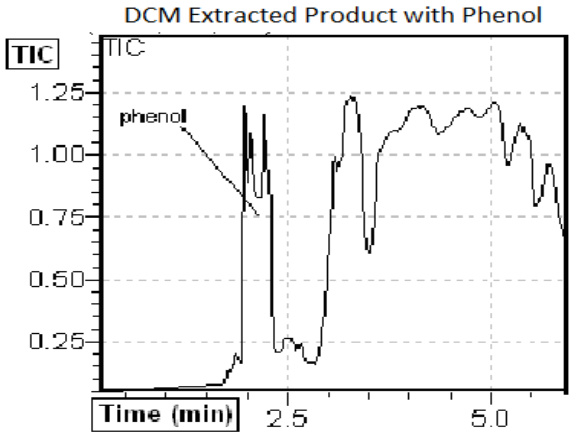
Overview of Prior Work



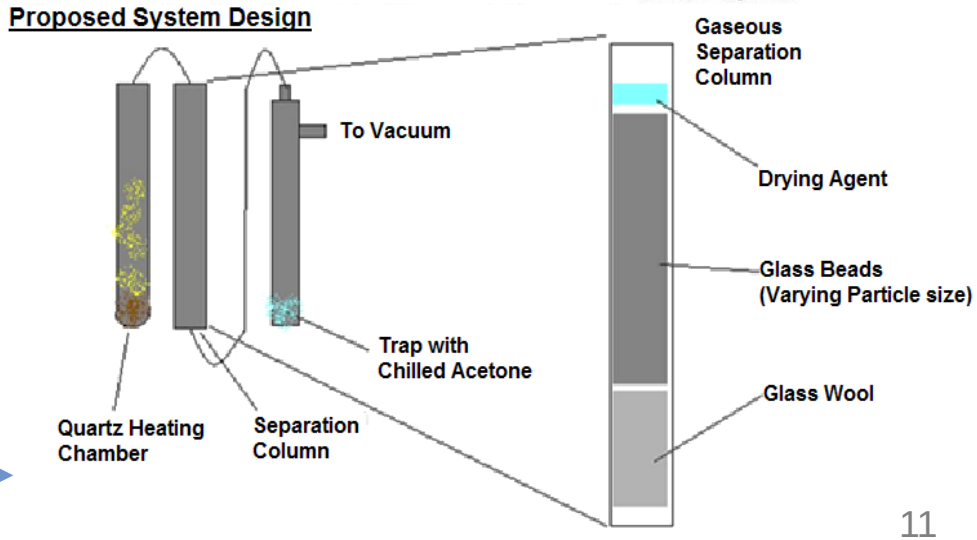
Supercritical Water Pyrolysis

Step 1. Isolation of Phenol from Lignin:





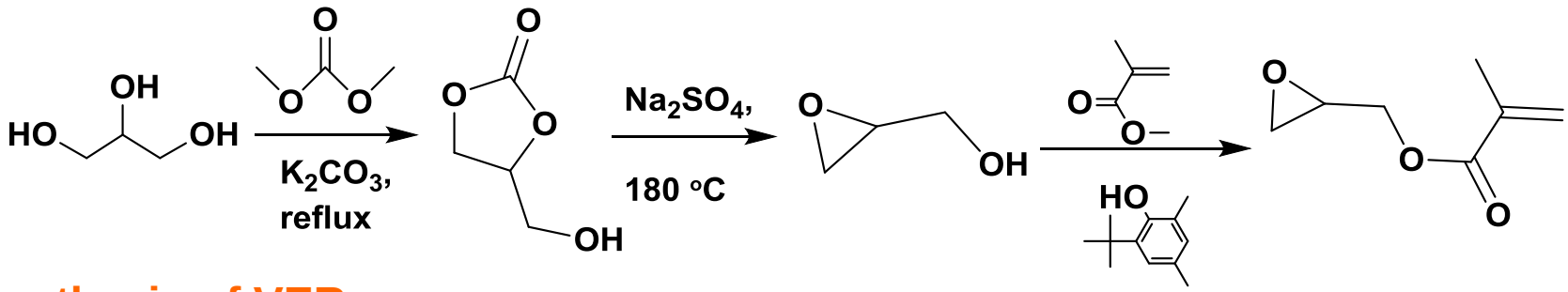
Flash Pyrolysis
(Proposed System in Phase-II)



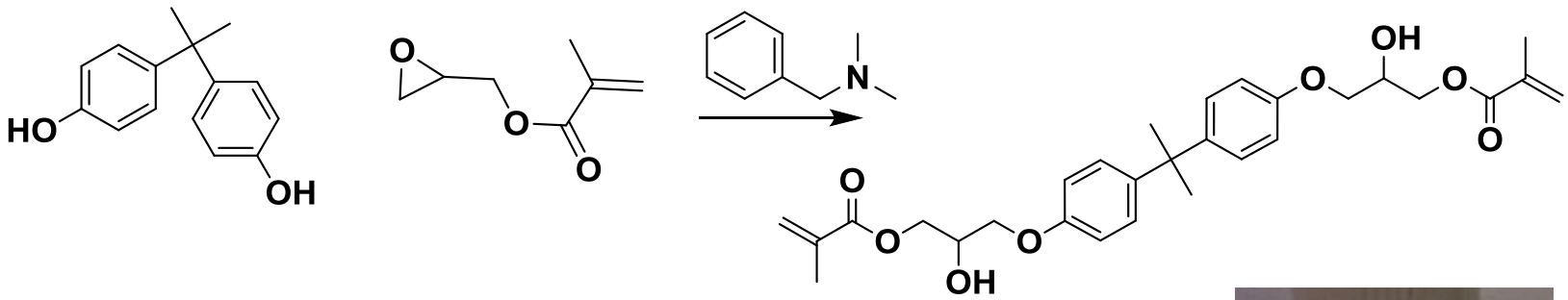
"Phenols from Lignin" ; M. Kleinert, T. Barth, Chem. Eng. Technol. 2008, 31, No. 5, 736-745

Overview of Prior Work

Synthesis of GMA



Synthesis of VER

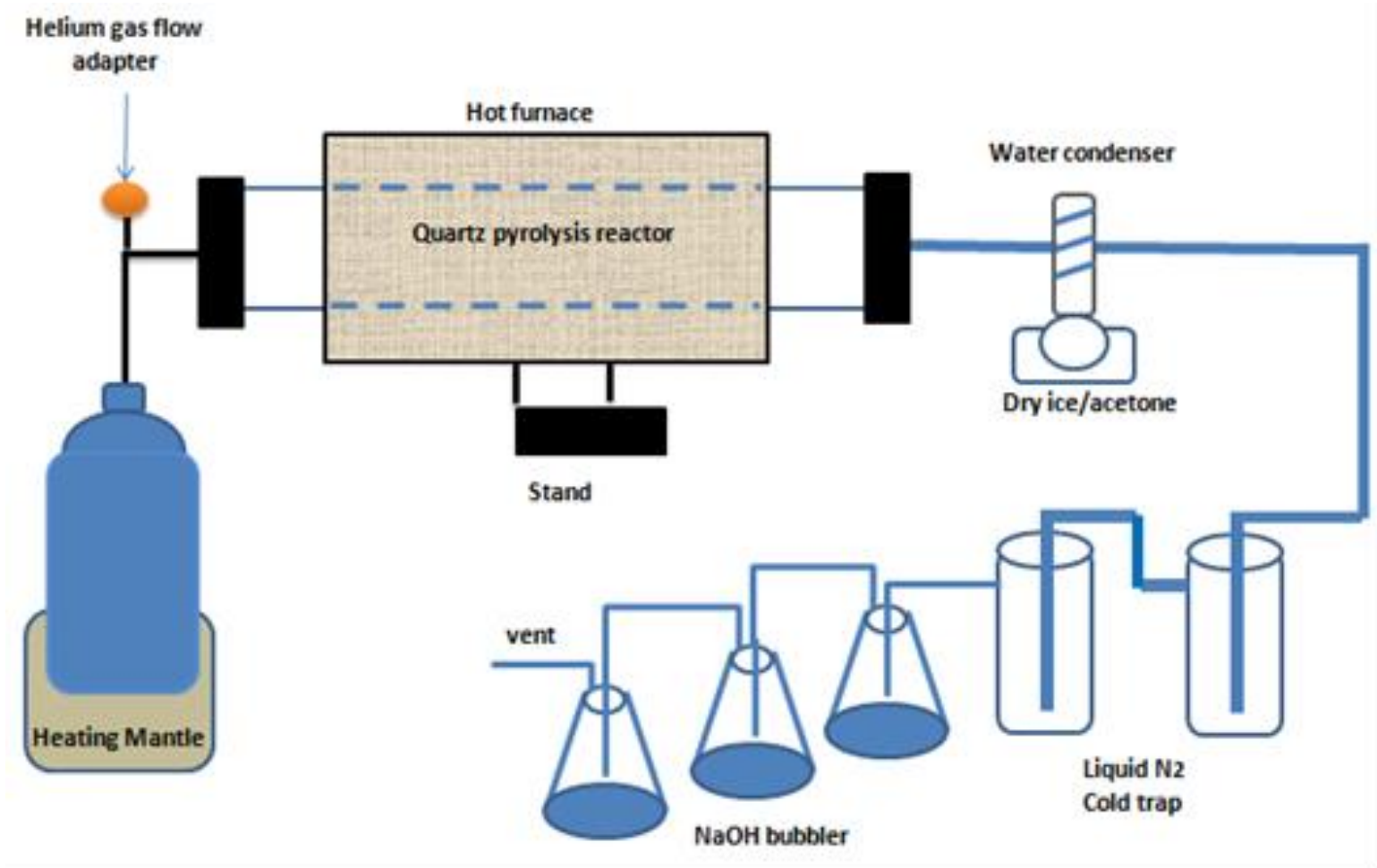


- **GMA and VER was successfully synthesized and characterized using commercially starting material and intermediates.**

- **GMA and VER was characterized using GC-MS, LC-MS and ^{1}H-NMR**

Current Pyrolysis Setup

Inspiration: Coal had been pyrolyzed to isolate phenol before WW-I and during WW-II, when there was a shortage of petroleum feed-stock

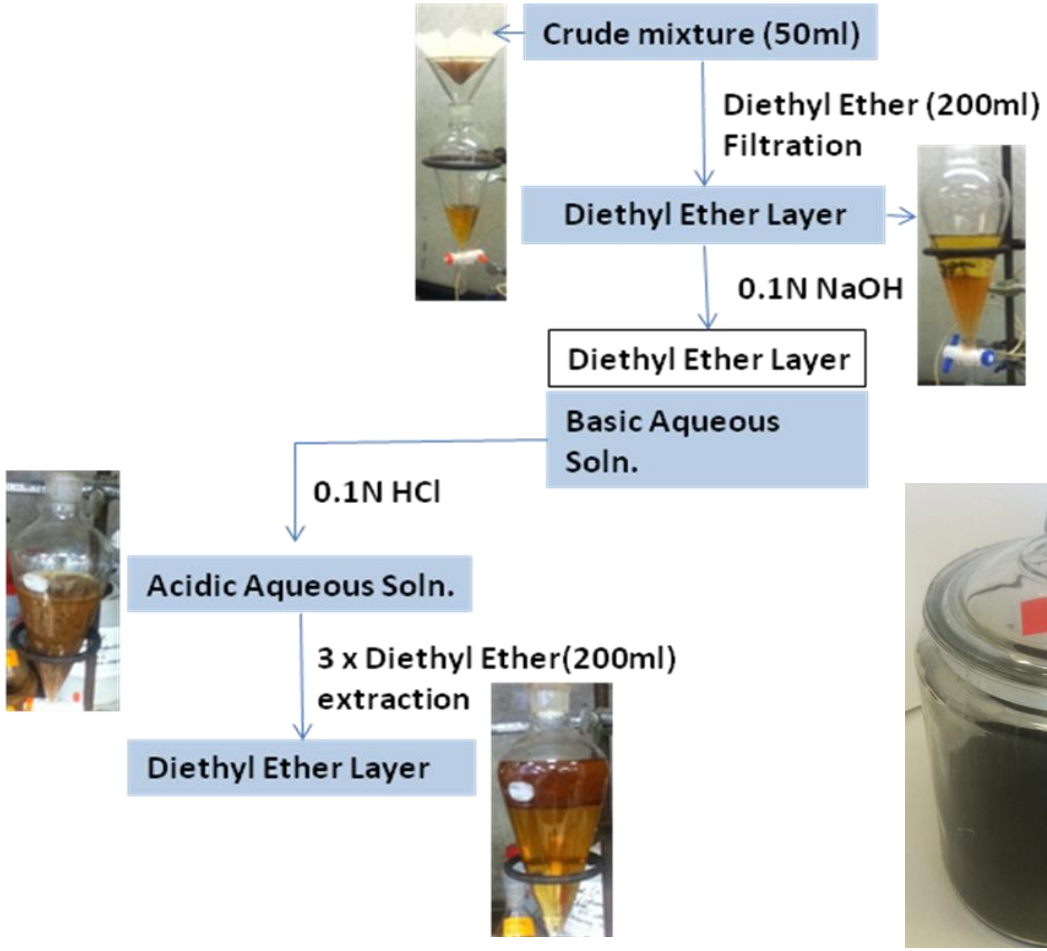


"Advanced Organic Chemistry"; Louis F. Fieser and Mary Fieser, New York, Reinhold Publishing Corporation, Chapman & Hall, Ltd., London, 1961, pp.640-645.

Gravimetric and GC-MS Data of Pyrolysis

Mass balance between different phases	Vacuum Setup (SA)	Helium Setup			
		SA	TCI (*alk*)	TCI (*dealk*)	FRP-LLC
Char (Solid) (wt. %)	55.0	54.9	62.6	54.9	52.7
Phenolics (Liquid) (wt. %)	7.1	12.6	11.5	3.2	17.9
(Gases)	37.9	32.5	25.9	41.9	29.4
Main phenolics identified					
Guaiacol	31.43	10.32	9.48	2.84	4.35
Butylated hydroxytoluene	7.03	16.33	28.21	69.05	22.20
2-methoxy-4-methylphenol	9.40	1.95	1.34	0.45	0.65
Phenol	6.30	9.41	**20.22**	4.59	3.97
4-ethyl-2-methoxyphenol	6.83	1.85	0.91	0.40	0.58
2-methoxy-4-vinylphenol	3.70	0.66	1.44	0.00	0.22
2,6-dimethoxyphenol	0.53	0.57	0.25	0.15	0.64
vanillin	0.87	0.03	0.92	0.89	0.83
4-hydroxy-3-methoxyacetaphenone	0.63	0.55	0.61	0.46	0.37
catechol	0.10	11.66	2.27	2.02	4.15
Homovanillic acid	1.40	0.50	0.43	0.22	0.18

Purification of Phenolics

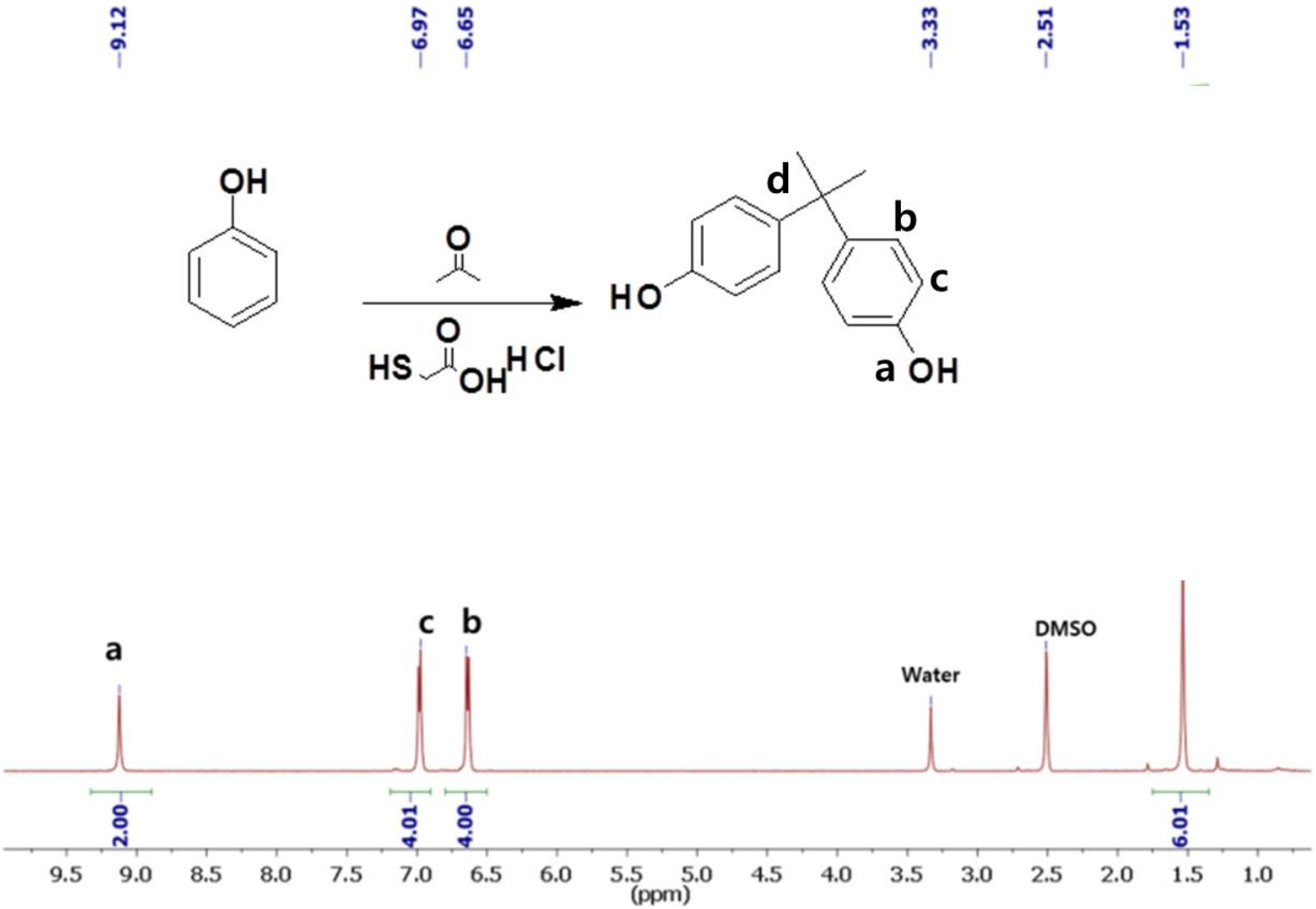


Char

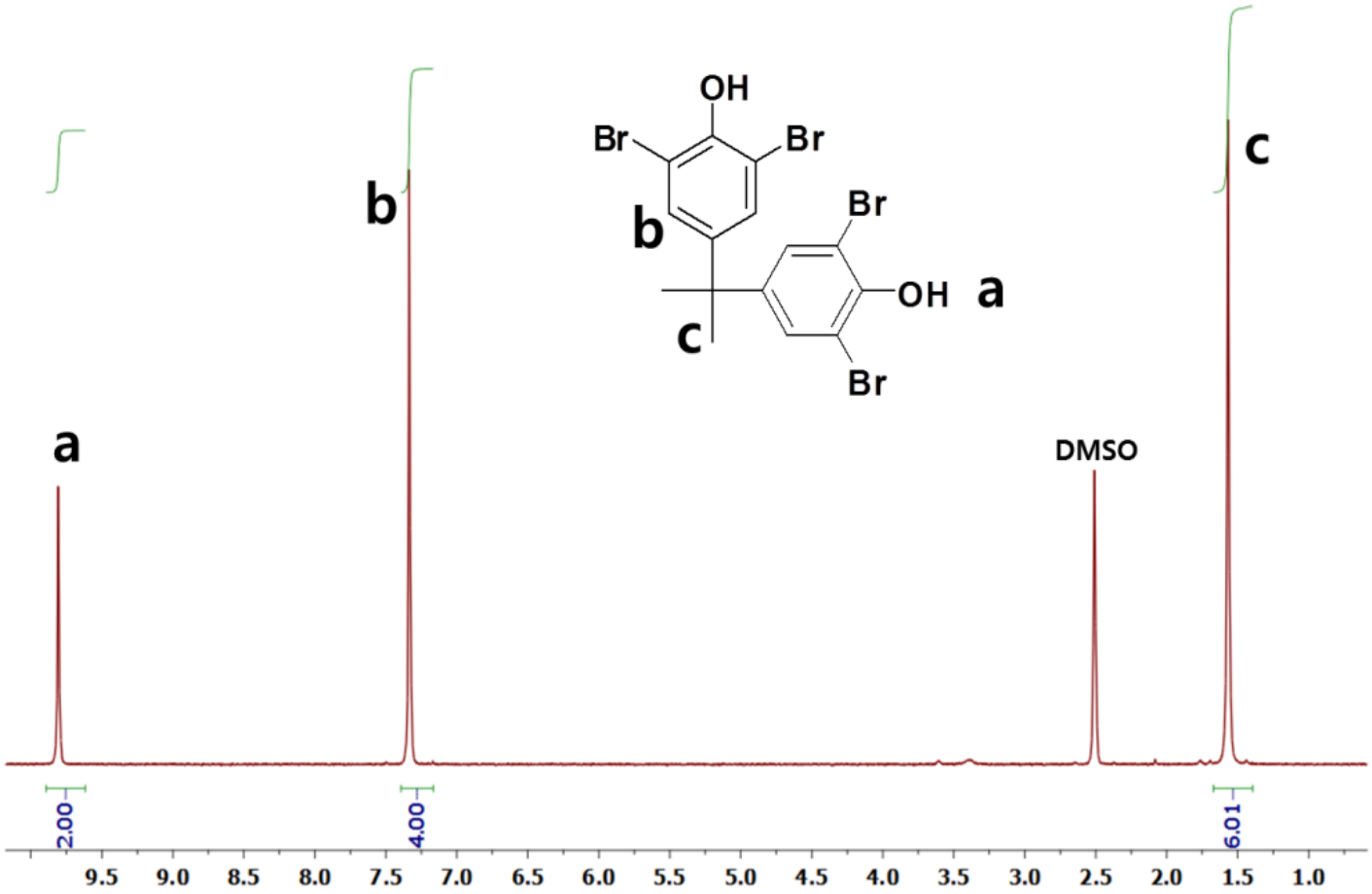
Isolated liquid

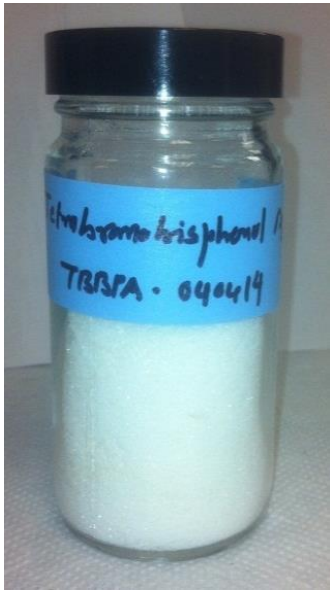
Purified product after solvent extraction

Synthesis of BPA

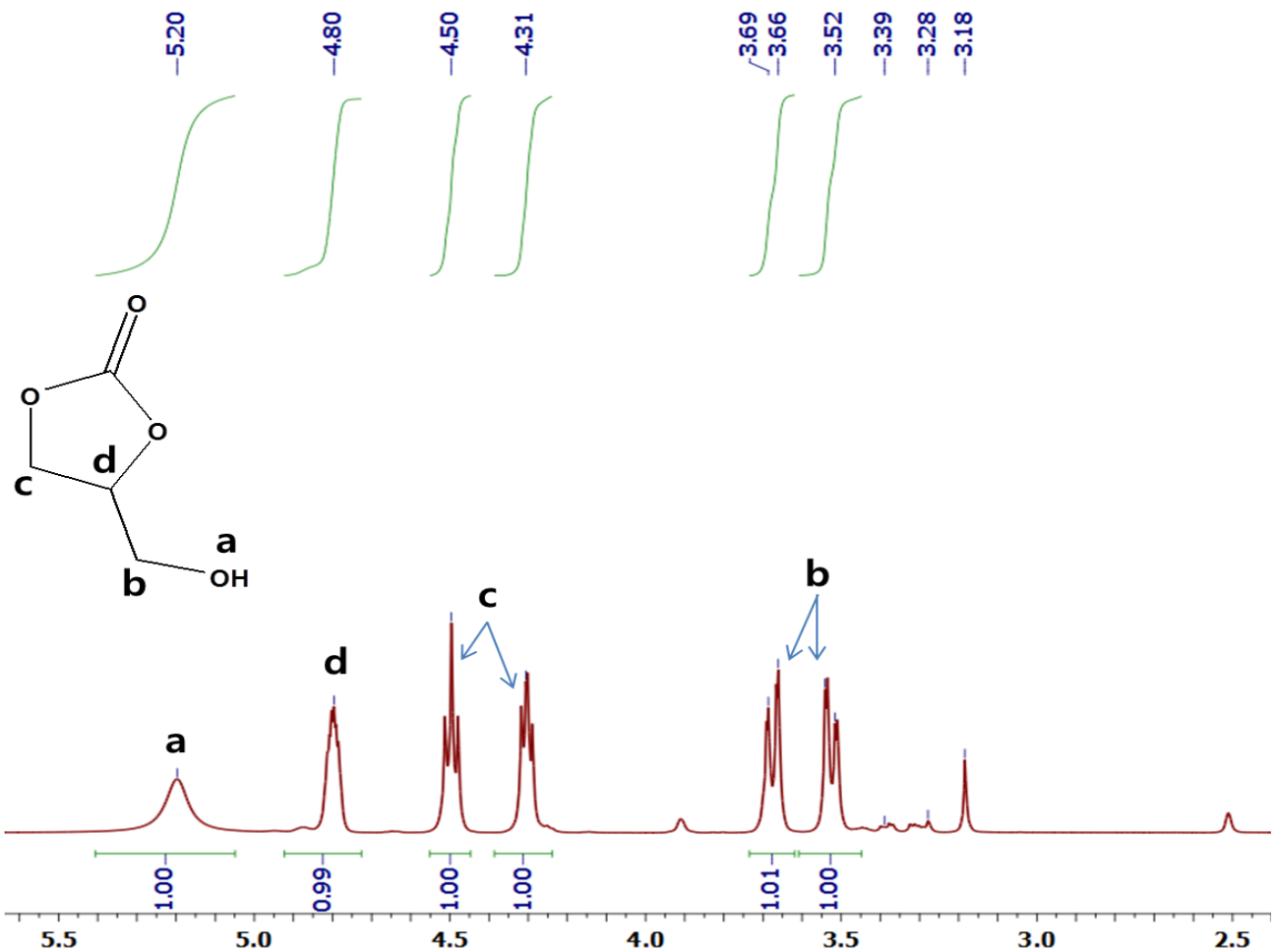


Synthesis of TBBPA



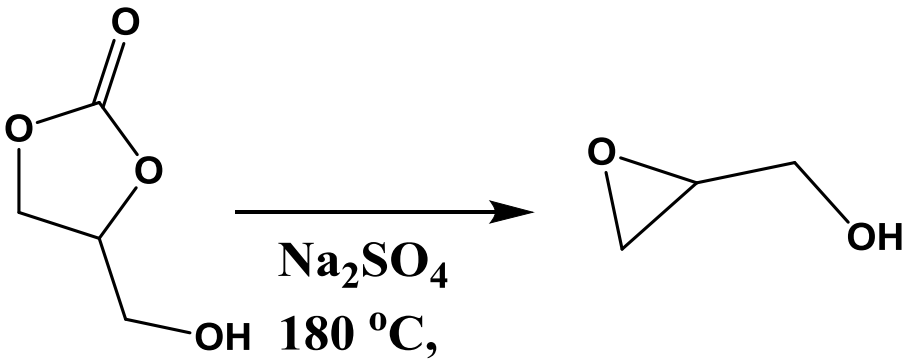


Synthesis of Glycerol Carbonate

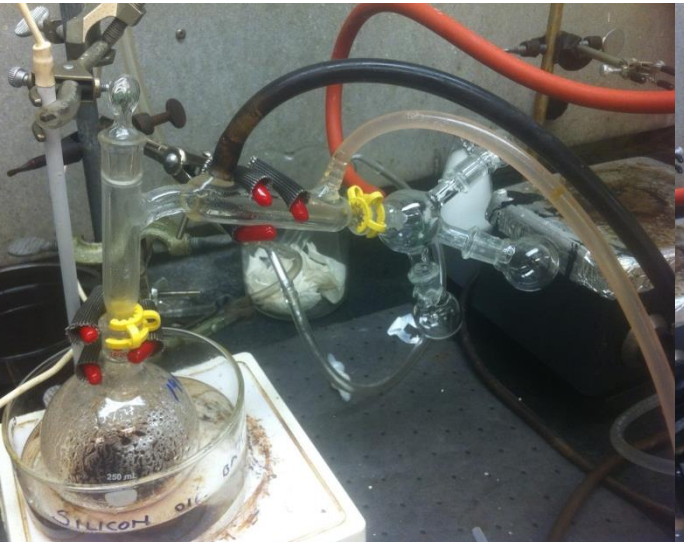


Neutralization using Ambelite IR 120-acidic resins

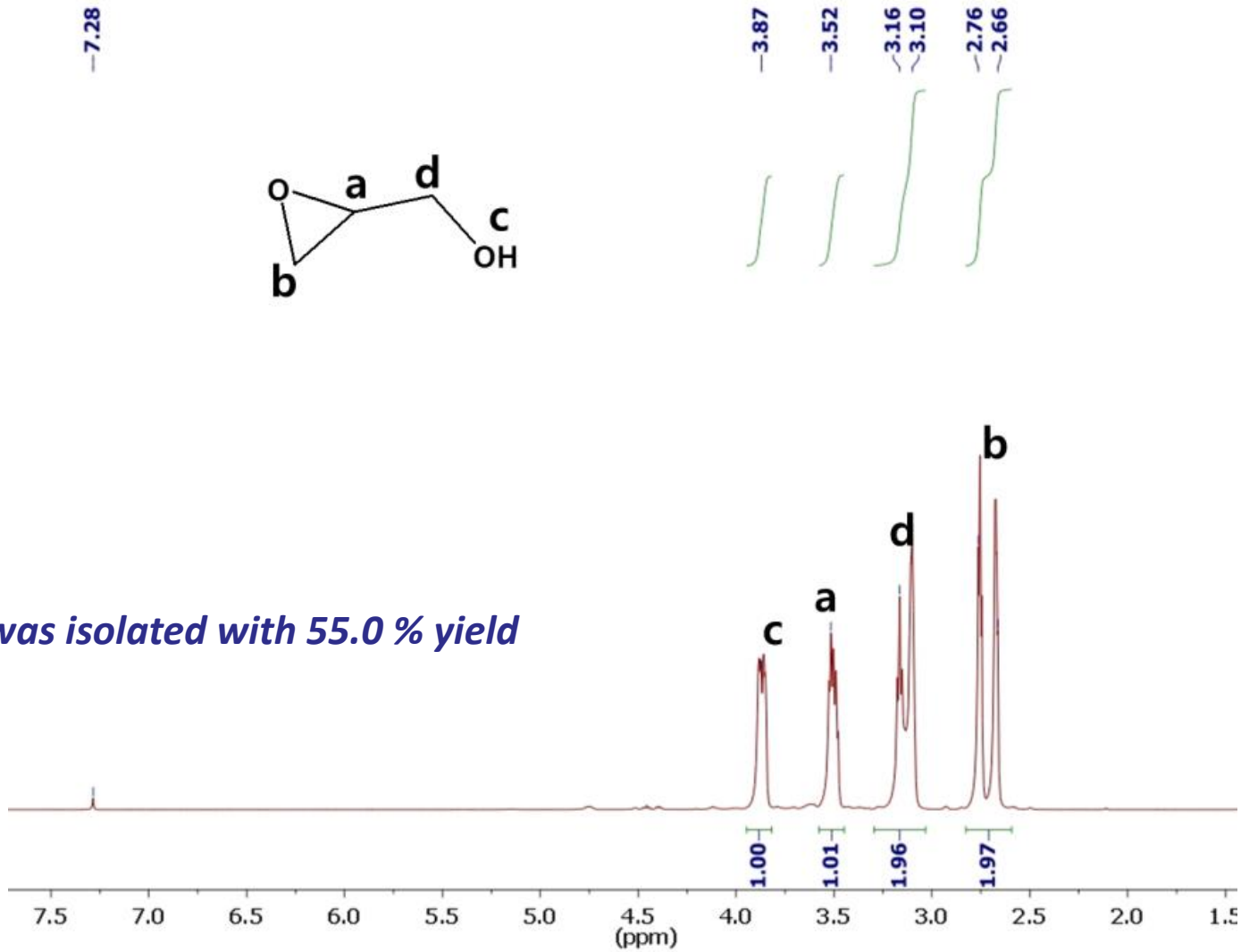
Synthesis of Glycidol



Glycerol carbonate was heated with sodium sulfate at 180 ˚C for 3 h and glycidol was distilled-off under mild vacuum condition.



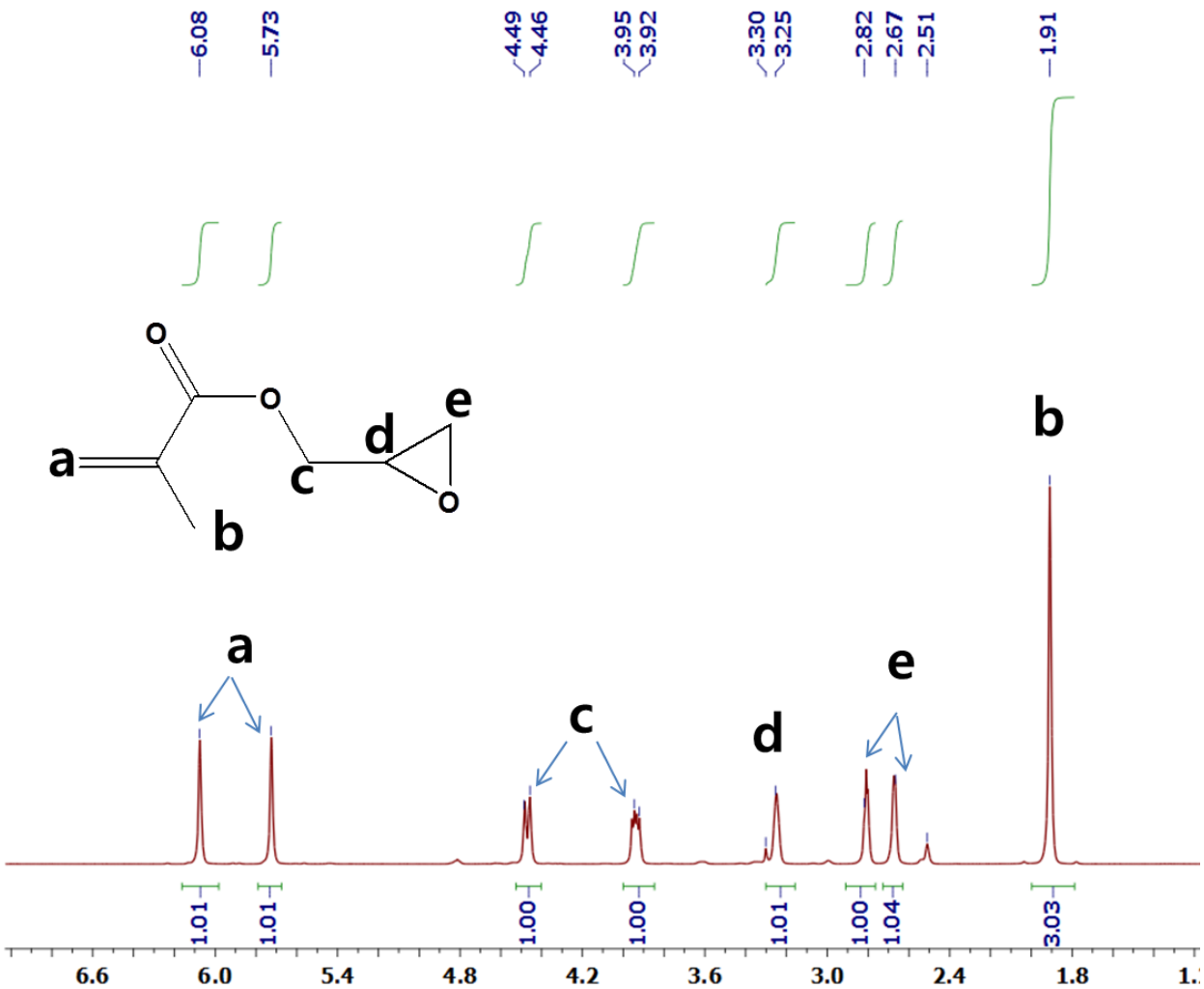
Synthesis of Glycidol



Product was isolated with 55.0 % yield

Synthesis of Glycidyl Methacrylate

GMA was obtained with 25.3 % yield



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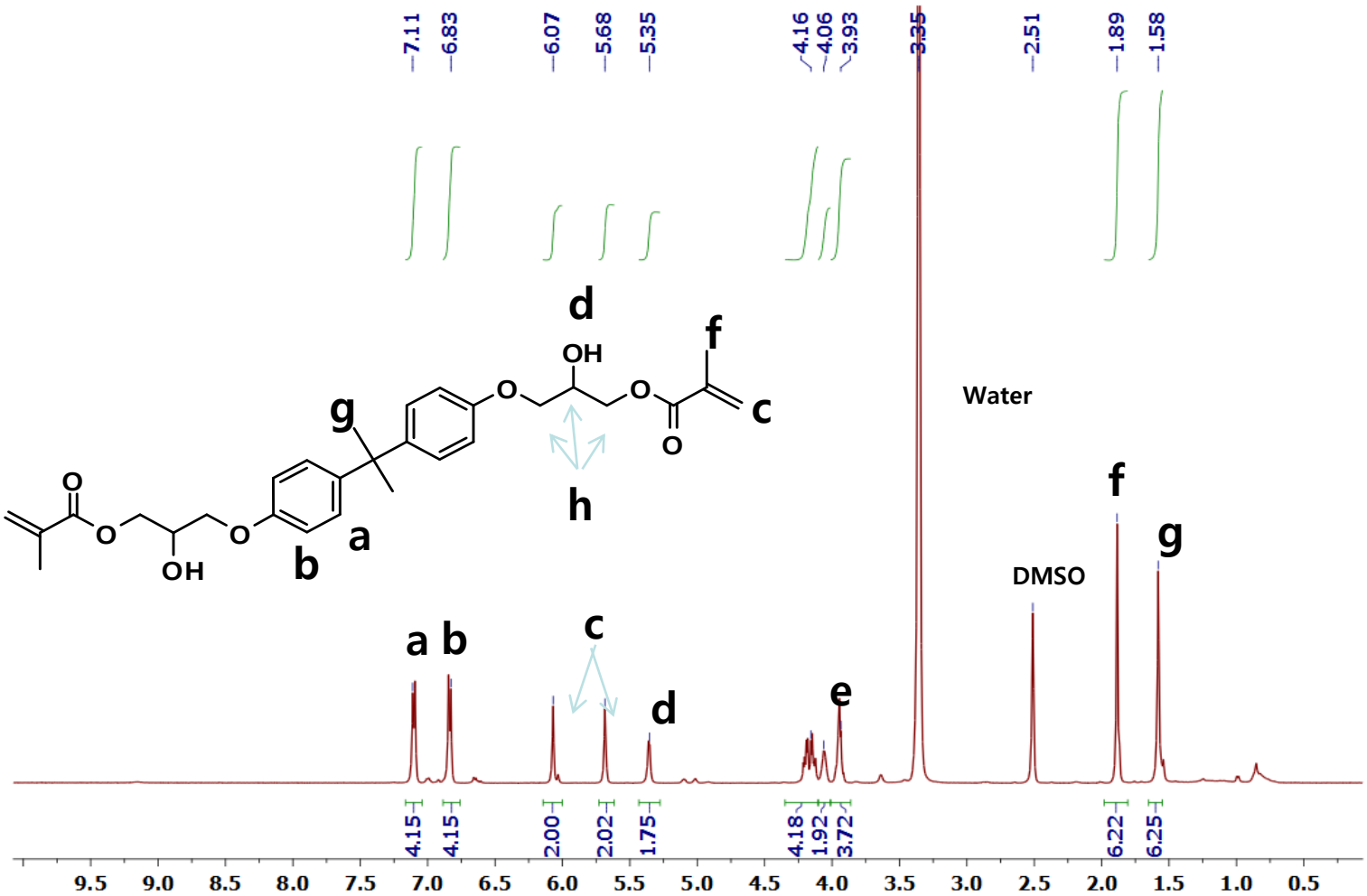
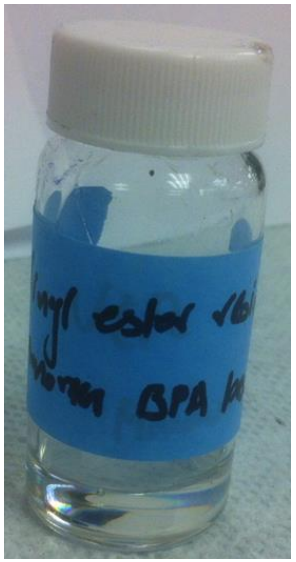
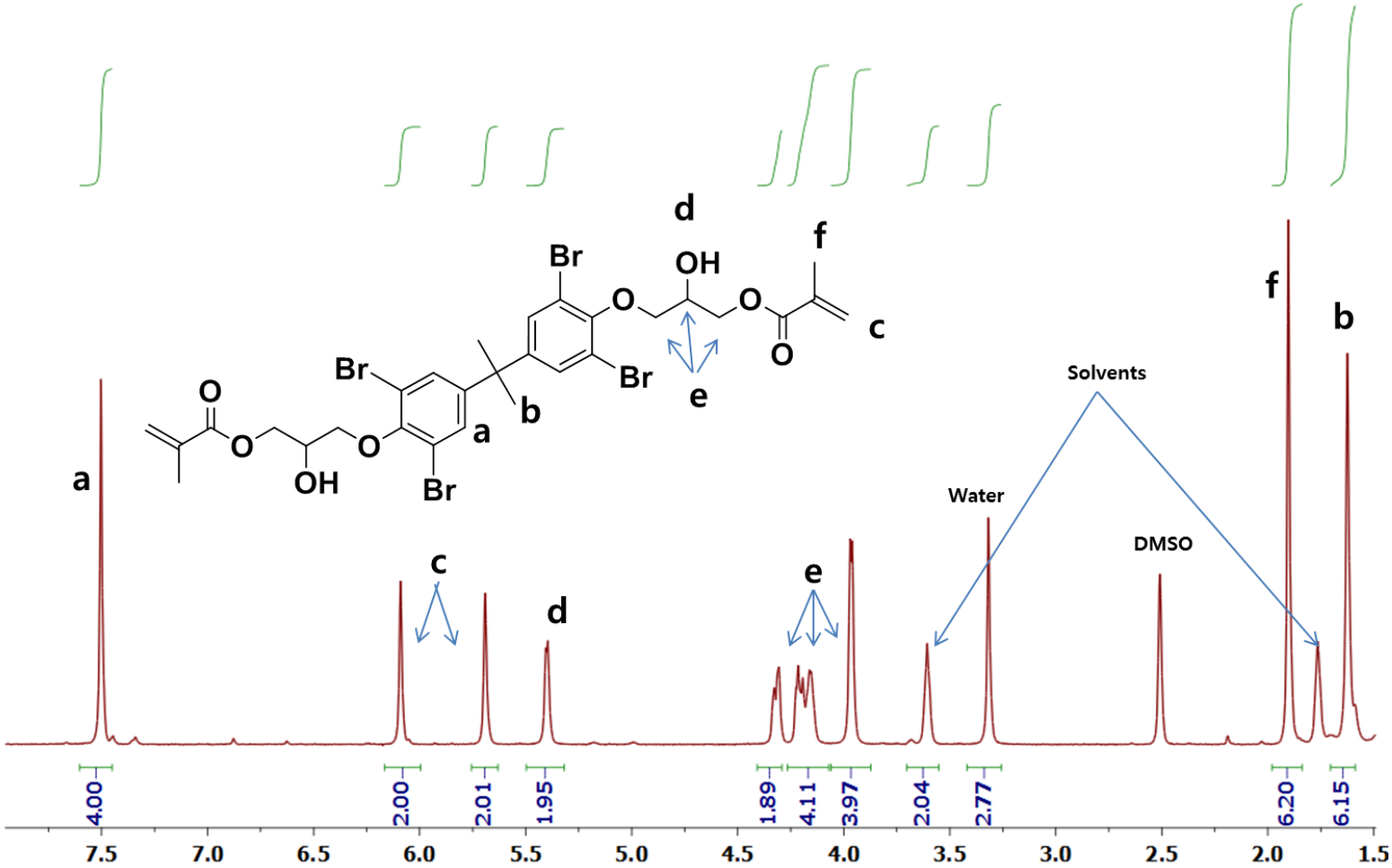
Synthesis of VER Monomer





The reaction was performed at 60 ˚C under inert condition

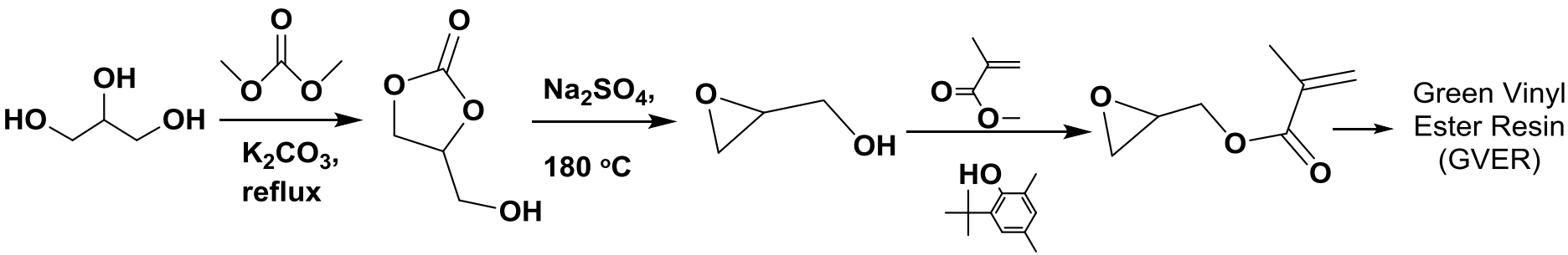
Synthesis of Br-VER Monomer

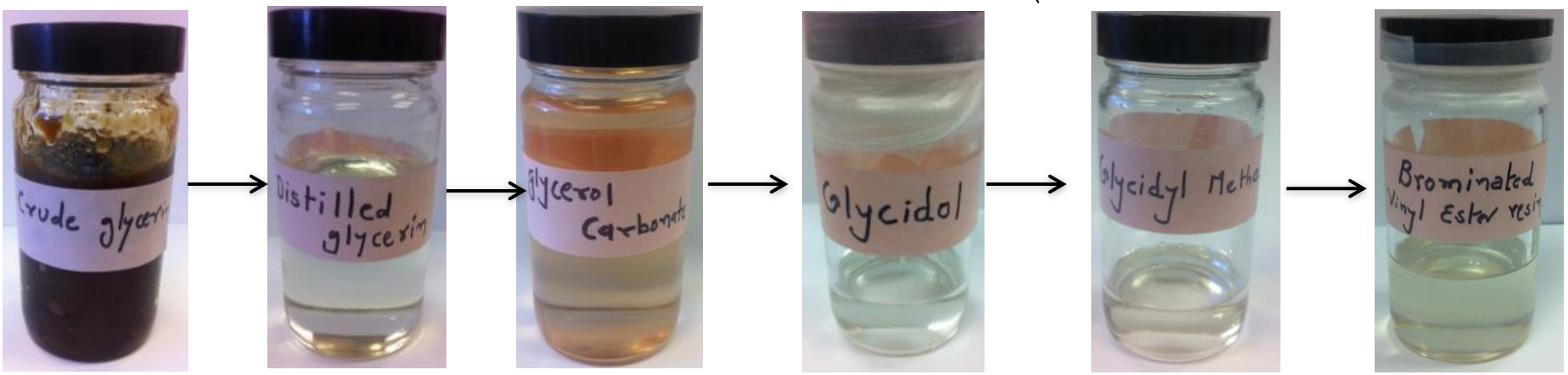


The reaction was performed at 60 ℃ under inert condition

University of Massachusetts Lowell

Green Vinyl Ester Resin from Biodiesel Glycerin

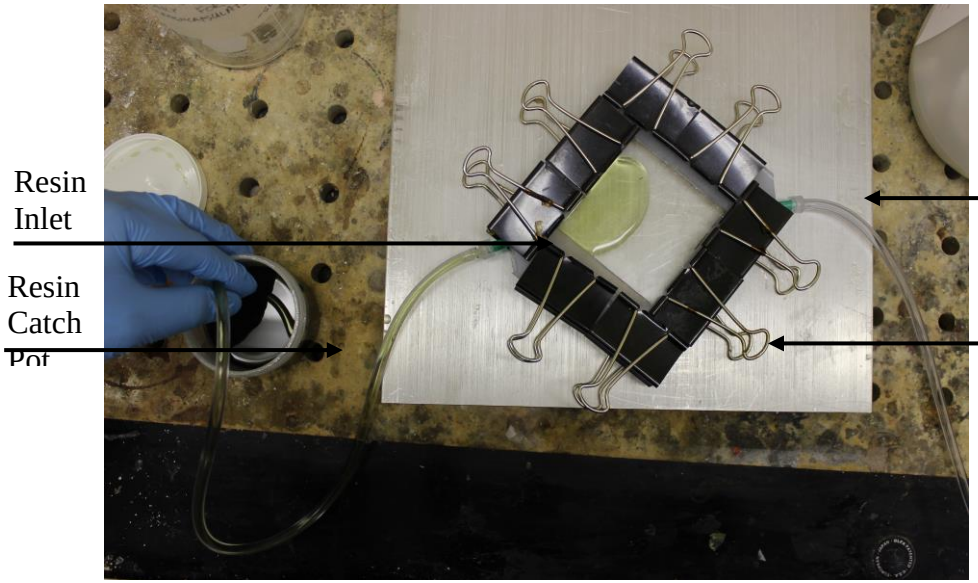


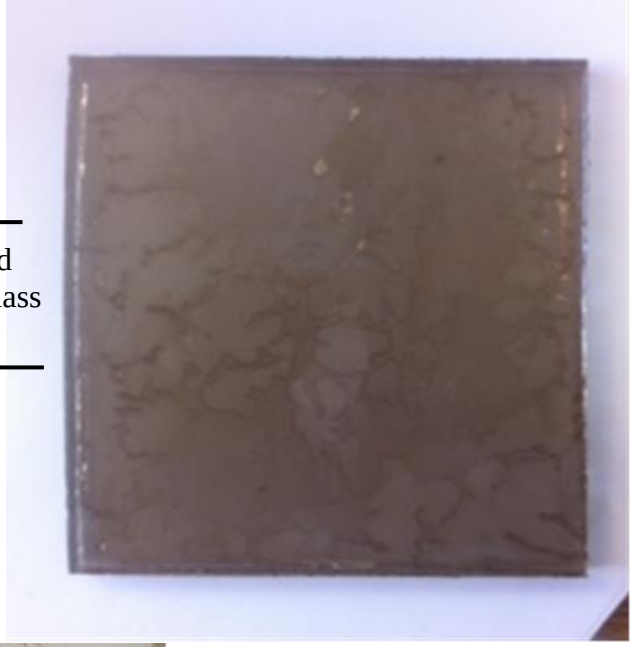


Crude Glycerin → *Distilled Glycerin* → *Glycerol Carbonate* → *Glycidol* → *Glycidyl Methacrylate* → *Green Vinyl Ester Resin*

University of Massachusetts Lowell

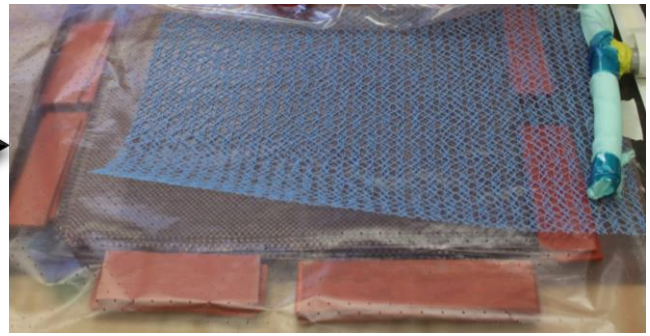
Neat Resin Coupons Fabrication





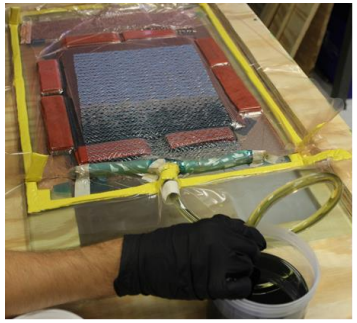
Carbon Fabric Reinforced Coupon Fabrication

Stacking of multiple layers of carbon fabric ply →



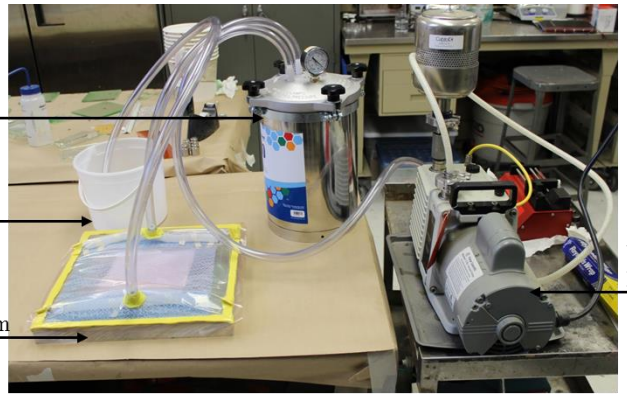
Covering of the stacked carbon fabric ply with peel-ply and resin flow media →

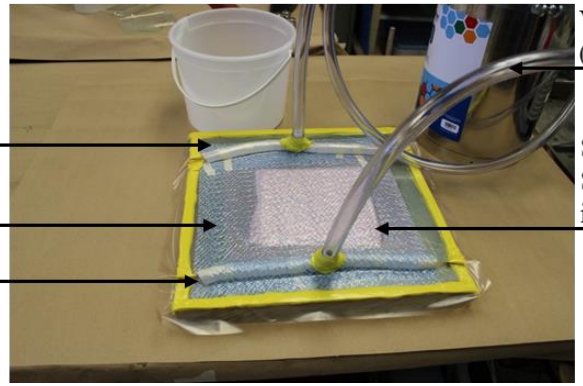
Vacuum was applied and the bag was inspected for leaks →



Resin flow across the plate.

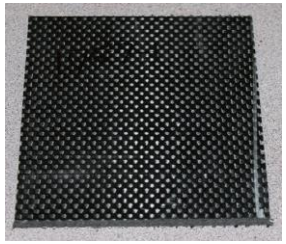
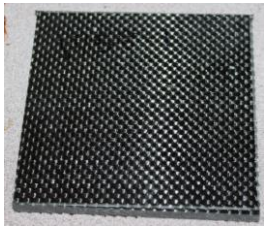
VARTM of VER Resins



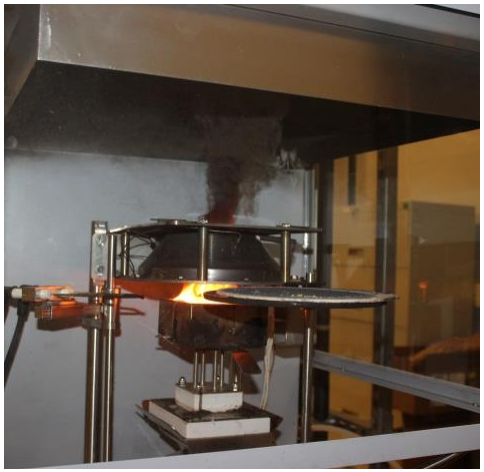


Flammability Testing

Cone Calorimetry Test Samples

Material ID Material Description	Umass Lowell				NAVAIR	
	1742 Brominated VER	1750 VER	1757 'C' Fabric Reinforced / Brominated VER	1758 'C' Fabric Reinforced VER	1760 'C' Fabric Reinforced VER	1763 'C' Fabric Reinforced Brominated VER
Photo						

Maximum burning of the sample during cone calorimetry testing



Maximum generation of smoke during cone calorimetry testing

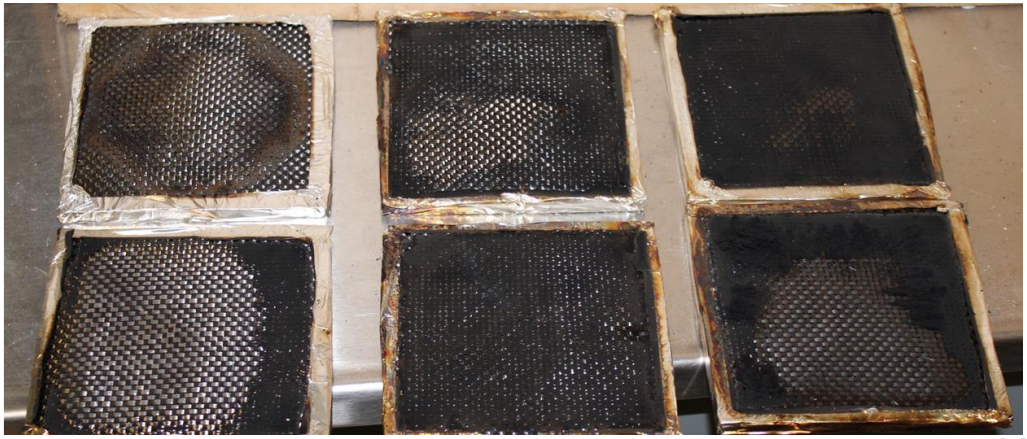
Flammability Testing

Cone Calorimetry Test Results

Sample ID	Time to Ign. (sec)	Flame Duration (sec)	% Mass Loss	Average Effective Heat of Combustion (MJ/kg)	Avg. HRR at 60 sec (kW/m^2)	Avg. HRR at 180 sec (kW/m^2)	Avg. HRR at 300 sec (kW/m^2)	Peak HRR (kW/m^2)	Time of Peak HRR (sec)	Total HRR/A (MJ/m^2)	SEA (m^2/kg)	CO Yield (kg/kg)	CO_2 Yield (kg/kg)
Neat Resin Panel													
Brominated	49	651	94	12	167	191	227	331	282	107	2067	0.17	0.78
Non-Brominated	59	897	100	36	391	528	664	1043	325	295	1274	0.13	4.10
Carbon Fabric Reinforced Resin Panel (UML)													
Brominated	91	339	29	13	108	119	128	159	318	41	1809	0.16	0.72
Non-Brominated	103	408	25	30	144	183	224	317	341	80	1327	0.06	2.27
Carbon Fabric Reinforced Resin Panel (NAVAIR)													
Brominated	97	419	29	14	102	119	127	158	284	43	1556	0.22	0.89
Non-Brominated	106	415	26	30	169	208	228	302	313	80	1296	0.08	2.30

Brominated Resin

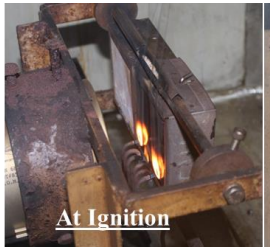
Non-Brominated Resin



Flammability Testing

Smoke Density Test Results

Sample ID	Mode of Combustion	D_m	$D_{m,corr}$	CO (ppm)	CO_2 (%)	HCN (ppm)	HCl (ppm)
			UML_Samples				
Br-VER	Non-Flaming	380	N/R	233	Trace	Trace	N/D
	Flaming	>924*	895	1833	1.17	0.5	1
VER	Non-Flaming	193	187	117	N/D	N/D	0.5
	Flaming	>924*	788	1000	1	N/D	5
C-Fabric reinforced Br-VER	Non-Flaming	134	131	10	N/D	1	0.2
	Flaming	559	542	150	0.5	2	Trace
C-Fabric Reinforced VER	Non-Flaming	25	25	10	N/D	1	N/D
	Flaming	330	298	367	1	4	N/D
			NAVAIR_Samples				
C-Fabric reinforced Br-VER	Non-Flaming	87	83	23	N/D	1	N/D
	Flaming	772	750	2000	1.5	Trace	N/D
C-Fabric Reinforced VER	Non-Flaming	19	19	10	N/D	1	N/D
	Flaming	305	296	500	1.2	2	N/D



Non-flaming

Flaming

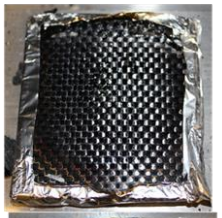
Brominated neat rein panels

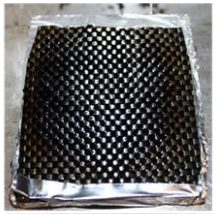
Brominated Resin

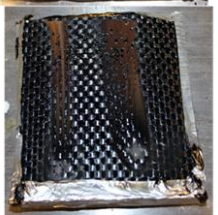
Non-brominated Resin

Non-Flaming

Flaming







Mechanical Testing

Tensile Testing

Sample	(Br-VER Composite)				
	Ultimate Tensile Strength (UTS)		Elastic Modulus		Strain to Failure
	psi	MPa	psi	GPa	e
AVERAGE	102000 ± 11000	704 ± 74	7520000 ± 511000	52 ± 3.5	0.0133 ± 0.00229
	(VER Composite)				
AVERAGE	100000 ± 6000	691 ± 41	7730000 ± 175000	53 ± 1.2	0.0138 ± 0.0003

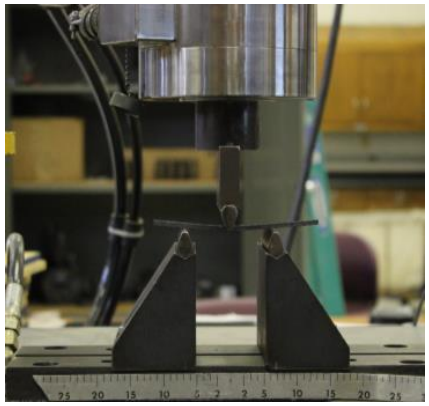
Setup for tensile testing of VER and Br-VER composite specimens.

Sample	Neat Br-VER specimen			
	Tensile Strength		Elastic Modulus	
	psi	MPa	psi	MPa
AVERAGE	3300 ± 800	23 ± 6	358000 ± 30000	2500 ± 200
	Neat VER specimen			
AVERAGE	4630 ± 60	31.8 ± 0.3	348000 ± 24000	2400 ± 162

Mechanical Testing

Flexural Testing

Br-VER carbon fabric reinforced samples				
Sample	Flexural Modulus (E)		Flexural Strength FS	
	psi	GPa	psi	MPa
AVERAGE	7140000 ± 660000	49 ± 4.5	29800 ± 2500	206 ± 18
VER carbon fabric reinforced samples				
AVERAGE	4640000 ± 225000	32.1 ± 1.6	30600 ± 547	211 ± 4



Setup for flexure testing of VER and Br-VER specimens.

Specimen of near Br-VER for flexure testing.

Br-VER neat resin specimen				
Sample	Flexural Modulus (E)		Flexural Strength (FS)	
	psi	Map	psi	MPa
AVERAGE	393000 ± 6000	2700 ± 42	3300 ± 380	21 ± 4
VER neat resin specimen				
AVERAGE	347698± 7111	2397±49	4767±26	33±0

Mechanical Testing

Short Beam Strength Testing

UML samples

Br-VER Composite		
Sample	SBS	
	ksi	MPa
AVERAGE	4.65 ± 0.18	32 ± 1

VER Composite		
Sample	SBS	
	ksi	MPa
AVERAGE	4.50 ± 0.46	32 ± 3

Short Beam Strength Testing

Barcol Hardness		
Sample	VER	Br-VER
AVERAGE	49 ± 1.3	50 ± 1.5
Error	2.6%	2.9%

NAVAIR samples

Br-VER Composite	
Specimen	SBS (ksi)
Mean	4.17
Standard Deviation	0.11
Coefficient of Variation	0.03
VER Composite	
Mean	4.15
Standard Deviation	0.33
Coefficient of Variation	0.08

DMA analysis

Br-VER Composite Tg	
Specimen	Glass Transition Temp.
1	118.65˚C
2	119.30˚C
VER Composite Tg	
1	118.28˚C
2	116.34˚C

Cost Analysis-I

Process Cost Calculation

Major Raw Materials	Amount (mol)	Amount (g)	Price ($/lb) *F.O.B Basis**	Material Cost
Glycerin to Glycidyl methacrylate				
Glycerin	10.70	985.63	$0.52	$1.12
Dimethyl carbonate	32.10	2891.6 (Recyclable)	$0.77	$1.60 consumed
Methyl methacrylate	28.85	2889.0 (Recyclable)	$1.35	$0.72 consumed
Phenol to Bisphenol A				
Phenol	9.288	874.09	$0.61	$1.17
Acetone	4.644	269.65	$0.54	$0.32
Material Cost ~ $4.93/kg F.O.B				
Transportation Estimate – 20% Material Cost ~ $0.986				
Total Material Cost ~ $5.92/kg = $2.69/lbs				

Raw Material Cost Information for production of 1 kg of VER

*Cost information based on Freight on Board (F.O.B) pricing from ICIS Chemical Review July 2014

Cost Analysis-II

Targeted Area of Cost Savings

Major Raw Materials	Amount (mol)	Amount (g)	Price ($/lb) ***F.O.B Basis****	Material Cost
Glycerin to Glycidyl methacrylate				
Glycerin	10.70	985.63	**$0.52**	$1.12
Crude Glycerin significantly cheaper at $0.09/lbs				
Phenol to Bisphenol A				
Phenol	9.288	874.09	**$0.61**	$1.17
Lignin Market ~ $0.09/lb price ***Equivalent heating value of $0.18/lb***				

Room to Maneuver for Cost Savings

Raw Material Cost Information for production of 1 kg of VER

*Cost information based on Freight on Board (F.O.B) pricing from ICIS Chemical Review July 2014

Project Funding

	FY13*	FY14*	FY15*	FY16	Total
Proposal Requested ($K)	380	438	434		1252
Funds Received ($K)	380				
% Expended	100				
Projected Out-Year Funds Required ($K)		438	434		1252

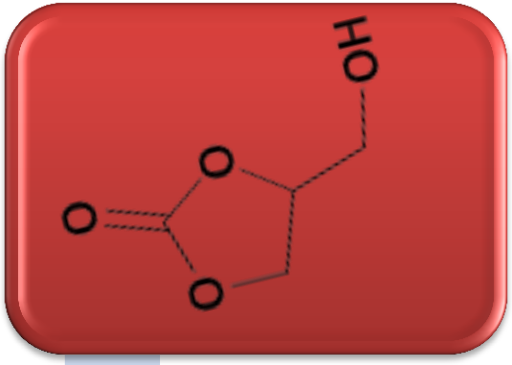
***NOTES:**

This table should reflect SERDP funds sent to all directly funded and second tier performers working on the project.

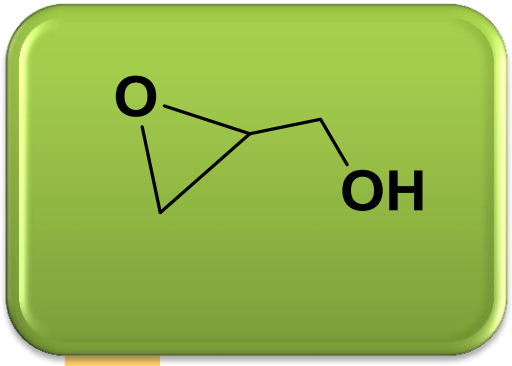
Include columns for all fiscal years for which funding has been received, is budgeted to be received, or is proposed to be received in the Revised Funding Profile. Add columns as needed.

Based on your spend rates for funding already received and any discussion with your program manager, identify your proposed out-year funding requirements. Total should not exceed current total project value.

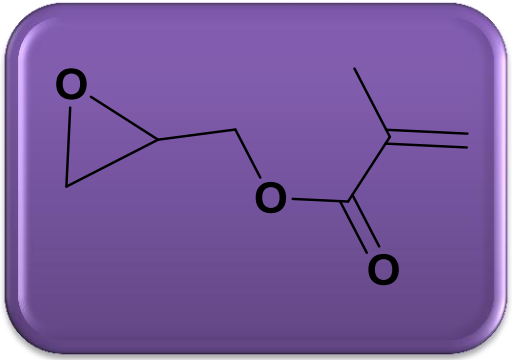
Transition Plan



- Solvent
- Batteries
- Cement
- Cosmetics
- Gas separation



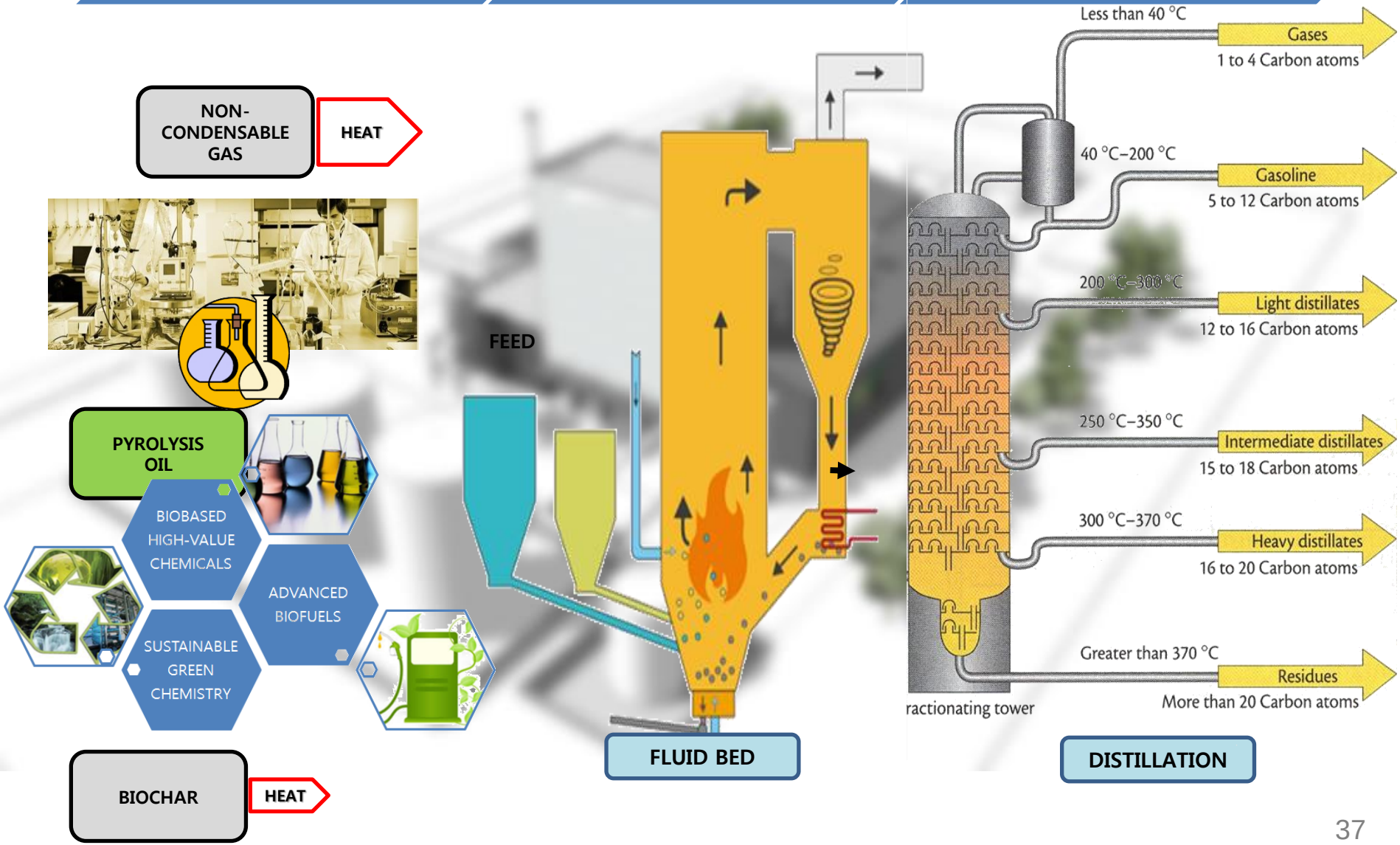
- Stabilizer
- Intermediate for many products
- Surface Coatings



- Dual functionality: epoxy and vinyl group
- Various applications

Ready to use materials synthesized from biodiesel glycerin

LAB-SCALE > SCALE-UP > REFINEMENT



Transition Plan

Pilot scale

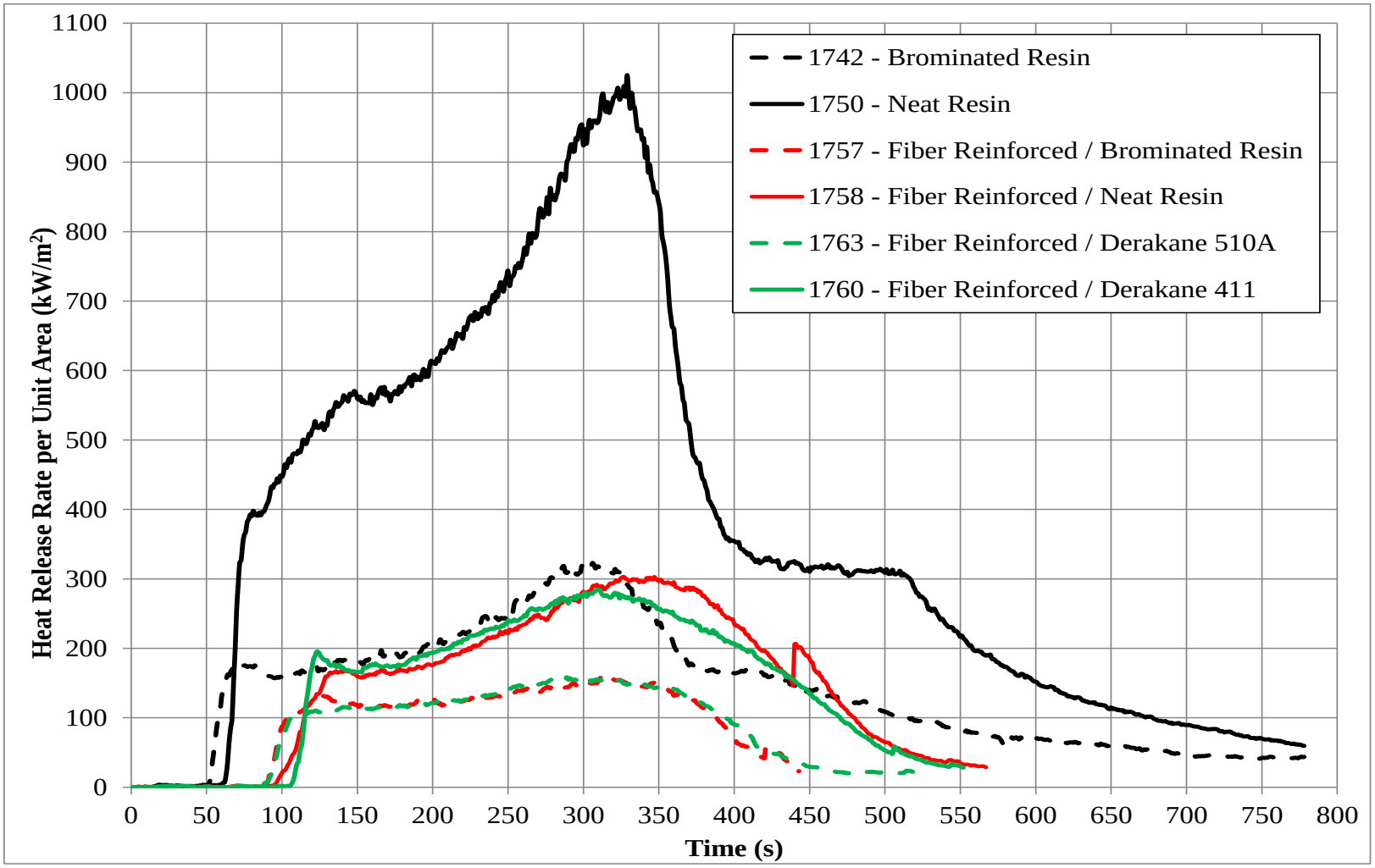
Reactor

Lab scale

BACKUP MATERIAL

These charts are required, but will only be briefed if questions arise.

ASTM E1354 Heat Release Rate Compilation



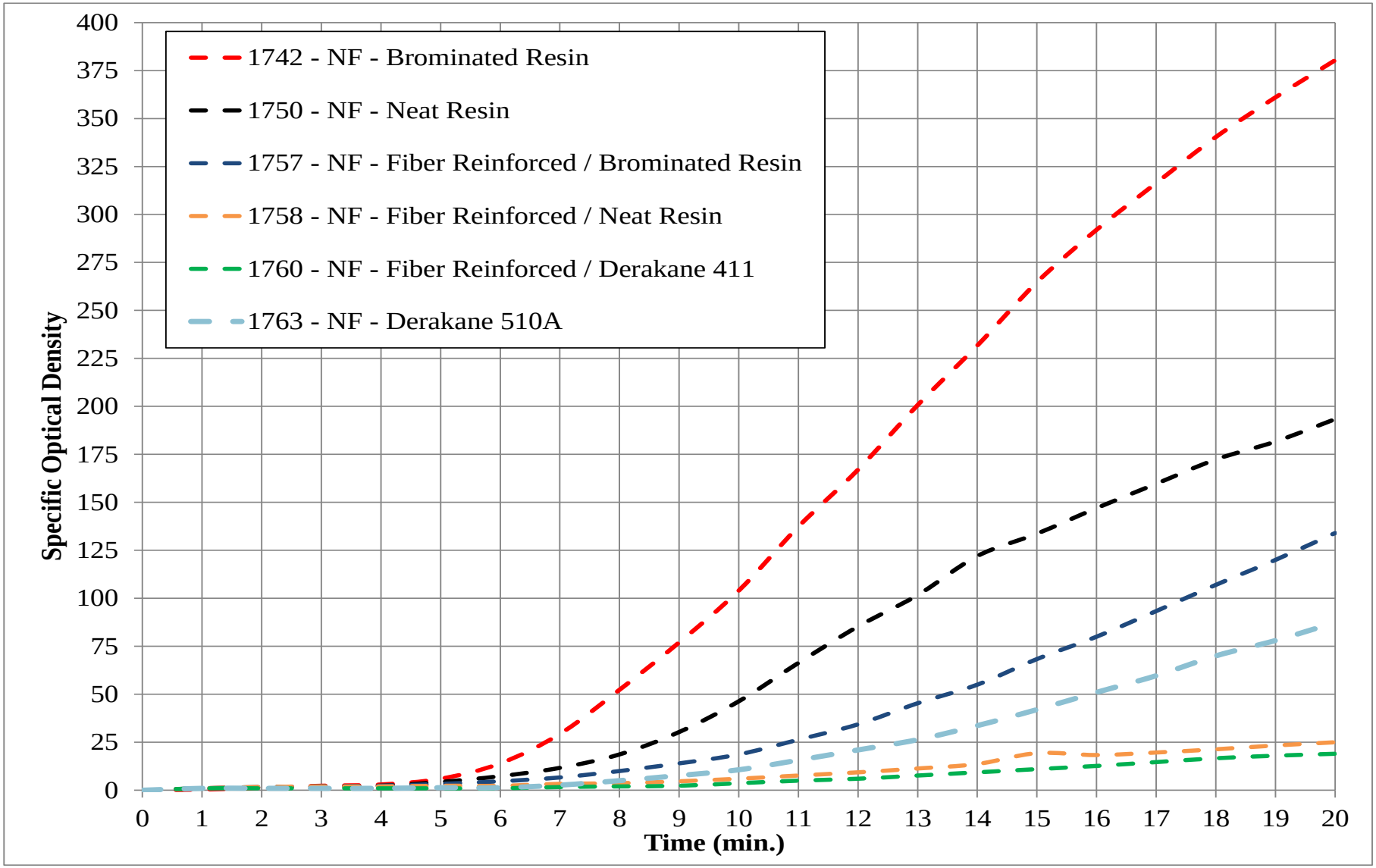
ASTM E1354 Data Compilation

Sample ID	Time to Ign. (sec)	Flame Duration (sec)	% Mass Loss	Average Effective Heat of Combustion (MJ/kg)	Avg. HRR at 60 sec (kW/m^2)	Avg. HRR at 180 sec (kW/m^2)	Avg. HRR at 300 sec (kW/m^2)	Peak HRR (kW/m^2)	Time of Peak HRR (sec)	Total HRR/A (MJ/m^2)	SEA (m^2/kg)	CO Yield (kg/kg)	CO2 Yield (kg/kg)
1742_1	51	723	95	11	142	167	207	310	304	102	2102	0.17	0.750
1742_2	50	529	91	12	170	197	238	353	280	102	2117	0.16	0.700
1742_3	47	702	95	13	188	208	236	329	262	117	1982	0.19	0.890
Average	**49**	**651**	**94**	**12**	**167**	**191**	**227**	**331**	**282**	**107**	**2067**	**0.17**	**0.78**
1750_1	61	985	99	36	382	517	658	1042	335	295	1222	0.14	4.4
1750_2	58	875	100	36	384	521	669	1083	330	303	1293	0.13	4.1
1750_3	59	830	100	35	406	547	664	1003	310	288	1306	0.12	3.8
Average	**59**	**897**	**100**	**36**	**391**	**528**	**664**	**1043**	**325**	**295**	**1274**	**0.13**	**4.10**
1757_1	99	18	4	4	N/A	N/A	N/A	124	106	2	568	0	0
1757_2	89	353	28	13	110	118	126	146	323	42	1796	0.16	0.77
1757_3	93	325	29	12	106	120	129	172	313	40	1823	0.16	0.67
Average	**91**	**339**	**29**	**13**	**108**	**119**	**128**	**159**	**318**	**41**	**1809**	**0.16**	**0.72**
1758_1	114	449	25	30	134	166	206	289	370	79	1320	0.06	2.3
1758_2	93	342	26	27	142	195	235	343	322	75	1245	0.04	1.8
1758_3	103	434	24	34	157	189	232	319	332	87	1417	0.07	2.7
Average	**103**	**408**	**25**	**30**	**144**	**183**	**224**	**317**	**341**	**80**	**1327**	**0.06**	**2.27**
1760_1	111	437	26	29	154	190	207	258	312	78	1381	0.07	2.2
1760_2	103	398	26	31	167	208	236	325	320	81	1345	0.08	2.3
1760_3	108	431	26	29	170	207	220	279	305	78	1246	0.08	2.3
Average	**106**	**415**	**26**	**30**	**169**	**208**	**228**	**302**	**313**	**80**	**1296**	**0.08**	**2.30**
1763_1	91	365	29	13	104	121	131	163	284	43	1464	0.18	0.79
1763_2	99	420	31	13	104	118	128	162	278	44	1412	0.19	0.78
1763_3	94	418	26	14	100	119	126	154	289	41	1700	0.25	1
Average	**97**	**419**	**29**	**14**	**102**	**119**	**127**	**158**	**284**	**43**	**1556**	**0.22**	**0.89**

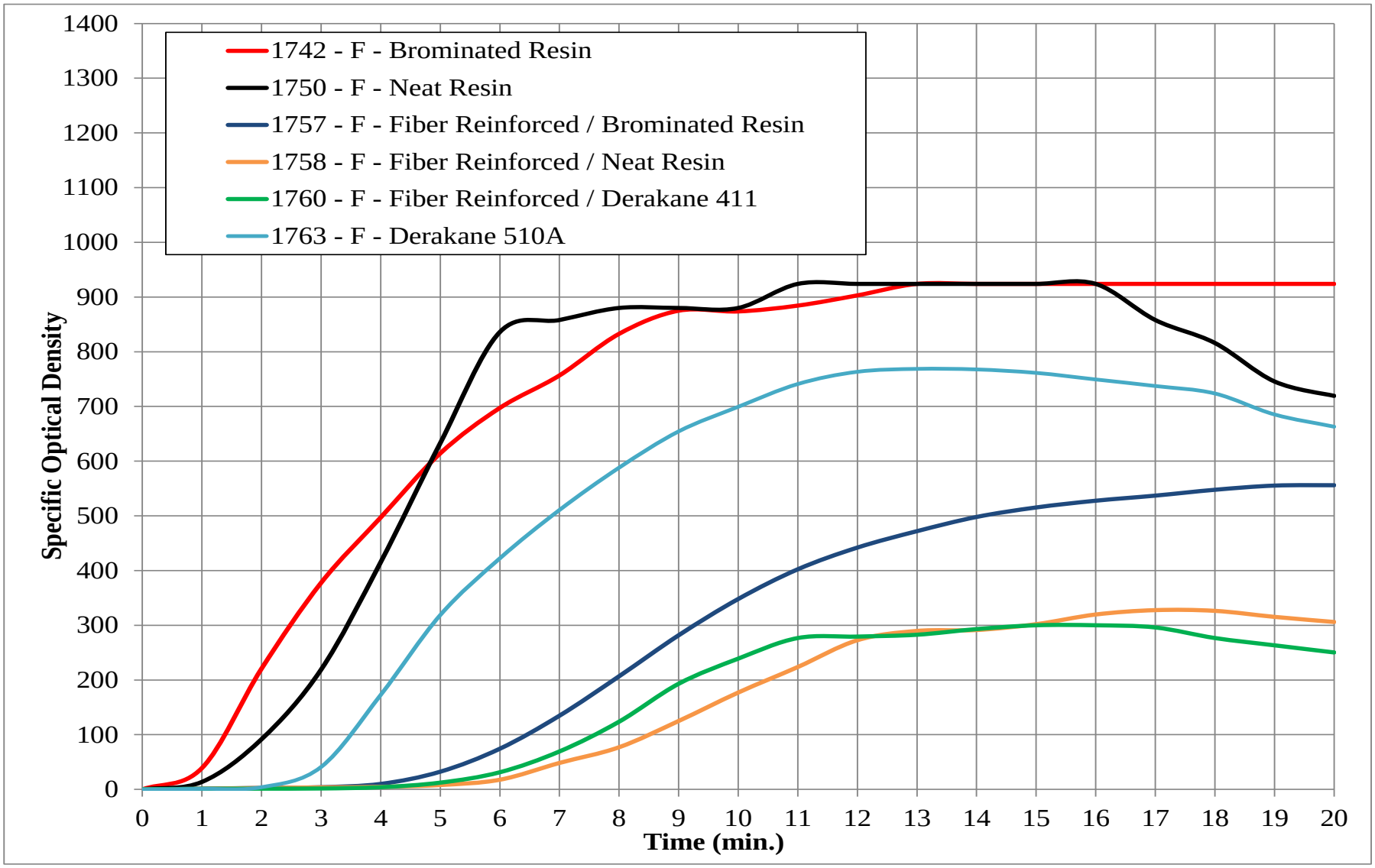
1742 – Brominated Vinyl Ester Resin (VER)
1757 – Brominated VER Composite with ‘C’ Fabric
1760 – Carbon Fiber Composite with Derakane 411

1750 – Neat VER
1758 – Neat VER with ‘C’ Fabric
1763 – Carbon Fiber Composite with Derakane510A

ASTM E662 Non-Flaming Smoke Compilation



ASTM E662 Flaming Smoke Compilation



Tensile Testing (Brominated & Non-Brominated Composite Specimens)

- Manufactured using VARTM
  - 12 plies of Carbon Fiber
- ASTM D3039
- 6” Gage length
- Targeted Specimen Dimensions
  - 10” X 1” X 0.10”
- Machine compliance an issue in strain measurement
- Samples Re-tested with strain gauges attached

Tensile Test: Brominated Carbon Fiber		
Sample	**Average w [in.]**	**Average t [in.]**
BT4	0.931	0.0930
BT8	0.900	0.1027
BT10	0.908	0.1017
BT11	0.901	0.1018
AVERAGE	**0.910 ± 0.013**	**0.0998 ± 0.004**

Tensile Test: Non Brominated Carbon Fiber		
Sample	Average w [in.]	Average t [in.]
NBR1	0.943	0.123
NBR2	0.902	0.125
NBR3	0.935	0.125
NBR4	0.891	0.118
NBR5	0.948	0.122
AVERAGE	**0.924 ± 0.023**	**0.123 ± 0.003**

Tensile Testing (Brominated & Non-Brominated Neat Specimens)

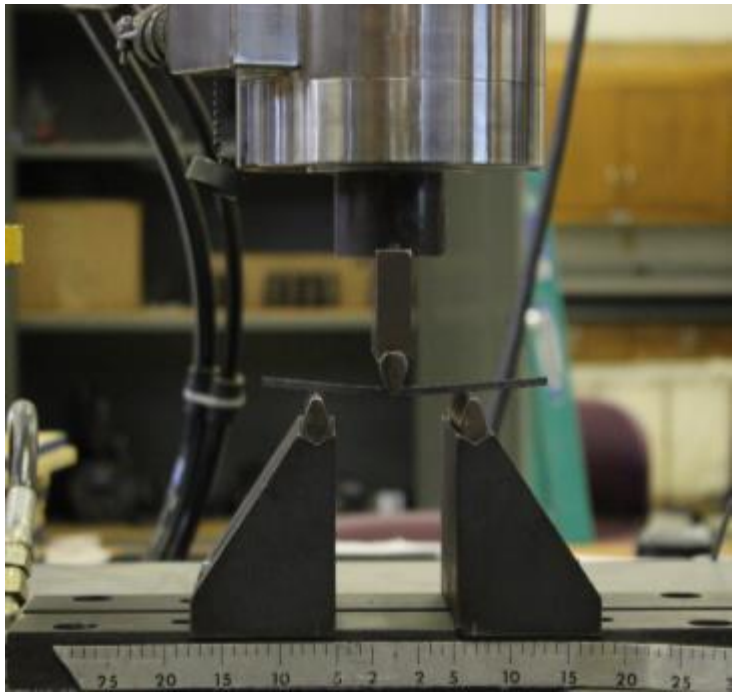
- Manufactured using open faced silicone molds
- ASTM D638
- 4.5” Gage Length
- Targeted Specimen Dimensions
  - ♦ Specimens molded on Type 1 High Impact Polystyrene Tensile Bars

Tensile Test: Brominated Neat		
Sample	**Average w [in.]**	**Average t [in.]**
BRN5 –T	0.516	0.129
BRN3 –T	0.508	0.133
BRN4 –T	0.513	0.136
BRN2 –T	0.507	0.126
AVERAGE	**0.511 ± 0.004**	**0.131 ± 0.004**

Tensile Test: Non Brominated Neat		
Sample	Average w [in.]	Average t [in.]
NBR1	0.526	0.132
NBR2	0.521	0.129
NBR3	0.525	0.127
NBR4	0.510	0.133
NBR5	0.507	0.122
AVERAGE	**0.518 ± 0.007**	**0.129 ± 0.004**

Flexure Testing (Brominated & Non-Brominated Composite Specimens)

- ASTM D790
- Three Point Bend Test
- Span Length : Thickness Ratio = 20:1
- Span Length for Brominated Carbon Fiber =2.70”
- Span Length for Non Brominated Carbon Fiber=3.60”
- Targeted Specimen Dimensions
  - 5” x 0.5” x 0.16”



Flexure Test: Brominated Carbon Fiber		
Sample	**Average w [in.]**	**Average t [in.]**
BF4	0.3750	0.1380
BF5	0.3510	0.1330
BF7	0.4520	0.1360
BF6	0.4120	0.1360
BF9	0.4390	0.1360
AVERAGE	**0.4058 ± 0.039**	**0.1358 ± 0.001**

Flexure Test: Non Brominated Carbon Fiber		
Sample	**Average w [in.]**	**Average t [in.]**
NLB1	0.490	0.183
NLB2	0.463	0.179
NLB3	0.520	0.185
NLB4	0.510	0.180
NLB5	0.525	0.180
AVERAGE	**0.502 ± 0.02**	**0.181 ± 0.002**

Flexure Testing (Brominated & Non-Brominated Neat Specimens)

- ASTM D790
- Three Point Bend Test
- Span Length : Thickness Ratio = 20:1
- Span Length: 2.7”
- Targeted Specimen Dimensions
  - 5” x 0.5” x 0.16”

Flexure Test: Brominated Neat		
Sample	**Average w [in.]**	**Average t [in.]**
BFN1	0.495	0.125
BFN2	0.494	0.126
BFN3	0.500	0.131
BFN4	0.496	0.154
AVERAGE	**0.496 ± 0.002**	**0.134 ± 0.012**

Flexure Test: Non Brominated Neat		
Sample	**Average w [in.]**	**Average t [in.]**
NNLB2	0.50	0.116
NNLB1	0.498	0.125
NNLB3	0.495	0.120
NNLB4	0.495	0.123
AVERAGE	**0.497 ± 0.002**	**0.121 ± 0.003**

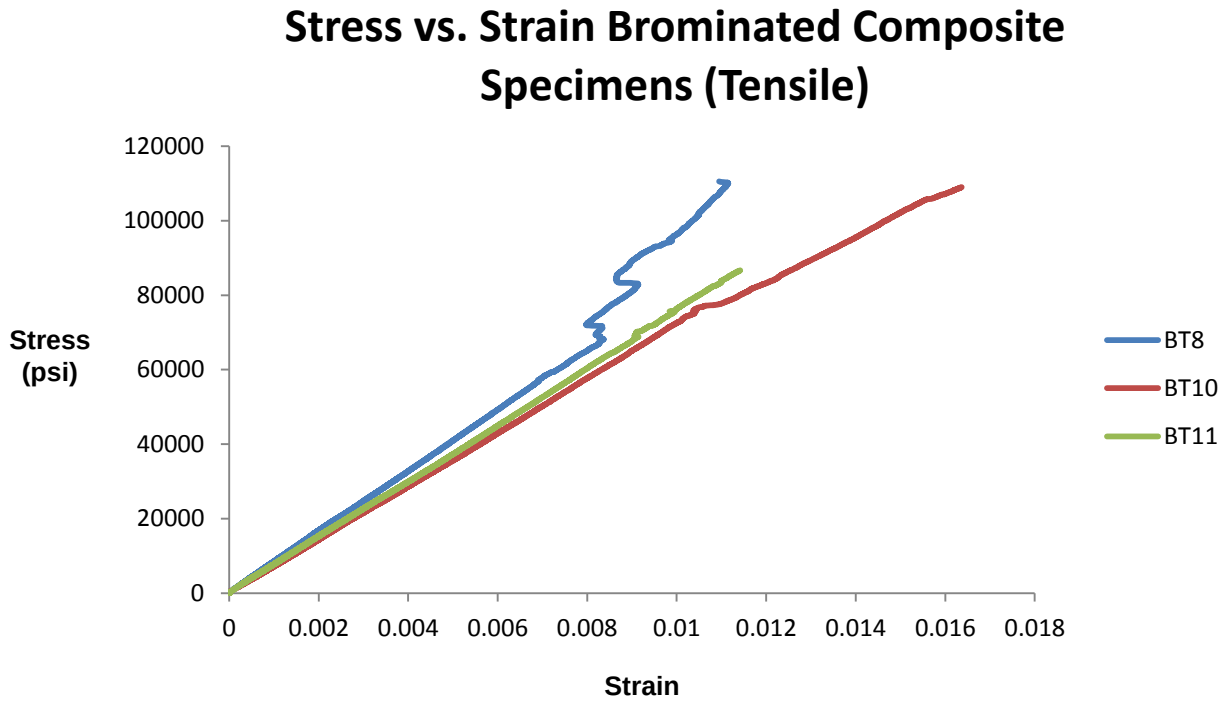
Short Beam Strength Testing (Brominated & Non-Brominated Composite Specimens)

- ASTM D2344
- Span Length: 1”
- Targeted Specimen Dimensions
  - 1.5” x 0.5” x 0.25”

Short Beam Test: Brominated Carbon Fiber		
Sample	**Average w [in.]**	**Average t [in.]**
1	0.562	0.261
2	0.655	0.262
3	0.513	0.257
4	0.597	0.256
5	0.498	0.256
AVERAGE	**0.565 ± 0.057**	**0.257±0.003**

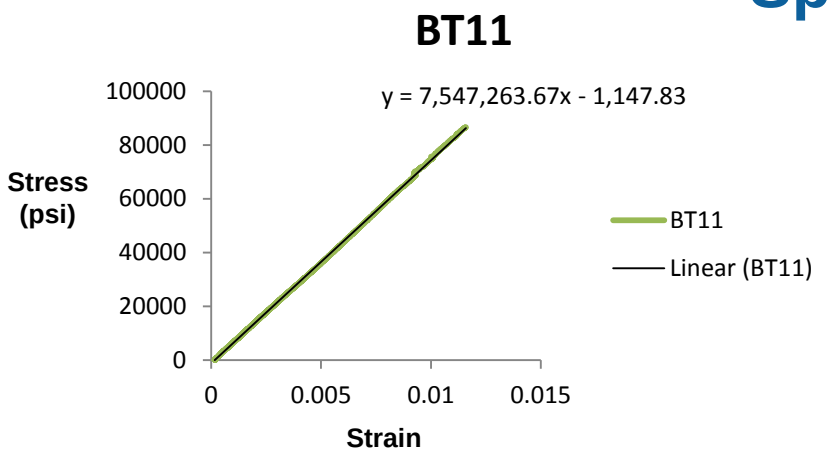
Short Beam Test: Non Brominated Carbon Fiber		
Sample	**Average w [in.]**	**Average t [in.]**
NSBS1	0.595	0.25
NSBS2	0.563	0.252
NSBS3	0.575	0.255
NSBS4	0.577	0.255
NSBS5	0.573	0.253
AVERAGE	**0.577 ± 0.010**	**0.253 ± 0.0019**

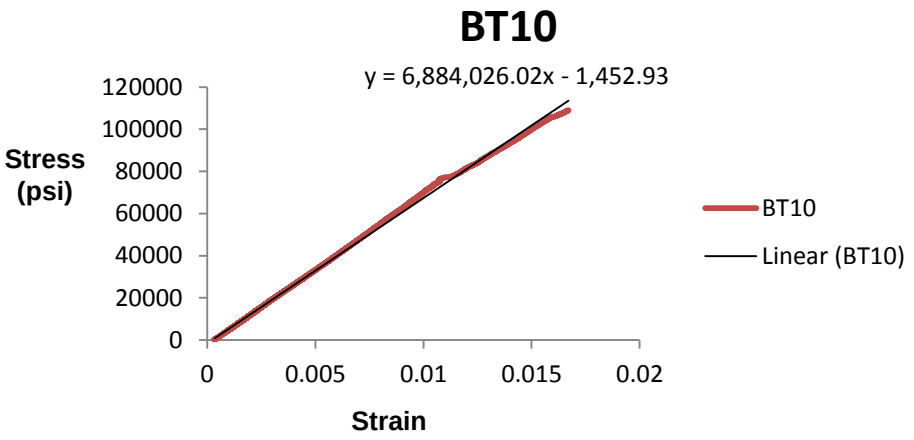
Tensile Testing Results (Brominated Composite Specimens)

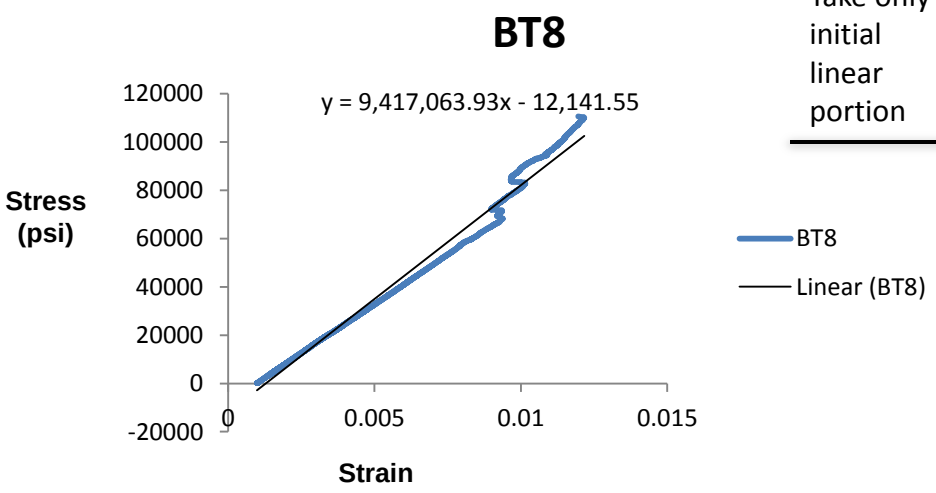


Ultimate Tensile Strength (Brominated Composite)		
Sample	UTS	
	psi	MPa
BT8	110510	762
BT10	109023	751
BT11	86641	598
AVERAGE	102000 ± 11000	704 ± 74

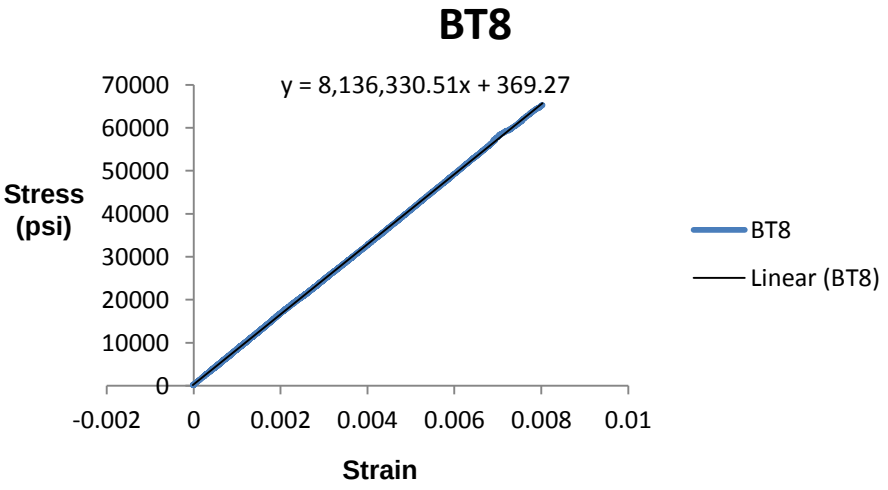
Tensile Testing Results (Brominated Composite Specimens)







Take only initial linear portion

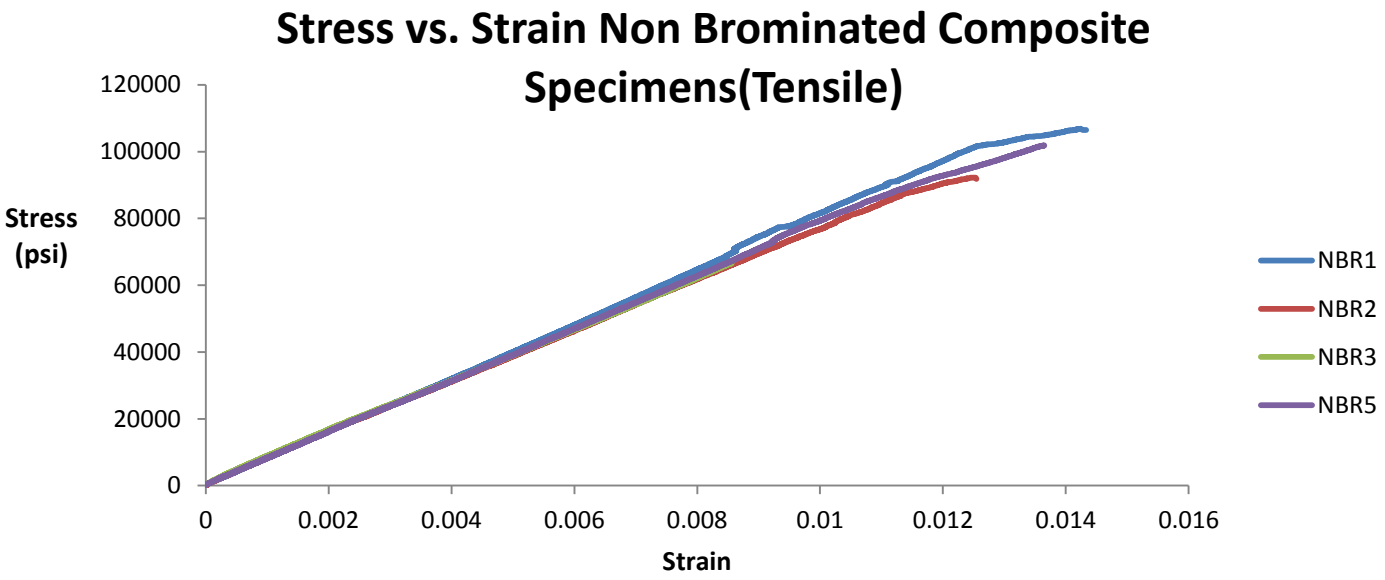


Tensile Testing Results (Brominated Composite Specimens)

Elastic Modulus (Brominated Composite)		
Sample	E	
	psi	GPa
NBR1	7547263	52.0
NBR2	6884026	47.5
NBR3	8136330	56.1
AVERAGE	**7520000 ± 511000**	**52 ± 3.5**

Strain to Failure (Brominated Composite)	
Sample	ε
NBR1	0.0110
NBR2	0.0164
NBR5	0.0124
AVERAGE	**0.0133 ± 0.00229**

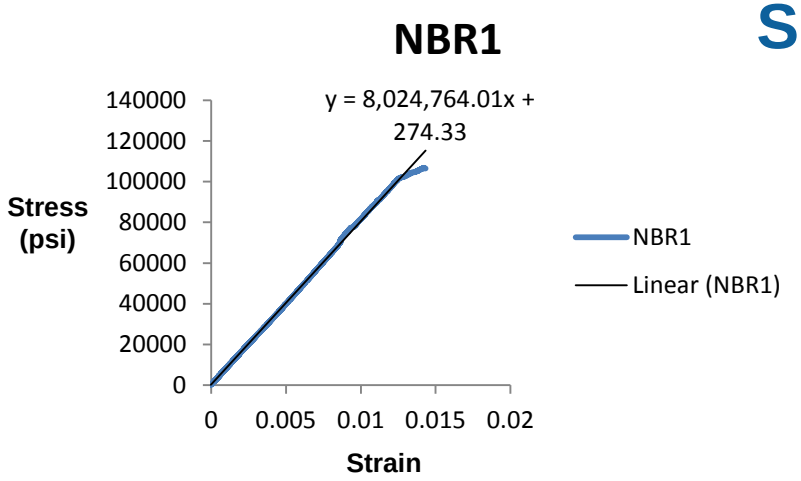
Tensile Testing Results (Non-Brominated Composite Specimens)

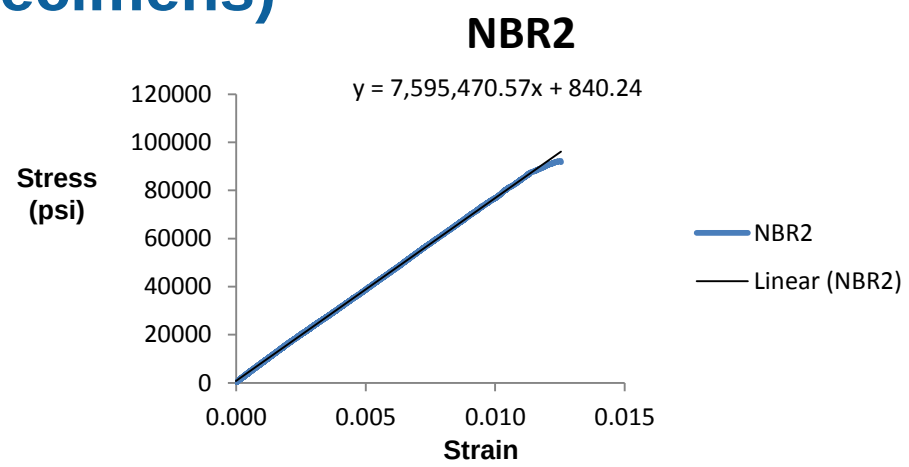


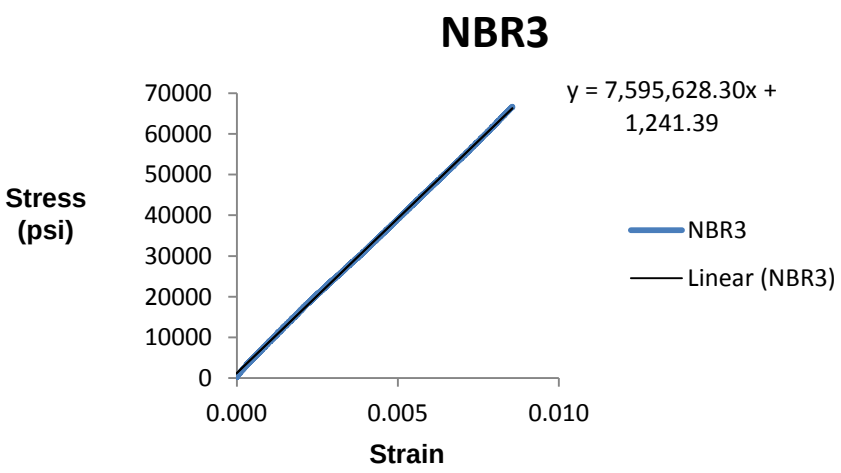
Ultimate Tensile Strength (Non – Brominated Composite)		
Sample	UTS	
	psi	MPa
NBR1	106824	736
NBR2	92220	635
NBR3	66662	459
NBR5	101817	702
AVERAGE	100000 ± 6000	691 ± 41

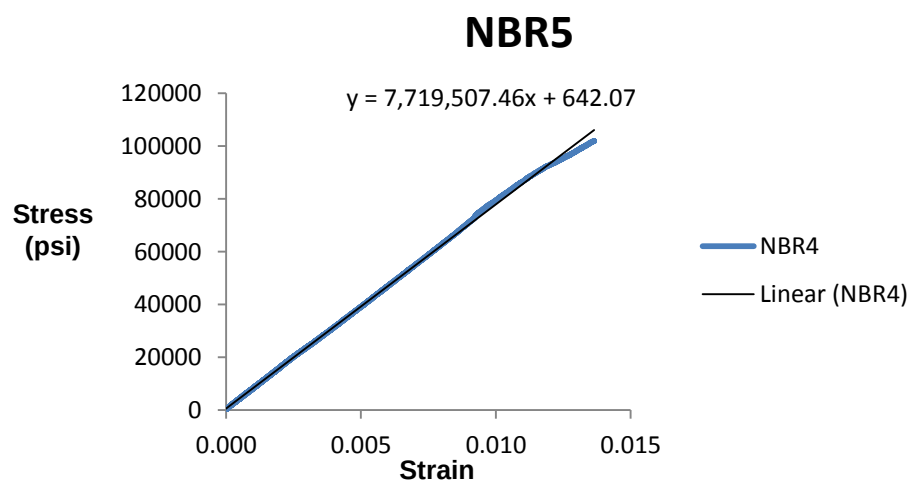
Outlier with similar modulus but lower ultimate strength.

Tensile Testing Results (Non-Brominated Composite Specimens)









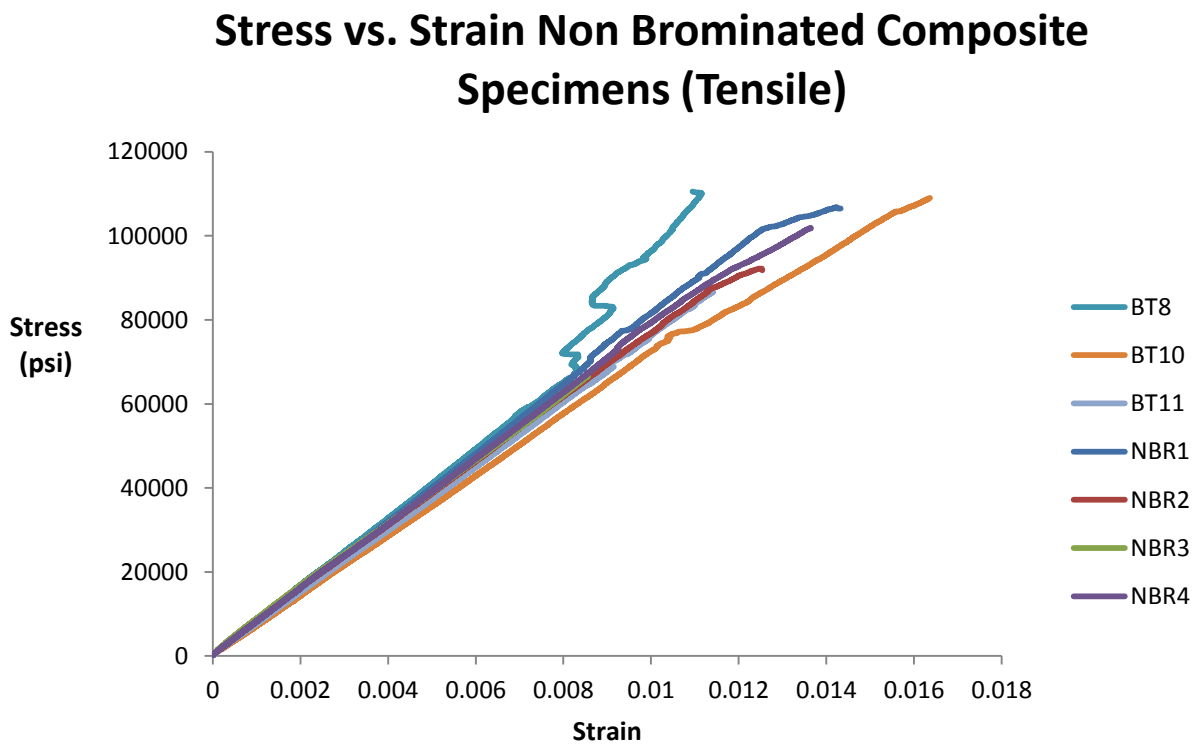
Tensile Testing Results (Non-Brominated Composite Specimens)

Elastic Modulus (Non – Brominated Composite)		
Sample	E	
	psi	GPa
NBR1	8024764	55.3
NBR2	7595470	52.3
NBR3	7595628	52.3
NBR5	7719507	53.2
AVERAGE	**7730000 ± 175000**	**53 ± 1.2**

Strain to Failure (Non – Brominated Composite)	
Sample	ε
NBR1	0.0142
NBR2	0.0135
NBR3	0.00876
NBR5	0.0137
AVERAGE	**0.0138 ± 0.0003**

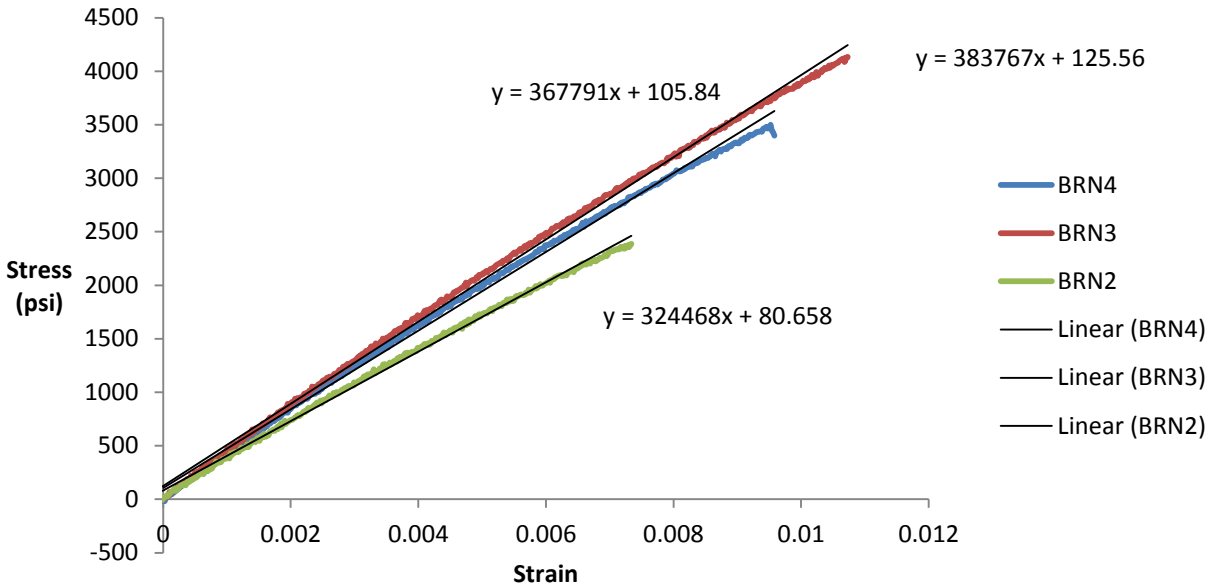
Outlier because sample failed at a lower than expected load.

Brominated and Non Brominated Data Plotted on one graph shows strong similarity in modulus values



Tensile Testing Results (Neat Brominated Specimens)

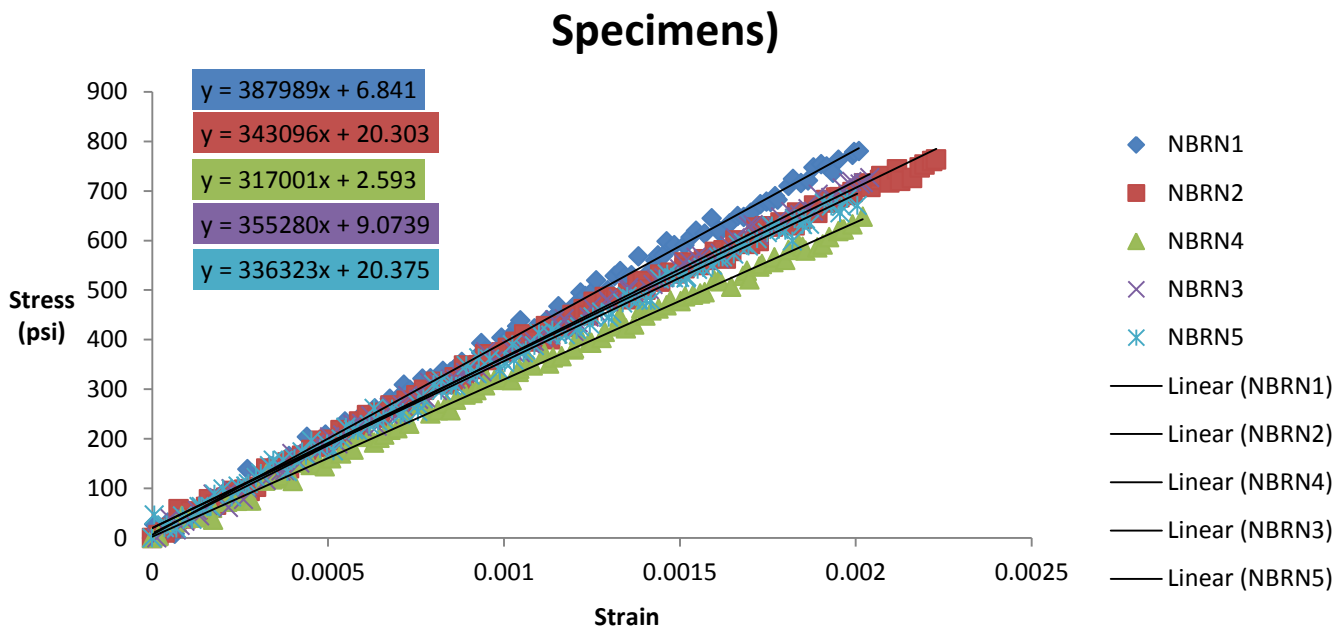
Stress vs. Strain (Brominated Tensile Neat Specimens)



Elastic Modulus (Brominated Neat)		
Sample	E	
	psi	MPa
BRN 4	367791	2535
BRN 3	383767	2645
BRN 2	324468	2237
AVERAGE	358000 ± 30000	2500 ± 200

Tensile Strength (Brominated Neat)		
Sample	UTS	
	psi	MPa
BRN 4	3500	24
BRN 3	4135	28
BRN 2	2388	16
AVERAGE	3300 ± 800	23 ± 6

Tensile Testing Results (Neat Non-Brominated Specimens)

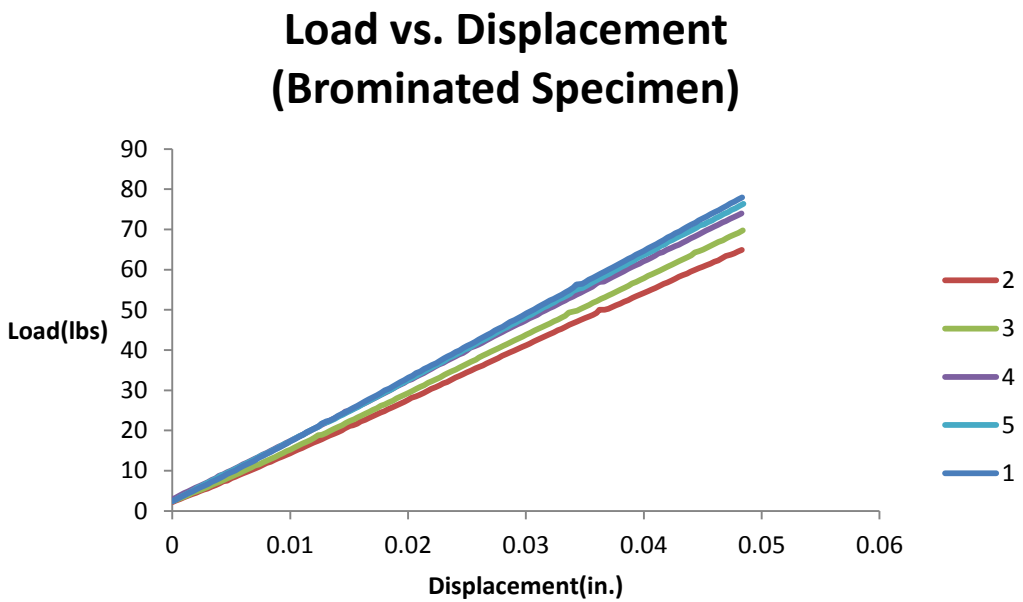


Elastic Modulus (Non-Brominated Neat)		
Sample	E	
	Psi	MPa
NBR-N1	387989	2675
NBR-N2	343096	2365
NBR-N3	355280	2450
NBR-N4	317001	2186
NBR-N5	336323	2319
AVERAGE	348000 ± 24000	2400 ± 162

Tensile Strength (Non-Brominated Neat)		
Sample	UTS	
	psi	MPa
NBR-N1	4694	32
NBR-N2	1170	8
NBR-N3	1799	12
NBR-N4	4574	31.5
NBR-N5	1792	12
AVERAGE	4630 ± 60	31.8 ± 0.3

Potential Outliers because of low failure strength

Flexure Testing Results (Brominated Composite Specimens)

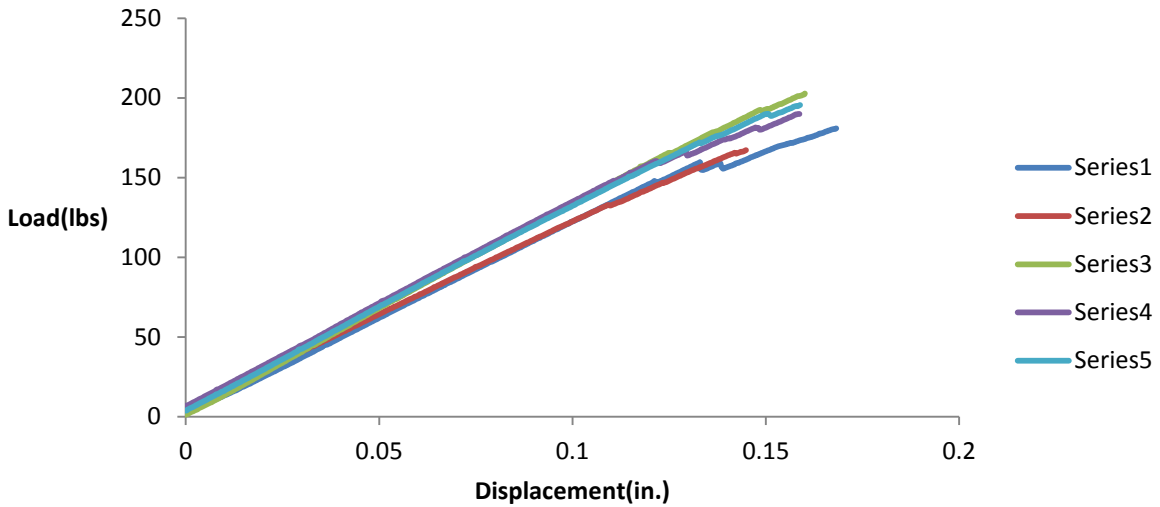


Flexural Modulus (Brominated Composite)		
Sample	E	
	psi	GPa
1	6585785	45.4
2	8412836	58.0
3	7041392	48.6
4	6644176	45.8
5	7024072	48.4
AVERAGE	7140000 ± 660000	49 ± 4.5

Flexural Strength (Brominated Composite)		
Sample	FS	
	psi	MPa
1	29427	203
2	34219	236
3	30539	211
4	26757	184
5	28123	194
AVERAGE	29800 ± 2500	206 ± 18

Flexure Testing Results (Non-Brominated Composite Specimens)

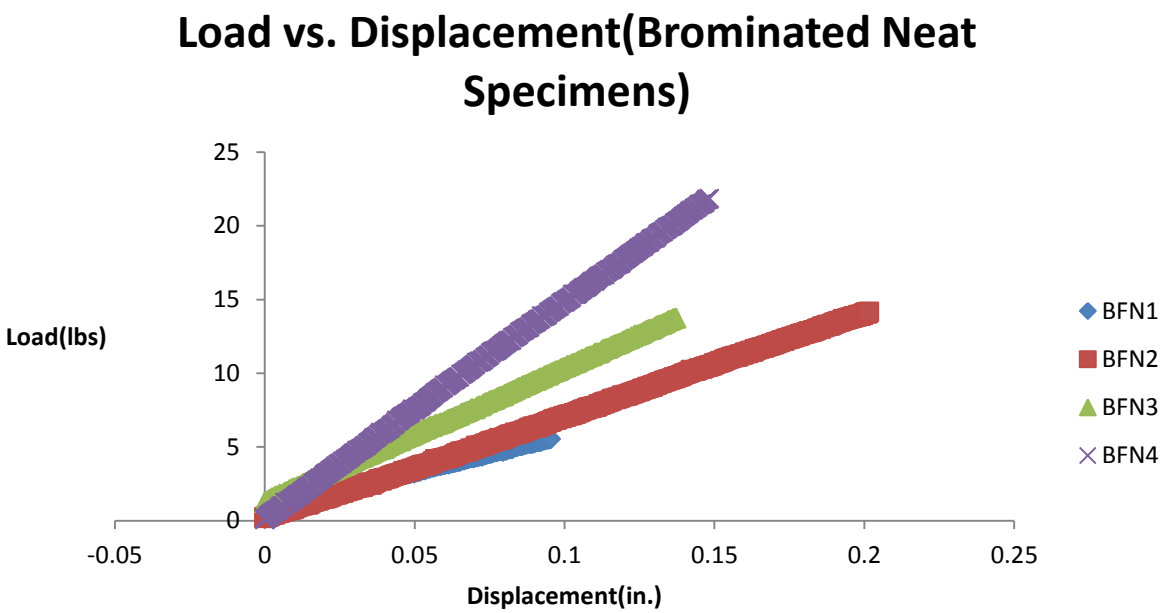
Load vs. Displacement (Non-Brominated Specimen)



Flexural Modulus (Non-Brominated Composite)		
Sample	E	
	psi	GPa
1	4292007	29.6
2	4985438	34.4
3	4562921	31.5
4	4680392	32.3
5	4727619	32.6
AVERAGE	4640000 ± 225000	32.1 ± 1.6

Flexural Strength (Non-Brominated Composite)		
Sample	FS	
	psi	MPa
1	29768	205
2	30420	210
3	30773	212
4	31039	214
5	31103	214
AVERAGE	30600 ± 547	211 ± 4

Flexure Testing Results (Brominated Neat Specimens)

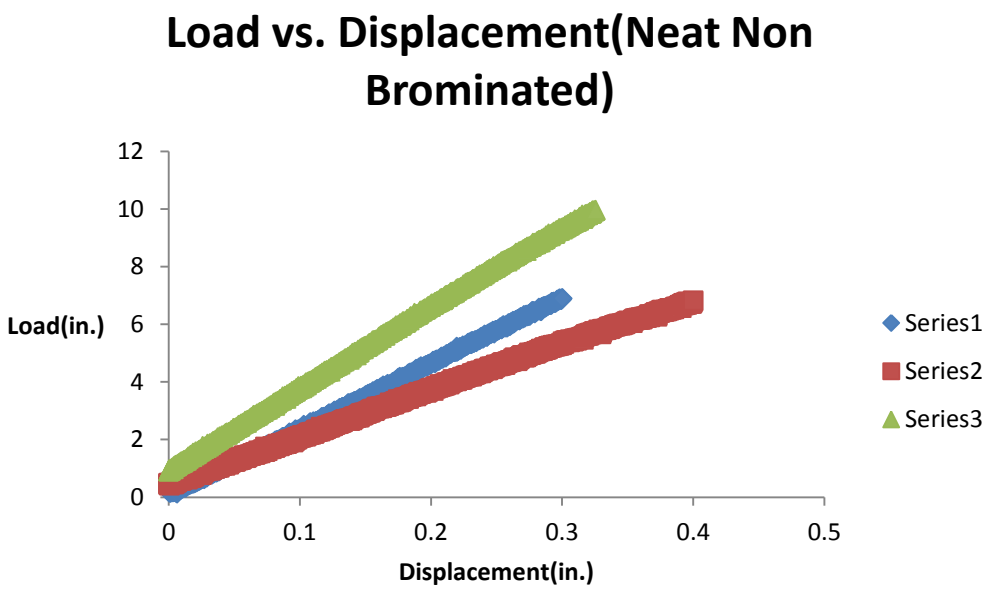


Flexural Modulus (Brominated Neat)		
Sample	E	
	psi	Mpa
1	257525	1775
2	384167	2648
3	396744	2735
4	397229	2738
AVERAGE	393000 ± 6000	2700 ± 42

Flexural Strength (Brominated Neat)		
Sample	FS	
	psi	MPa
1	1452	10
2	2835	16
3	3238	22
4	3760	26
AVERAGE	3300 ± 380	21 ± 4

Outlier with lower flexural strength and flexural modulus

Flexure Testing Results (Non-Brominated Neat Specimens)



Flexural Modulus (Non-Brominated Neat)		
Sample	E	
	psi	Mpa
1	340587	2348
2	193467	1333
3	354809	2446
AVERAGE	347698± 7111	2397±49

Flexural Strength (Non-Brominated Neat)		
Sample	FS	
	psi	MPa
1	4792	33
2	3173	22
3	4741	33
AVERAGE	4767± 26	33 ±0

Potential Outlier with lower flexural strength and flexural modulus

Short Beam Strength Results (Brominated and Non-Brominated Composite Specimens)

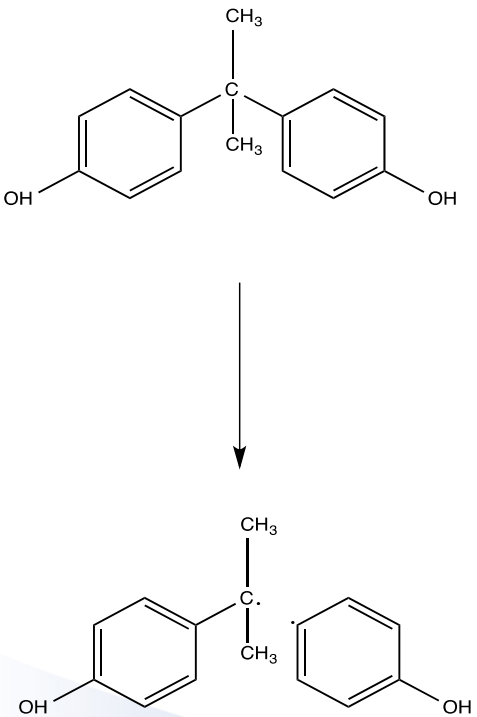
Short Beam Strength (Brominated Composite)		
Sample	E	
	psi	MPa
1	4434	31
2	4625	32
3	4715	33
4	4507	31
5	4961	34
AVERAGE	4650 ± 180	32 ± 1

Short Beam Strength (Non-Brominated Composite)		
Sample	E	
	psi	MPa
1	5215	36
2	4312	30
3	4067	28
4	4733	33
5	3946	27
AVERAGE	4500 ± 460	32 ± 3

Hardness Testing (Brominated & Non-Brominated Composite Specimens)

- ASTM D2583
- Barcol Hardness
- Sample Size = 10
- Non-Brominated Sample Thickness: 0.258”
- Brominated Sample Thickness: 0.137”
- Specimens met minimum thickness requirement of 0.0625”

Barcol Hardness		
Sample	**Non-Brominated**	**Brominated**
1	49	50
2	50	51
3	47	50
4	47	47
5	50	51
6	48	49
7	49	51
8	50	52
9	50	49
10	47	52
AVERAGE	**49 ± 1.3**	**50 ± 1.5**
Error	**2.6%**	**2.9%**



Chemical Formula: $C_9H_{11}O^{\bullet}$
Exact Mass: 135.08

Chemical Formula: $C_6H_5O^{\bullet}$
Exact Mass: 93.03

- The given samples were analyzed at the same GC-MS conditions hoping to observe two peaks at the same retention times as observed in BPA standard to confirm the presence of BPA in the samples.
- Since the BPA concentrations in samples were very low, both “total ion” and “selective ion” chromatograms were obtained.
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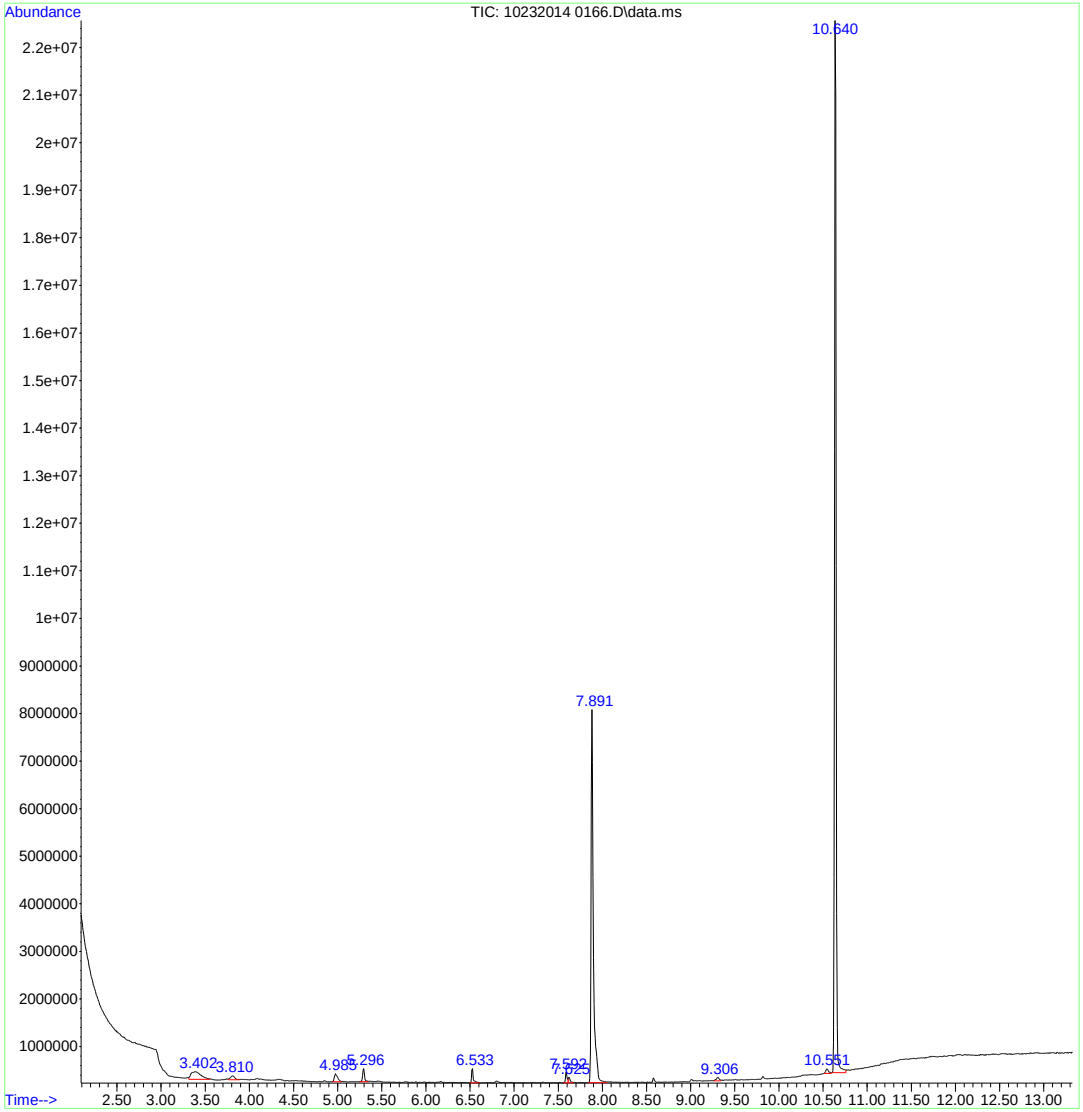
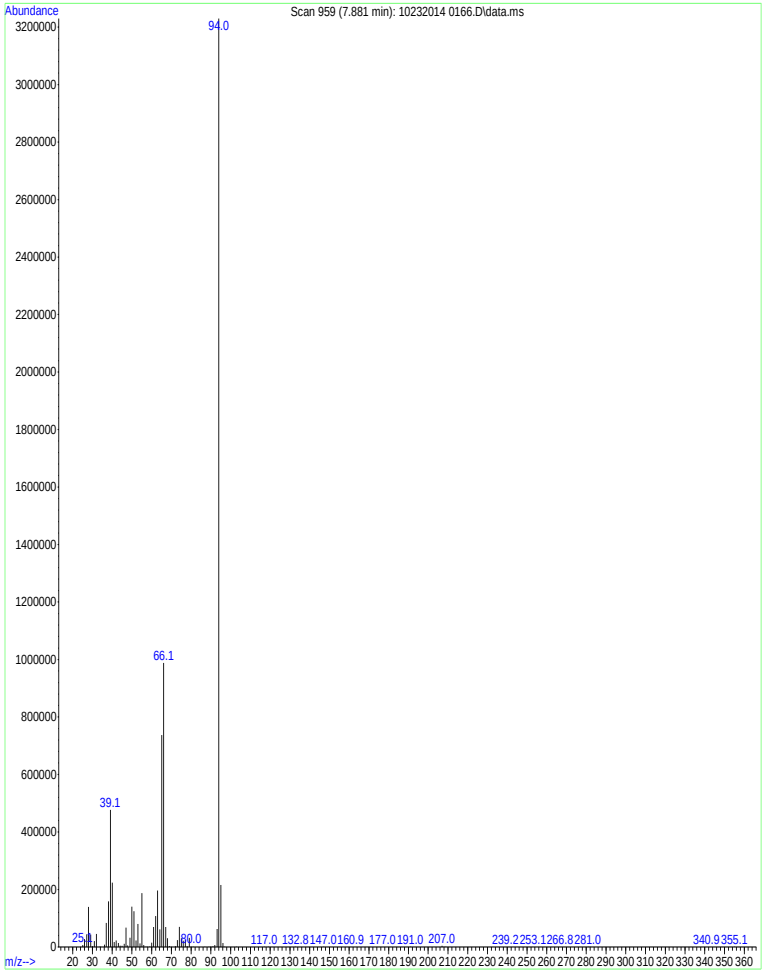
SERDP
DOD ▪ EPA ▪ DOE

File :C:\msdchem\1\DATA\MAHESH\LIGNINE PYROLYSIS\10232014 0166.D
Operator :
Acquired : 24 Oct 2014 2:52 pm using AcqMethod BPA_ANALYSIS_DB_WAX.M
Instrument : GCMS
Sample Name: BPA (1160 PPM)
Misc Info :
Vial Number: 2



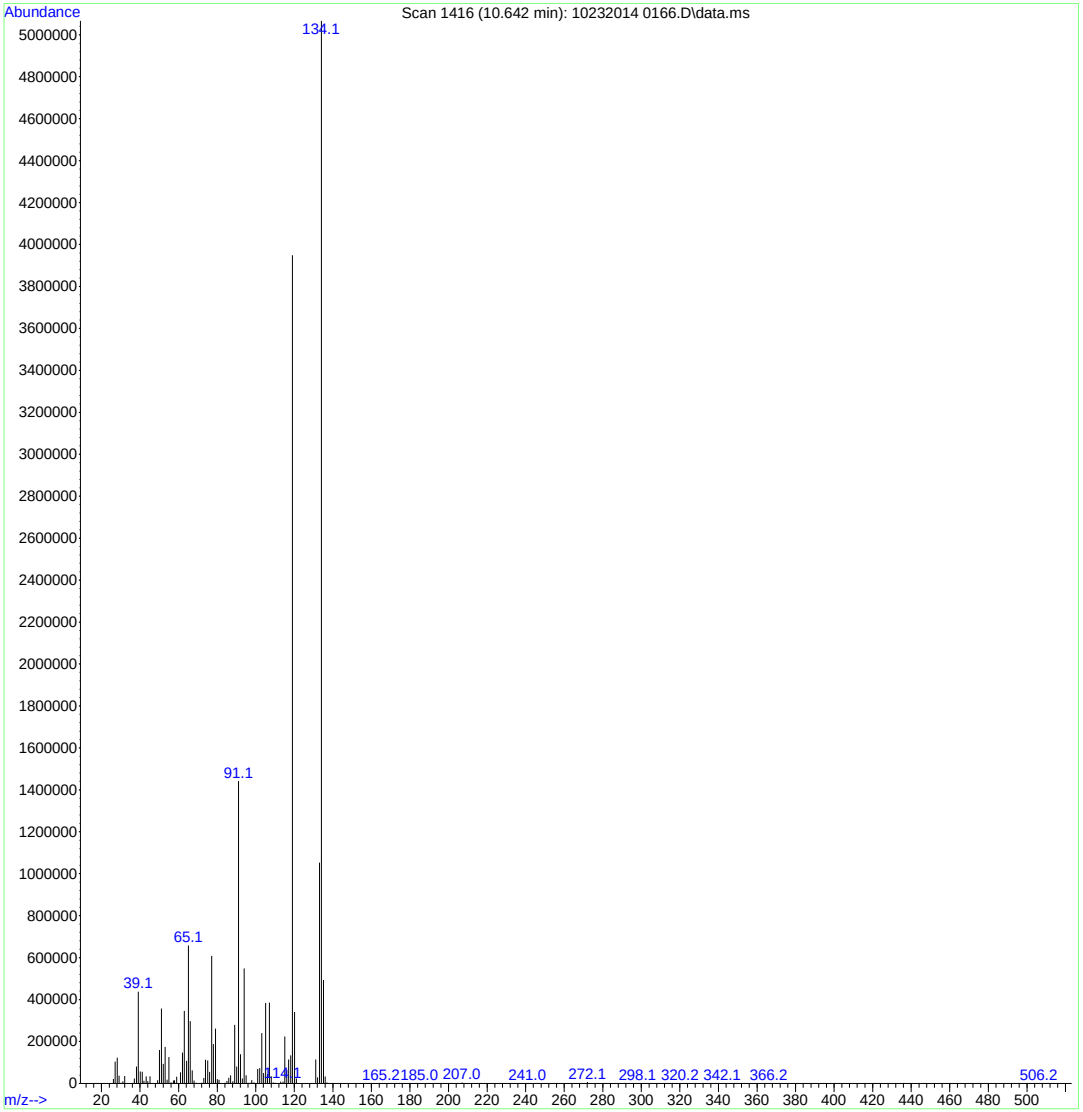
File :C:\msdchem\1\DATA\MAHESH\LIGNINE PYROLYSIS\10232014 0166.D
Operator :
Acquired : 24 Oct 2014 2:52 pm using AcqMethod BPA_ANALYSIS_DB_WAX.M
Instrument : GCMS
Sample Name: BPA (1160 PPM)
Misc Info :
Vial Number: 2



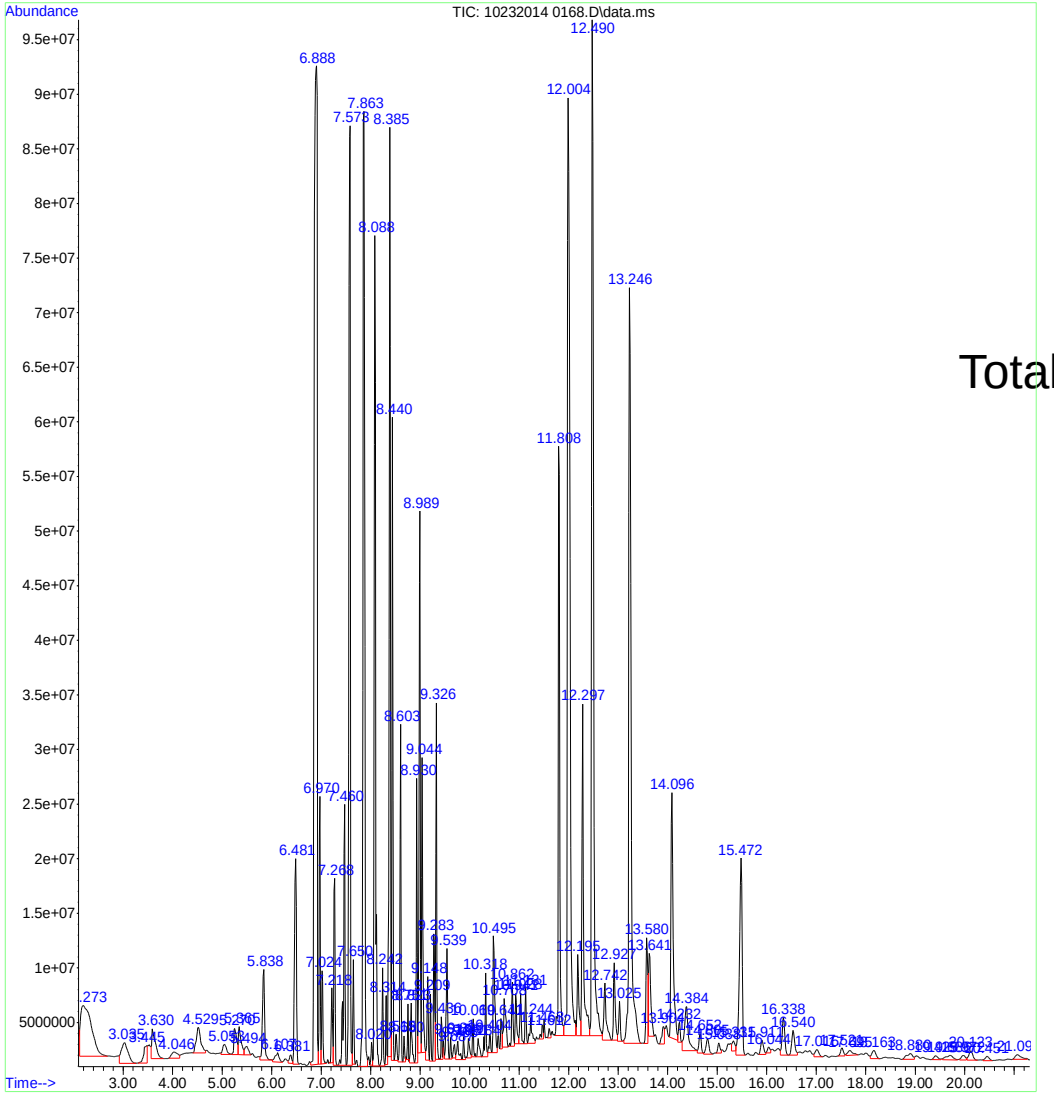
Mass spectrum of the peak observed at 7.881 min.

File :C:\msdchem\1\DATA\MAHESH\LIGNINE PYROLYSIS\10232014 0166.D
Operator : [redacted]
Acquired : 24 Oct 2014 2:52 pm using AcqMethod BPA_ANALYSIS_DB_WAX.M
Instrument : GCMS[redacted]
Sample Name: BPA (1160 PPM)
Misc Info :
Vial Number: 2

Mass spectrum of the peak observed at 10.642 min.



File :C:\msdchem\1\DATA\MAHESH\LIGNINE PYROLYSIS\10232014 0168.D
Operator :
Acquired : 24 Oct 2014 5:12 pm using AcqMethod BPA_ANALYSIS_DB_WAX.M
Instrument : GCMS
Sample Name: LOW ACETONE
Misc Info :
Vial Number: 3



Total ion chromatogram of sample

File :C:\msdchem\1\DATA\MAHESH\LIGNINE PYROLYSIS\10232014 0168.D
Operator :
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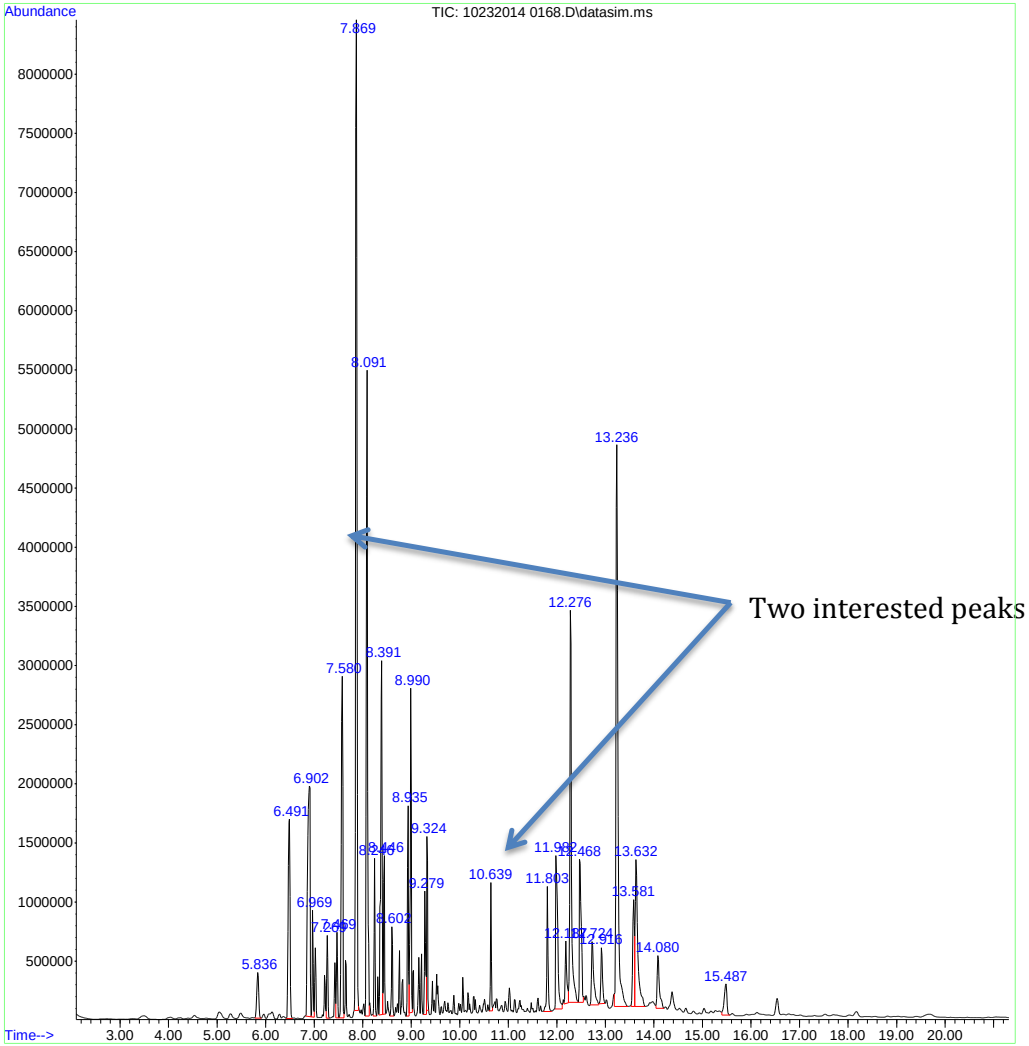
Instrument : GCMS
Sample Name: LOW ACETONE
Misc Info :
Vial Number: 3



Selective ion chromatogram of sample “

File :C:\msdchem\1\DATA\MAHESH\LIGNINE PYROLYSIS\10232014 0168.D
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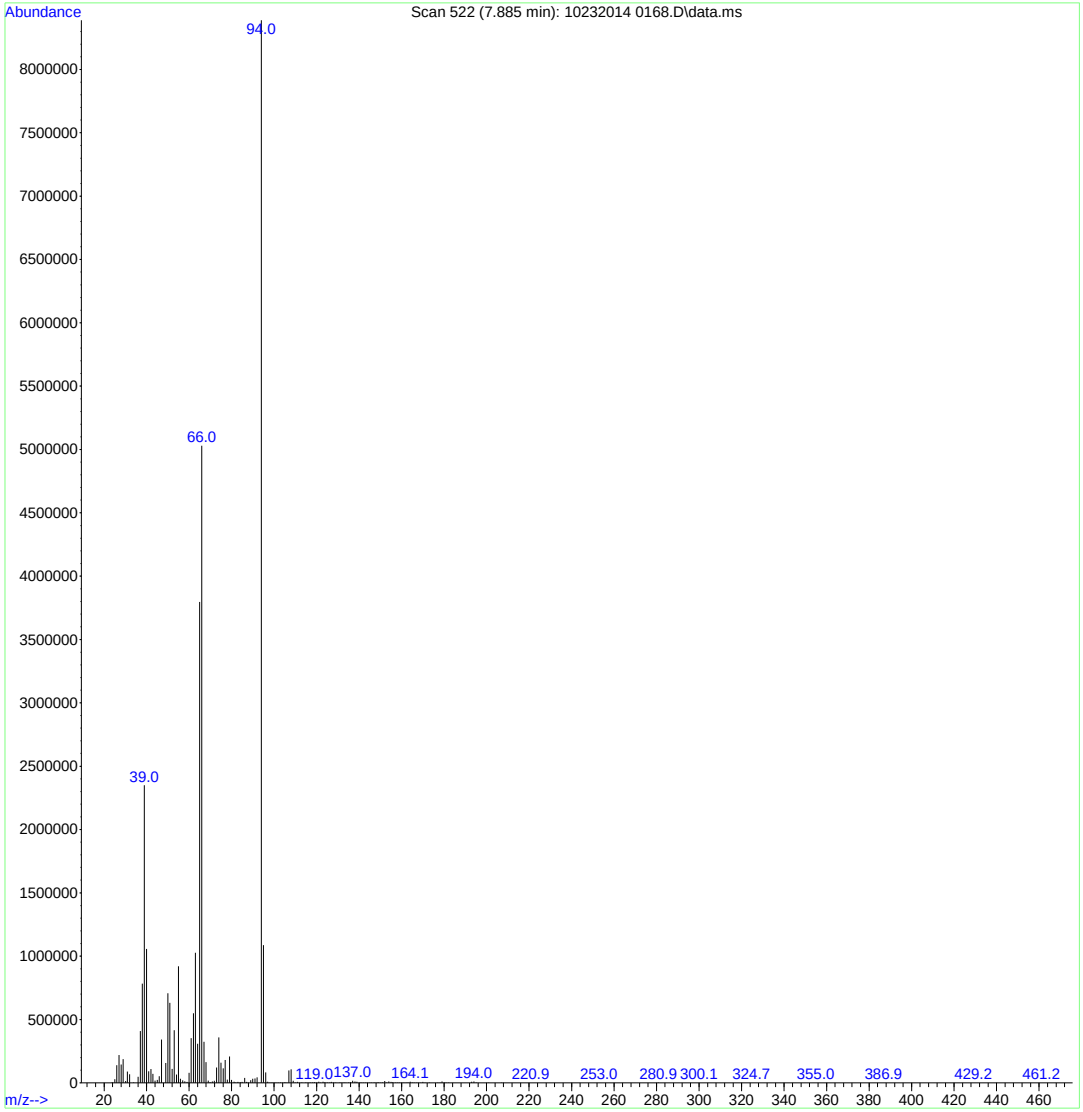
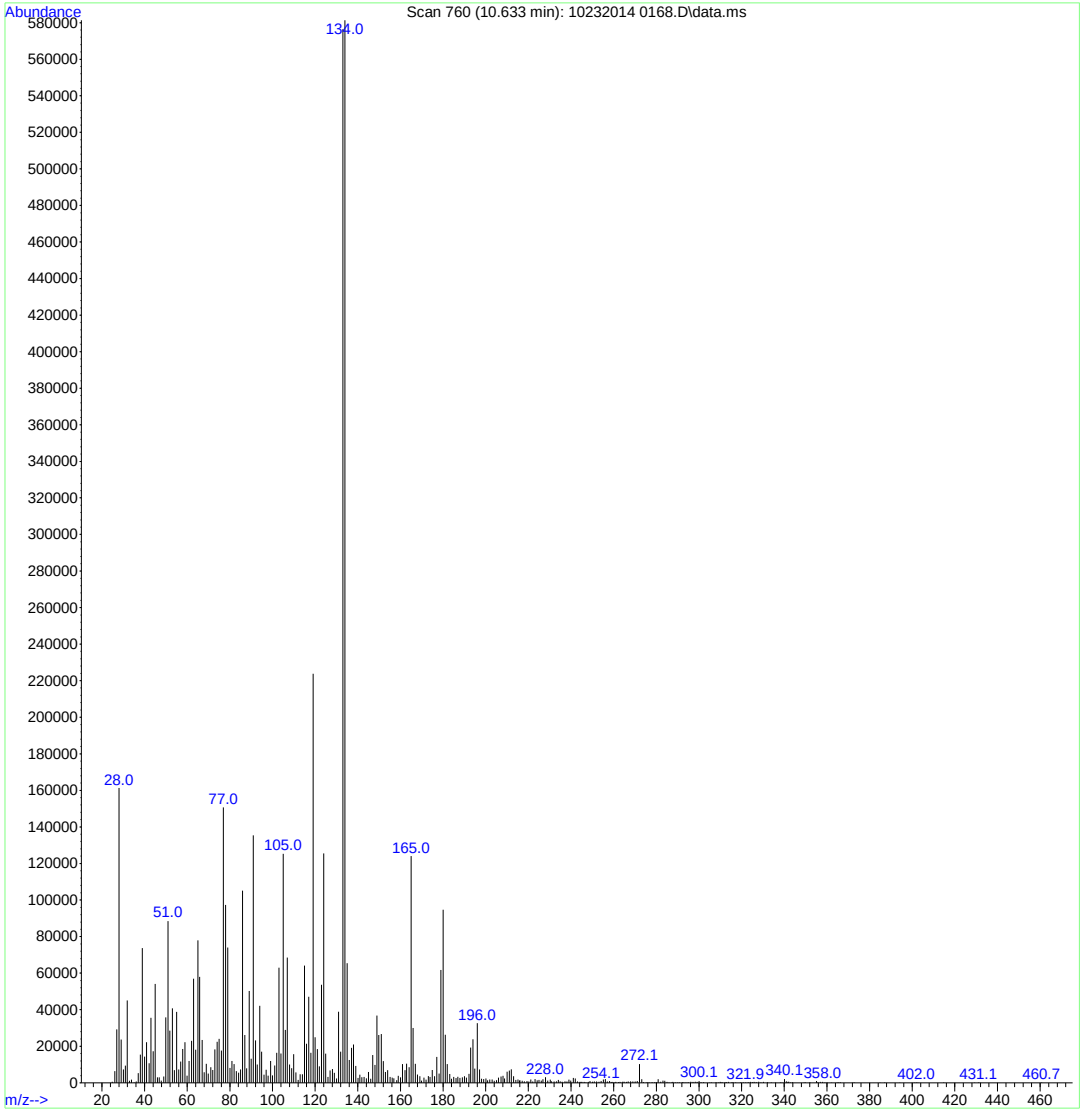
Instrument : GCMS
Sample Name: LOW ACETONE
Misc Info :
Vial Number: 3



File :C:\msdchem\1\DATA\MAHESH\LIGNINE PYROLYSIS\10232014 0168.D
Operator :
Acquired : 24 Oct 2014 5:12 pm using AcqMethod BPA_ANALYSIS_DB_WAX.M
Instrument : GCMS
Sample Name: LOW ACETONE
Misc Info :
Vial Number: 3



Acronyms and Symbols

- VER: Vinyl ester resin
- Br-VER: Brominated vinyl ester resin
- GVER: Green vinyl ester resin
- GMA: Glycidyl methacrylate
- VARTM: Vacuum assisted resin transfer molding
- BPA: Bisphenol A
- TBBPA: Tetrabromobisphenol A

Publications

- ***<u>Prepared manuscript to be submitted after IP issues resolved:</u>***

- Manuscript is prepared for synthesis of vinyl ester resin "*Synthesis of Flame Retardant Vinyl Ester Resin from Renewable Biowaste*" with author list of *Priyank N. Shah, Namjoon Kim, Robert F. Kovar and Yongwoo Lee**.
- Manuscript is prepared for synthesis of vinyl ester resin "*Glycidyl Methacrylate: A Precursor for Vinyl Ester Resin from Renewable Biowaste Glycerine*" with author list of *Priyank N. Shah, Namjoon Kim, Zhuangrong Huang, Mahesh Jayamanna, Edwin Jahngen, David K. Ryan, Seongkyu Yoon, Robert F. Kovar and Yongwoo Lee.*

- ***<u>Invention Disclosure to UML:</u>***

- High Value Phenol Enriched Phenolics by Cost-Effective Pyrolysis of Biowaste Lignin: Yongwoo Lee, Robert F. Kovar, Priyank N. Shah, Namjoon Kim, Akshay Kokil, Edwin Jahngen, David K. Ryan; *Invention Disclosure*, UML- 2015-007.
- • Sustainable "Green" Vinyl Ester Resin (VER) from Renewable Resources, Name: Yongwoo Lee, Robert F. Kovar, Priyank N. Shah, Namjoon Kim, Akshay Kokil, Edwin Jahngen; *Invention Disclosure*, UML- 2015-008.

Appendix R

Sustainable "Green" Vinyl Ester Resin (GVER) from Renewable Resources

WP 2317

Yongwoo Lee
University of Massachusetts Lowell

In-Progress Review Meeting
April 22, 2015

SERDP
DOD ▪ EPA ▪ DOE

Content

Introduction

- Project overview
- Project team
- Technological objective

Technical Approach

- Pyrolysis of lignin and synthesis of BPA and TBBPA
- Synthesis of GMA from biodiesel glycerin
- Environmental and technical advantages

Overview of Prior Work

- A brief overview of phase-I work

Results

- Depolymerization of lignin under various conditions
- Various phenolic materials identified
- Purification of pyrolysates
- Scale-up of green VER
- Action items

Technology Transition

WP-2317: Sustainable "Green" Vinyl Ester Resin (GVER) from Renewable Resources

Performers:

Y. Lee, P. Shah, R. F. Kovar, and A. Kokil

Technology Focus

- *Synthetic protocol for GVER and its processing into VARTM composites, pyrolysis of lignin, extraction of phenol*

Research Objectives

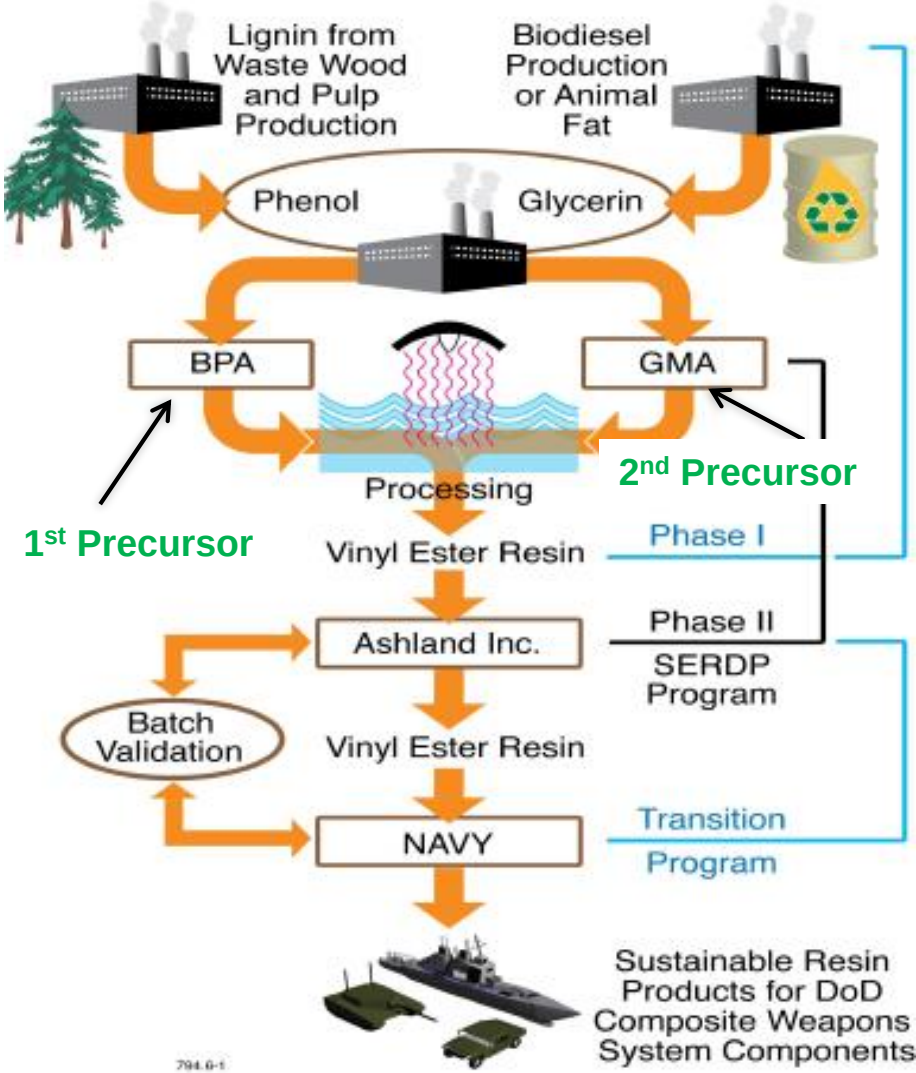
- *Demonstrate synthesis of GMA from glycerin.*
- *Isolation of phenol from lignin to get BPA and TBBPA.*
- *Demonstrate synthesis of GVER and VARTM processing.*

Project Progress and Results

- *Successfully scaled up synthesis of GMA and GVER from biowaste glycerin.*
- *Fabricated neat coupons using GVER and Br-GVER synthesized from bio-waste glycerin .*
- *Synthesized Green BPA using lignin pyrolysate.*
- *Developed alternate lignin depolymerization protocols for selective yield of constituent chemicals.*

Technology Transition

- *Working with Ashland Inc. to understand industrial demands.*
- *Working with paper and biodiesel company for procuring lignin and glycerin.*



Project Team

Team	Person In-Charge (Point of Contact)	Role
UMass Lowell	Dr. Yongwoo Lee (PI) Dr. Priyank Shah (Co-PI) Dr. Akshay Kokil	Developing GVER from biowaste and coordinating all research team
UMass Lowell	Prof. Chris Hansen	Developing GVER composites using and VARTM
UMass Lowell	Prof. David Ryan	Developing analytical technique for characterization of pyrolyzed material.
Bentley University	Prof. Ryan Bouldin	Business development
NAVAIR	Dr. John Brennan Ms. Emily Dumm	Developing composites with flame retardant ability and deliver coupons to NAVSEA
NAVSEA	Mr. Usman Sorathia	Examine flame retardant properties of the composites received from NAVAIR
R.F. Kovar & Associates	Dr. Robert F. Kovar	Provide technical expertise to UML team.
Ashland Inc.	Dr. Michael Stevens, Dr. Joe Fox, Dr. Charlie Lewis	Industrial teaming partner
Maine Standard Biofuels	Mr. Jarmin Kaltsas, Mr. Alex Pine	Provide unrefined glycerin obtained during biodiesel manufacturing
Flamebeau River Paper LLC	Mr. Bill Tomczak	Provide lignin from paper industry waste stream
Maine Seed Company	Mr. Tate McPherson	Provide lignin from different plant source

Technical Objective

- Refine Phenol from Lignin
- Refine GMA from Glycerin
- Scale up VER resin

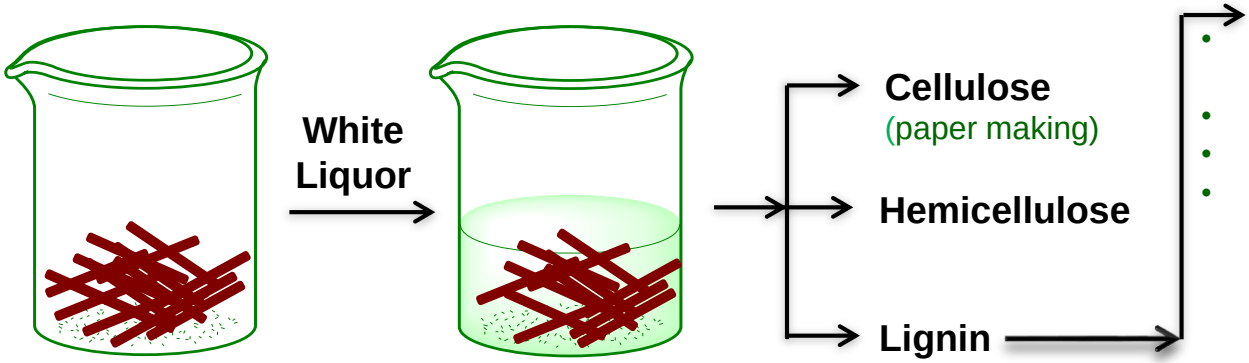
Year I

- Formulation with Derakane Vinyl Ester
- Fabricate composites with VARTM
- Conduct structural testing for equivalence

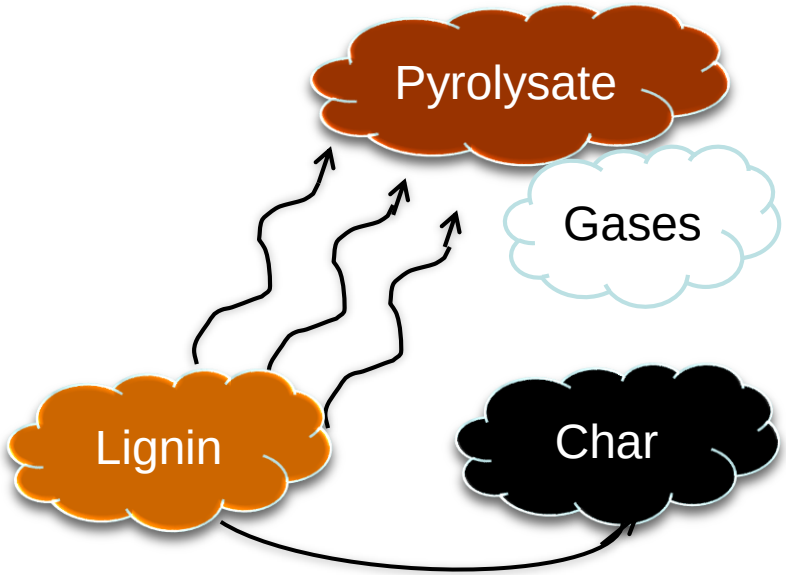
Year II & Year III

Technical Approach

Pyrolysis of Lignin



- Multi-polarity related products (surfactant/emulsifier and dispersant)
- Materials (Binders, thermosets)
- Agriculture
- High purity/value applications (food and cosmetics application, anti-oxidative and antibacterial)



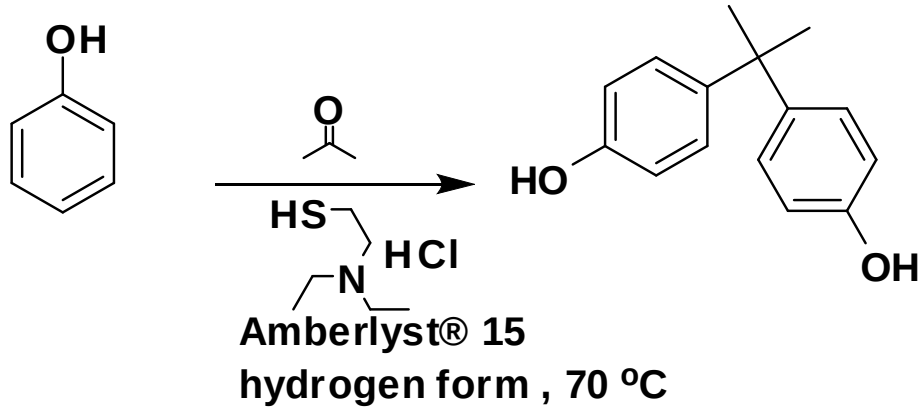
Pyrolysis Concept

Samples of lignin provided by Flambeau River Papers LLC (Park Falls, WI) and Maine Seed Company (Mapleton, ME)

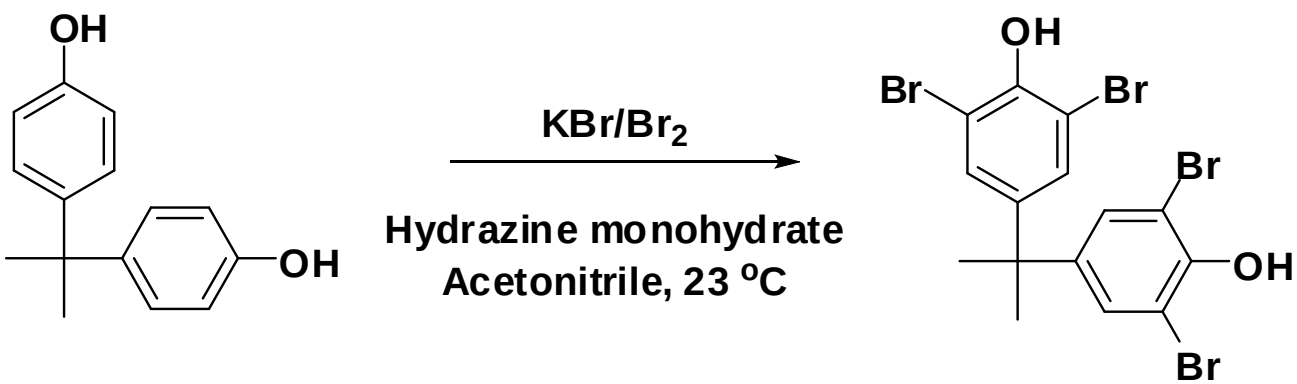
http://www.ili-lignin.com/

Technical Approach

Synthesis of BPA



Synthesis of TBBPA



Purification by precipitation in water

Technical Approach

Introduction to Glycerin

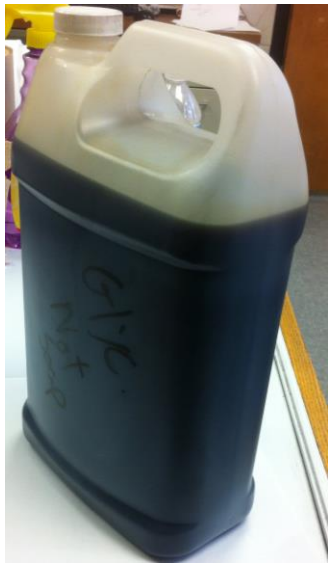
Vegetable Oil, Animal Fat (Triglycerides)[1] →

- **Water, NaOH (Hydrolysis, Saponification)** → **long-chain carboxylate salts used as soaps**
- **Alcohol, NaOH Transesterification** → **esters of fatty acids used as biodiesel**

+ glycerin

- By 2020, the production of glycerin will be six times higher than its demand. [2]
- Disposal of glycerin in the waste stream would require increasing expenditures for biodiesel industry

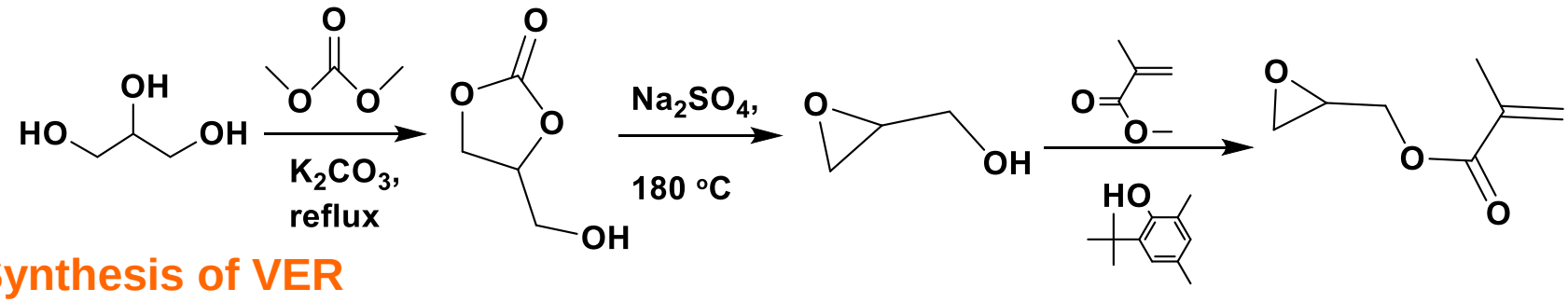
We are using crude glycerin from bio-diesel waster stream provided by Maine Standard Biofuels (Portland, Maine)



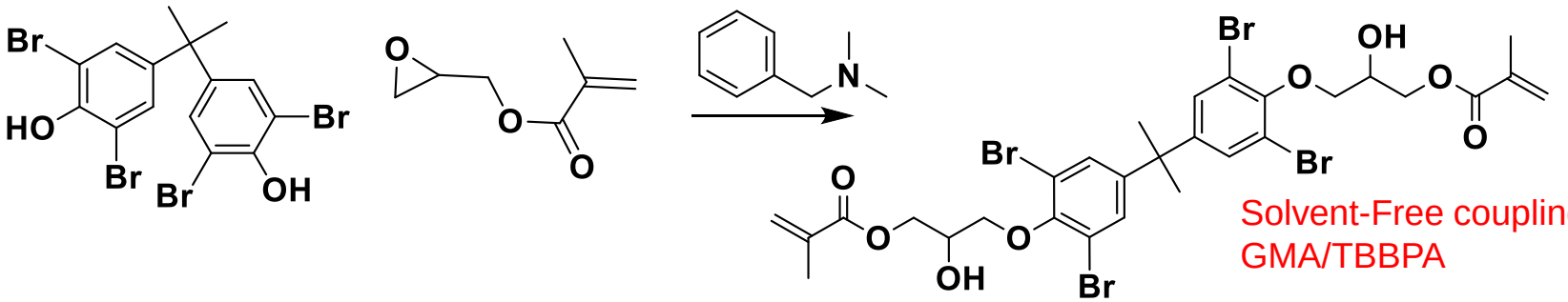
1. Sims, Bryan (2011-10-25). "Clearing the Way for Byproduct Quality: Why quality for glycerin is just as important for biodiesel". Biodiesel Magazine
2. Christoph, Ralf; Schmidt, Bernd; Steinberner, Udo; Dilla, Wolfgang; Karinen, Reetta (2006). "Glycerol". Ullmann's Encyclopedia of Industrial Chemistry. doi:10.1002/14356007.a12_477.pub2. ISBN 3527306730.

Technical Approach

Synthesis of GMA

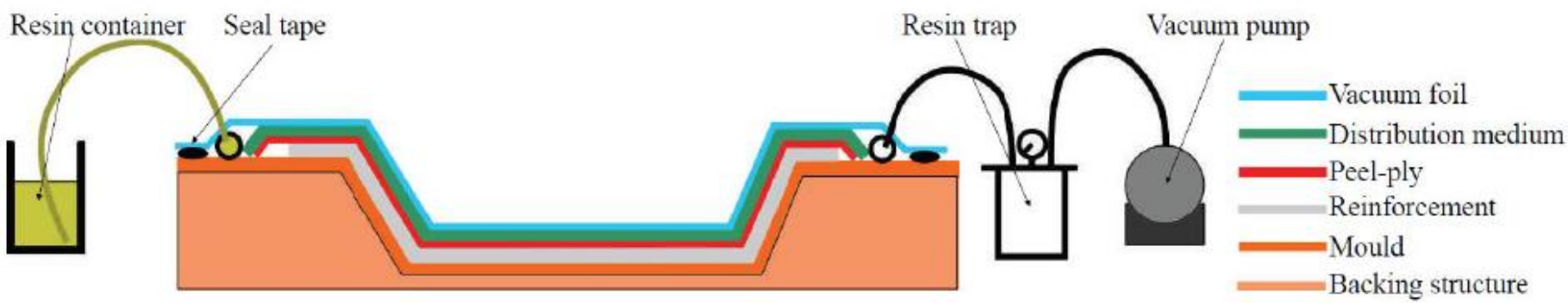


Synthesis of VER



Solvent-Free coupling of GMA/TBBPA

Carbon fabric reinforced panel fabrication by VARTM

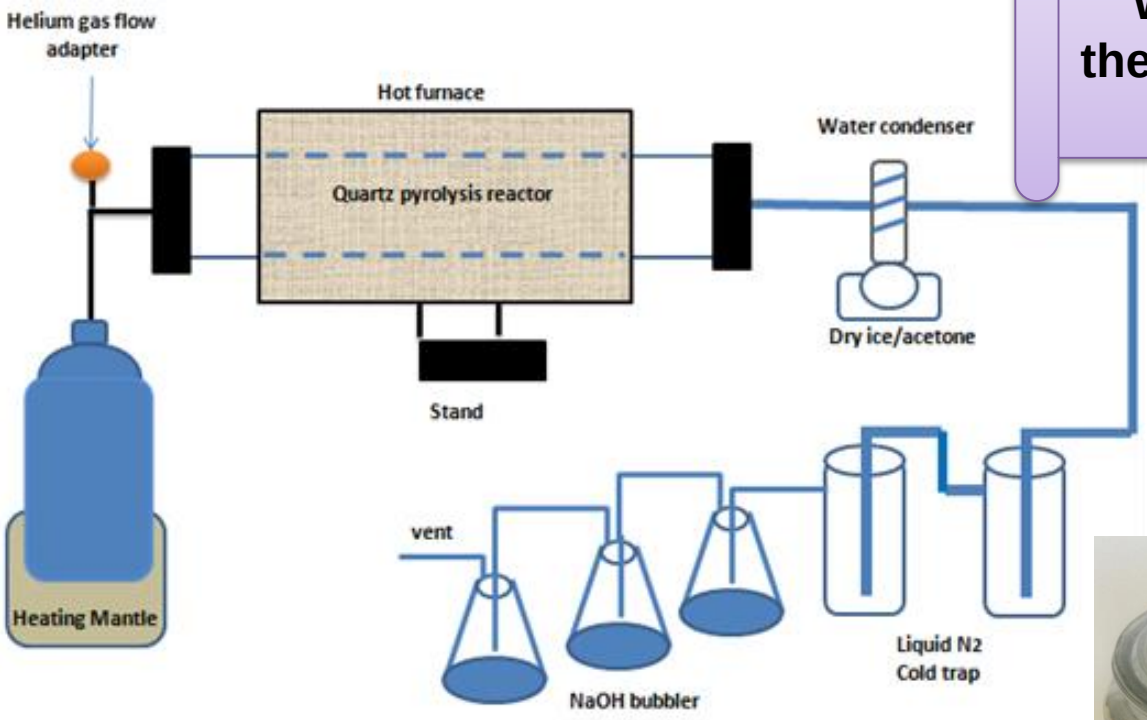


Significance

- **Environmental Advantages**
- **Elimination of US dependence upon foreign oil** in manufacturing critical military composites.
- **Replacement of epichlorohydrin** with GMA yields an environmentally benign synthesis.
- Production of green BPA and GMA will provide raw materials **for other high-value chemical products**.
- Finally, the proposed use of biomass waste **will not affect the nation's food supply**.
- Pyrolysis of lignin produces **many other valuable phenolic derivatives**.
- **Technical Advantages**
- **Solvent-free** synthesis of vinyl ester resin monomer.
- GVER from TBBPA and GMA forms only **pure, low molecular weight product**,
  - Good for VARTM processing
  - Reduces usage of reactive diluent (styrene)
  - Increases wetting of resins and decrease voids/bubbles in composites

Overview of Prior Work

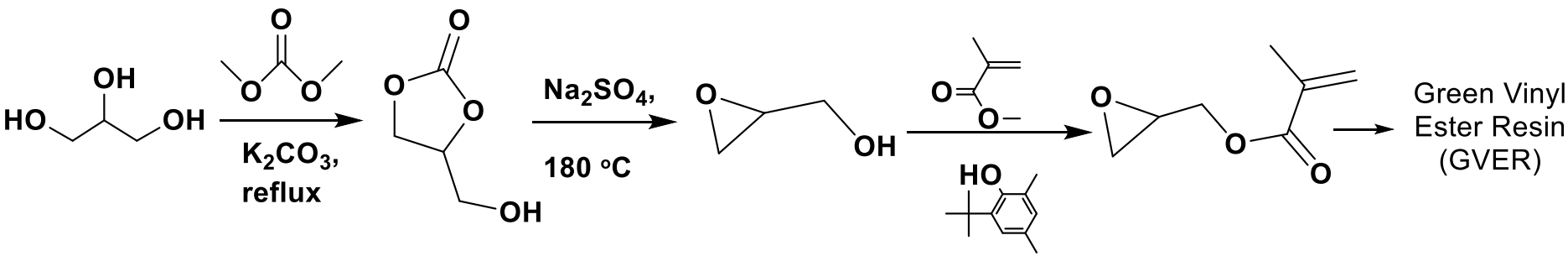
Inspiration: Coal had been pyrolyzed to isolate phenol before WW-I and during WW-II, when there was a shortage of petroleum feed-stock

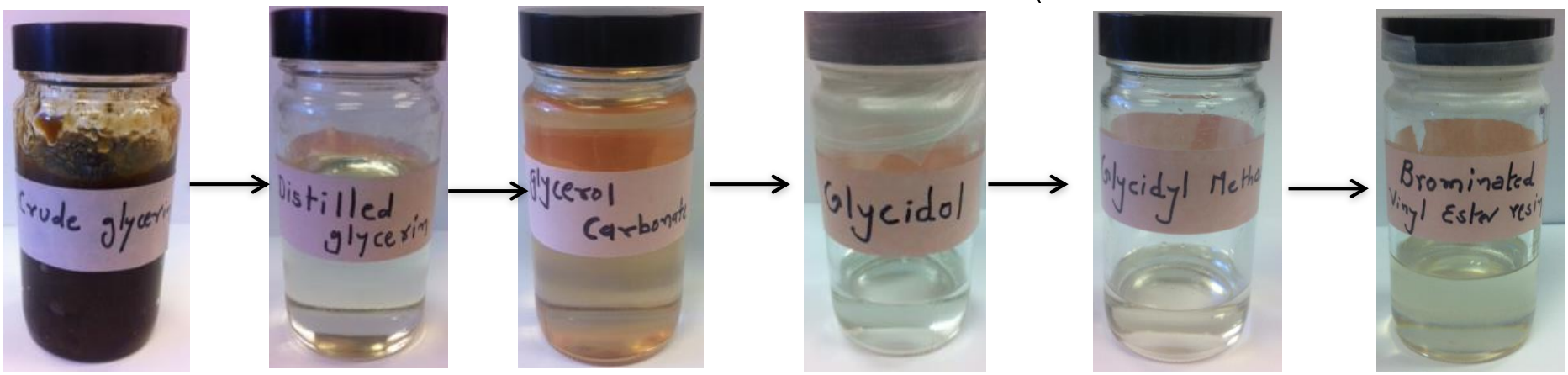


Purified product after solvent extraction

"Advanced Organic Chemistry"; Louis F. Fieser and Mary Fieser, New York, Reinhold Publishing Corporation, Chapman & Hall, Ltd., London, 1961, pp.640-645.

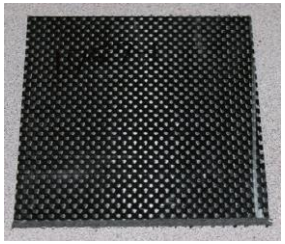
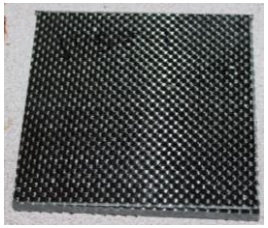
Green Vinyl Ester Resin from Biodiesel Glycerin



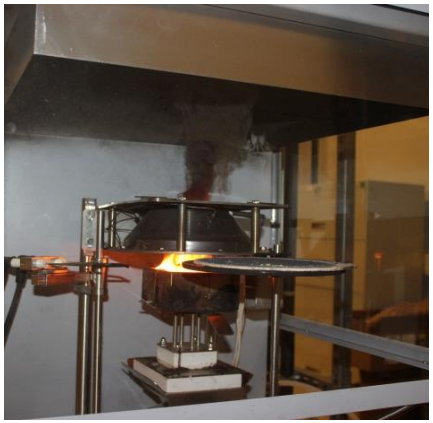


Crude Glycerin → *Distilled Glycerin* → *Glycerol Carbonate* → *Glycidol* → *Glycidyl Methacrylate* → *Green Vinyl Ester Resin*

Flammability and Mechanical Testing

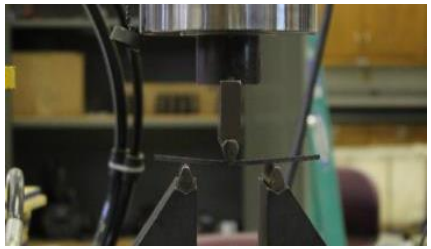
Material ID Material Description	Umass Lowell				NAVAIR	
	1742 Brominated VER	1750 VER	1757 'C' Fabric Reinforced / Brominated VER	1758 'C' Fabric Reinforced VER	1760 'C' Fabric Reinforced VER	1763 'C' Fabric Reinforced Brominated VER
Photo						

Maximum burning of the sample during cone calorimetry testing



Maximum generation of smoke during cone calorimetry testing

Setup for tensile testing of VER and Br-VER composite.



Setup for flexure testing of VER and Br-VER specimens.

Short Beam Strength Testing

Pyrolysis of Lignin from Various Sources

Mass balance between different phases	*Vacuum Setup (SA)*	*Helium Setup*					
		SA	**TCI (alk)**	**TCI (dealk)**	**FRP-LLC**	**MSC-SL***	**MSC-BL***
Char (Solid) (wt %)	55.0	54.9	62.6	54.9	52.7	-	-
Phenolics (Liquid) (wt %)	7.1	12.6	11.5	3.2	17.9	-	-
(Gases)	37.9	32.5	25.9	41.9	29.4	-	-
Main phenolics identified							
Guaiacol	31.43	10.3	9.48	2.84	4.35	5.13	6.59
2-methoxy-4-methylphenol	9.40	1.95	1.34	0.45	0.65	0.46	0.64
Phenol	6.30	9.41	20.2	4.59	3.97	13.4	10.7
4-ethyl-2-methoxyphenol	6.83	1.85	0.91	0.40	0.58	0.68	0.71
2-methoxy-4-vinylphenol	3.70	0.66	1.44	0.00	0.22	0.22	0.62
2,6-dimethoxyphenol	0.53	0.57	0.25	0.15	0.64	1.50	0
vanillin	0.87	0.03	0.92	0.89	0.83	2.07	0
4-hydroxy-3-methoxyacetaphenone	0.63	0.55	0.61	0.46	0.37	2.71	0.39
catechol	0.10	11.7	2.27	2.02	4.15	4.93	4.82
Homovanillic acid	1.40	0.50	0.43	0.22	0.18	5.36	0

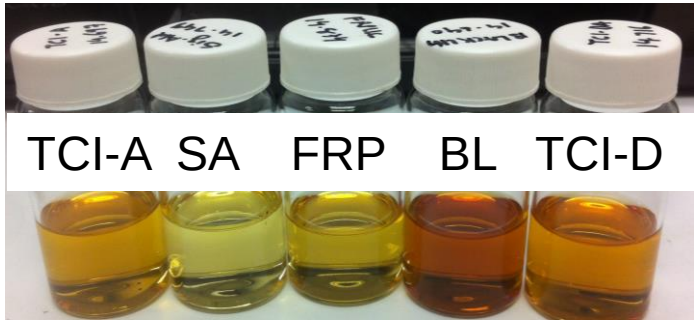
Lignin (left vial) strong liquor, (center vial) weak liquor and (right vial) black liquor obtained from Maine Seed Company

* *Waiting for Mass Balance Data*

Depolymerization of Lignin Using Microwave Irradiation

Phenolics	*Lignin Materials*				
	SA	**TCI (alk)**	**TCI (dealk)**	**FRP-LLC**	**MSC-BL***
Guaiacol	11.371	5.122	8.876	1.177	3.582
2-methoxy-4-methylphenol	4.742	1.420	2.878	0.000	0.805
Phenol	1.078	1.473	1.583	3.951	0.827
4-ethyl-2-methoxyphenol	8.265	2.552	3.868	1.346	2.827
2-methoxy-4-vinylphenol	0.000	0.000	0.000	0.000	0.000
2,6-dimethoxyphenol	0.000	0.692	1.611	3.519	8.432
vanillin	0.000	0.000	0.000	0.000	0.000
4-hydroxy-3-methoxyacetaphenone	0.000	0.000	0.000	0.000	0.000
catechol	1.693	4.436	3.762	0.000	1.464
Homovanillic acid	5.927	0.000	0.000	0.000	0.000

Microwave Reactor

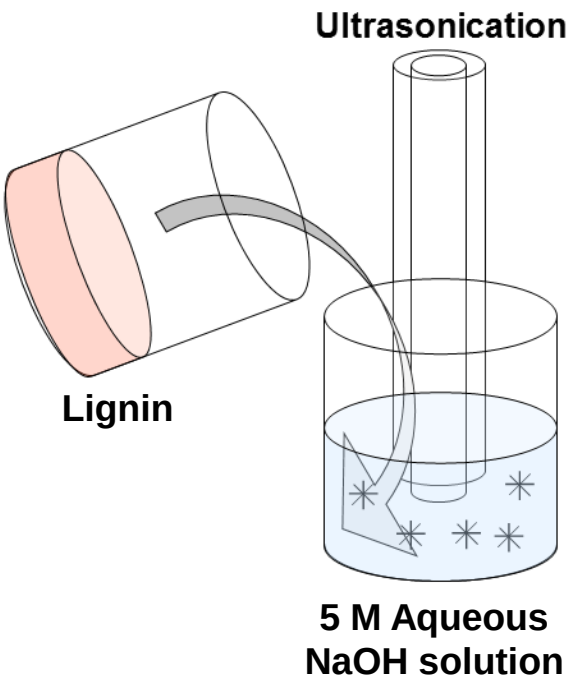


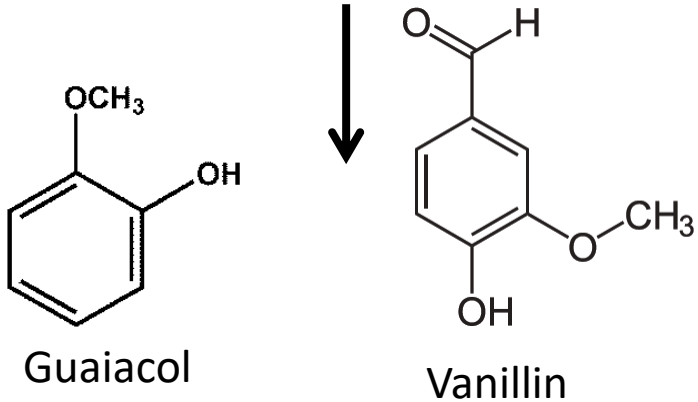
MOF Catalyzed Pyrolysis of Lignin

Phenolics	*Sigma-Aldrich lignin*			
	Without Catalyst	GO-Cu MOF	Ca-TA MOF	Iron Oxide NP
Guaiacol	10.32	2.82	4.81	12.7
2-methoxy-4-methylphenol	1.95	0.63	0.35	4.91
Phenol	9.41	10.73	3.83	5.16
4-ethyl-2-methoxyphenol	1.85	0.39	1.31	5.52
2-methoxy-4-vinylphenol	0.66	0.14	0.18	1.74
2,6-dimethoxyphenol	0.57	0	0	0.76
vanillin	0.03	0	0	0.80
4-hydroxy-3-methoxyacetaphenone	0.55	0.18	0.34	1.01
catechol	11.66	10.23	8.64	8.21
Homovanillic acid	0.50	0	0.28	2.47

- MOFs and Nanoparticles are considered excellent heterogeneous catalyst due to their unique properties.
- Graphene-Oxide based MOF has exhibited great selectivity towards cleaving of methoxy and converting it to hydroxy group as a result, high amount of phenol and catechol observed compared with guaiacol.

Sonication of Black Liquor





Compound name	Retention time (min)	% from the total
Guaiacol	27.917	5.647
2-methoxy-4-methylphenol	Not Detected	0.000
Phenol + Methylphenol	Not Detected	0.000
4-ethyl-2-methoxyphenol	Not Detected	0.000
2-methoxy-4-vinylphenol	Not Detected	0.000
2,6-dimethoxyphenol	Not Detected	0.000
Vanillin	39.149	17.060
4-hydroxy-3-methoxyacetaphenone	Not Detected	0.000
Catechol	Not Detected	0.000
Homovanillic acid	Not Detected	0.000

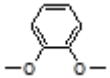
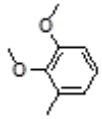
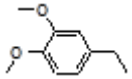
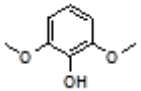
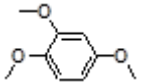
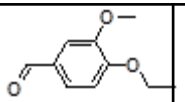
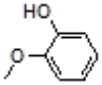
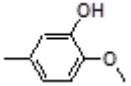
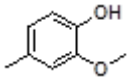
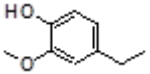
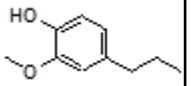
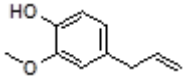
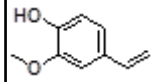
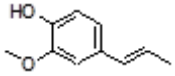
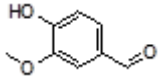
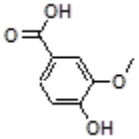
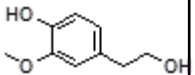
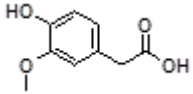
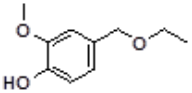
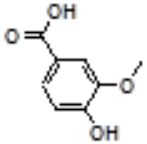
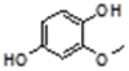
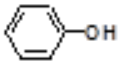
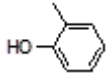
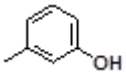
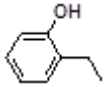
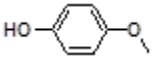
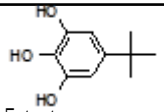
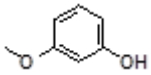
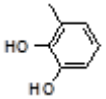
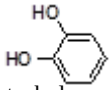
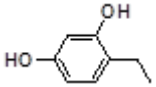
- Base catalyzed depolymerization of lignin can be assisted through ultrasonication.
- The temperature of the lignin dispersion was maintained at 23 °C using a water bath.

Oxidation of Lignin Using Potassium Permanganate

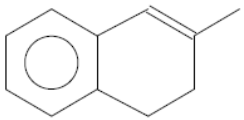
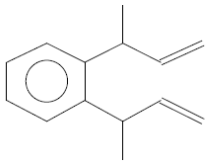
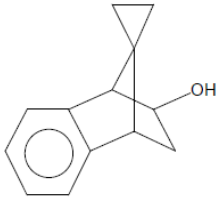
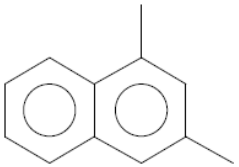
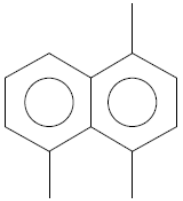
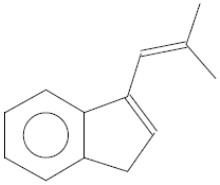
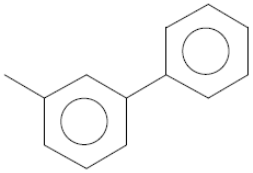
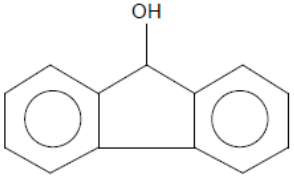
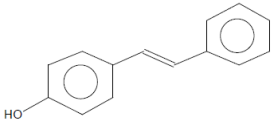
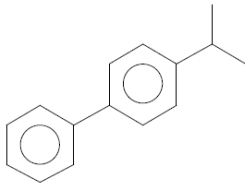
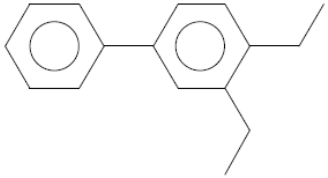
Phenolics	Types of lignin		
	Sigma-Aldrich	TCI (Alkaline)	TCI (Dealkaline)
Guaiacol	6.81	0.00	0.00
2-methoxy-4-methylphenol	0.00	0.00	0.00
Phenol	0.00	0.00	0.00
4-ethyl-2-methoxyphenol	0.44	0.00	0.00
2-methoxy-4-vinylphenol	1.40	0.00	0.00
2,6-dimethoxyphenol	0.00	0.00	0.00
Vanillin	10.4	32.0	17.7
4-hydroxy-3-methoxyacetaphenone	3.09	8.03	2.90
Catechol	0.00	0.00	0.00
Homovanillic acid	5.18	0.00	10.9

The oxidation of lignin using potassium permanganate produced vanillin dominantly.

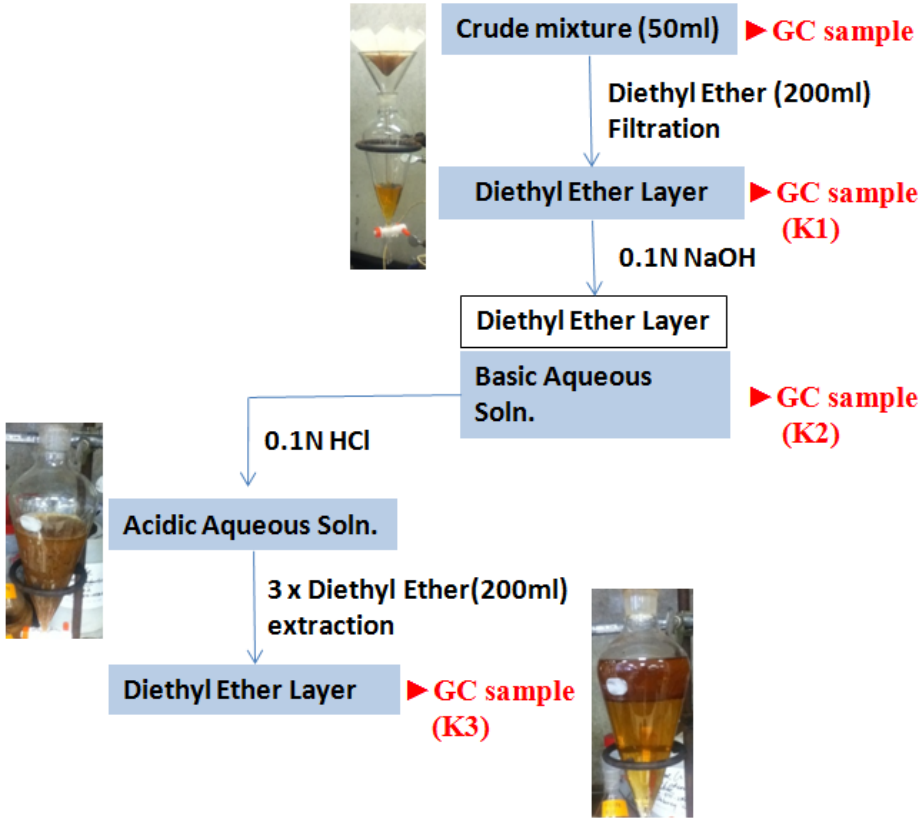
Various Phenolics Identified

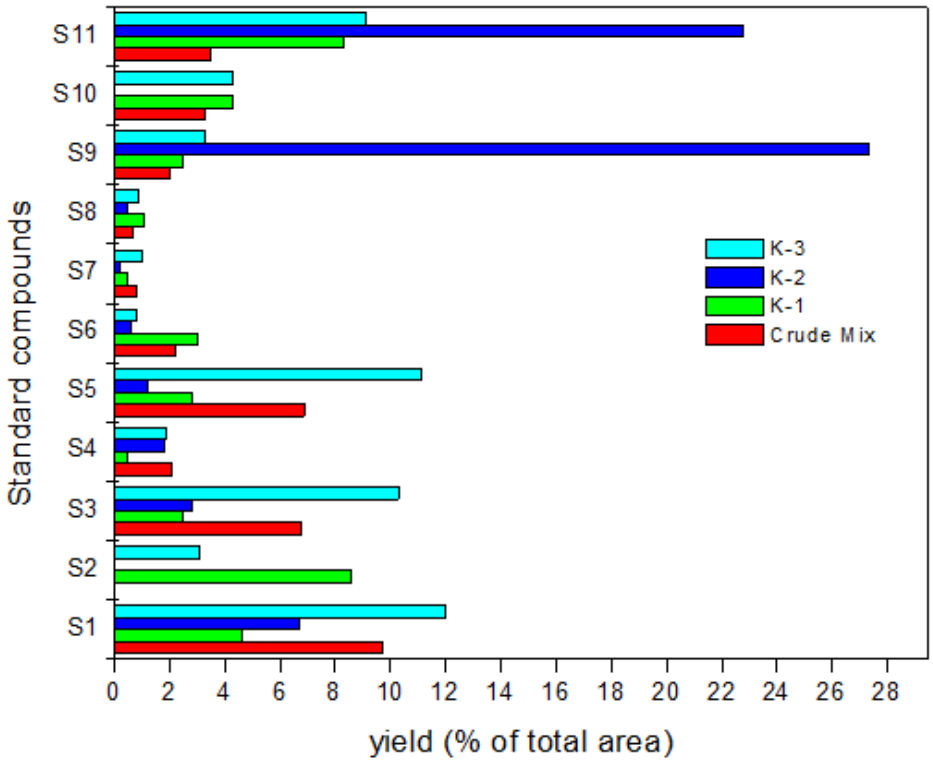
Syringol and Methoxy Containing Aromatics	 1,2-dimethoxy benzene (Veratrole) *25.380*	 2,3-Dimethoxy-toluene *27.416*	 1,2-dimethoxy, 4-ethyl benzene *32.104*	 2,6-dimethoxy-phenol *35.477*	 1,2,4-trimethoxy benzene *36.757*	 4-ethoxy-3-anisaldehyde *41.433*		
Guaiacol Derivatives	 Guaiacol *28.471*	2-methoxy-3-methylphenol *28.654*	 2-methoxy-5-methylphenol *30.032*	 2-methoxy-4-methylphenol *30.289*	 4-ethyl guaiacol *31.376*	 4-propyl guaiacol *33.023*	 4-allyl guaiacol *33.965*	 4-vinyl guaiacol *34.388*
	 4-propenyl-guaiacol *35.325*	 Vanillin *39.559*	 apocynin *40.569*	 Homovanilyl alcohol *43.228*	 Homovanillic acid *44.853*	 Phenol, 4-(ethoxymethyl)-2-methoxy *45.016*	 p-vanilic acid *52.182*	 2-Methoxyhydro quinone *27.253*
Phenol Derivatives	 Phenol *30.834*	 2 methyl phenol *32.563*	 3 methyl phenol *32.693*	 2-ethyl phenol *34.110*	 Mequinol *37.421*	 5-tert-butylpyrogallol *37.602*	 3-methoxy phenol *38.038*	 1,2-dihydroxy, 3-methyl benzene *40.956*
	 Catechol *41.523*	 1,3-dihydroxy,4-ethylbenzene *43.469*						

Possible Other Aromatic Compounds Identified During GC-MS

 Naphthalene, 1,2-dihydro-3-methyl- *24.129*	 Benzene, 1,2-bis(1-buten-3-yl)- *25.440*	 Spiro(tricyclo[6.2.1.0(2,7)]undeca -2,4,6-triene)-7,1'-cyclopropane *27.392*	 Naphthalene, 1,3-dimethyl- *29.706*	 Naphthalene, 1,4,5-trimethyl- *32.376*
 3-(2-Methyl-propenyl)-1H-indene *32.956*	 1,1'-Biphenyl, 3-methyl- *34.721*	 9H-Fluoren-9-ol *36.014*	 Phenol, 4-(2-phenylethenyl)- *37.814*	 1,1'-Biphenyl, 4-(1-methylethyl)- *37.893*
 1,1'-Biphenyl, 3,4-diethyl- *39.621*				

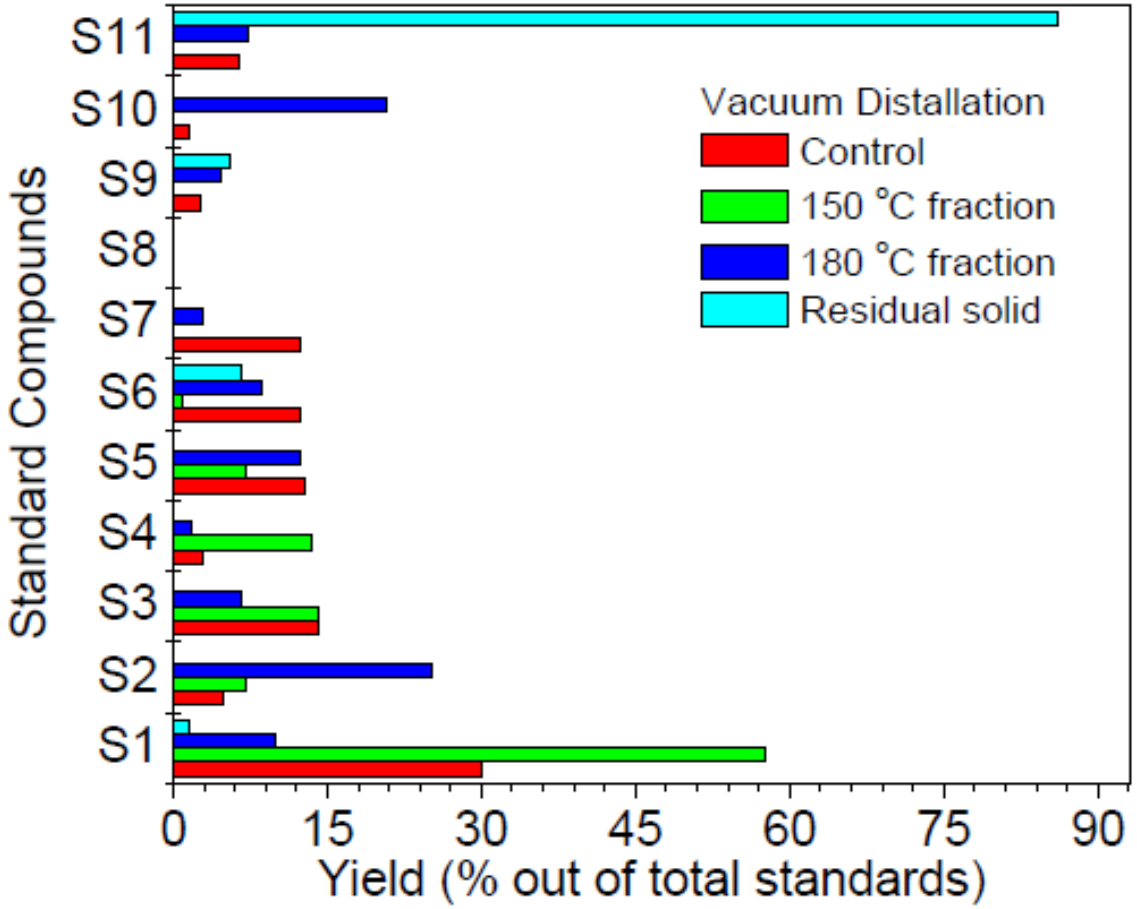
Purification of Pyrolysate Using Solvent Extraction



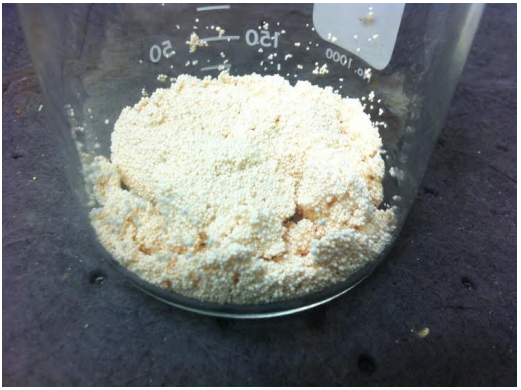


Purification of Pyrolysate by Fractional Vacuum Distillation

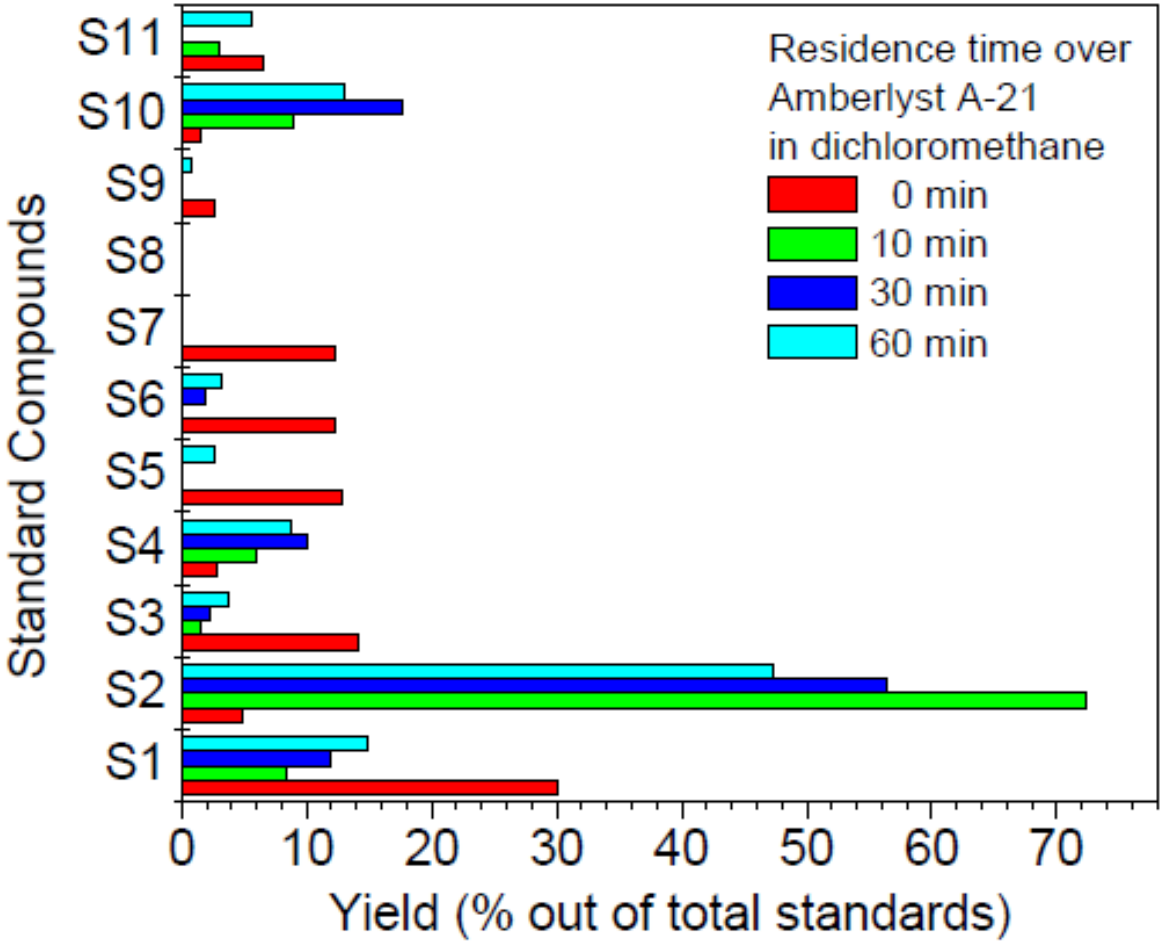
Typical Distillation Setup



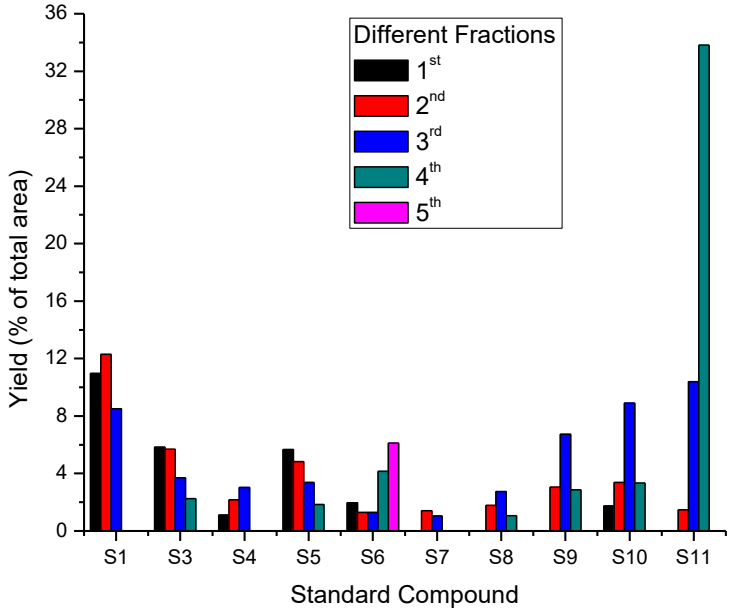
Purification of Pyrolysate by Resin Treatment

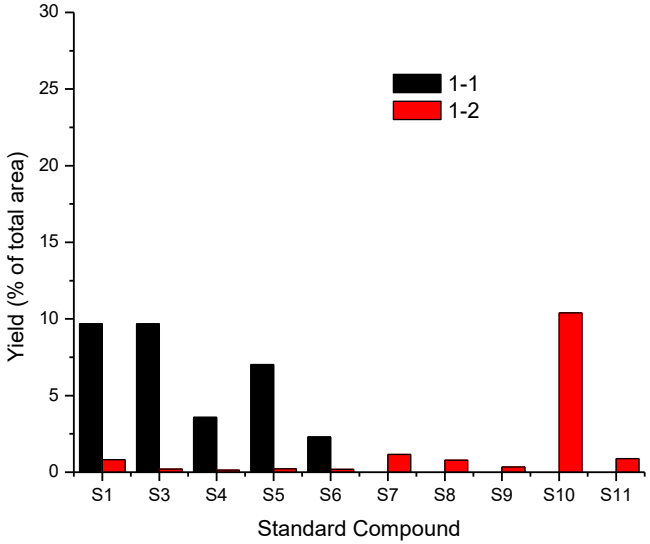


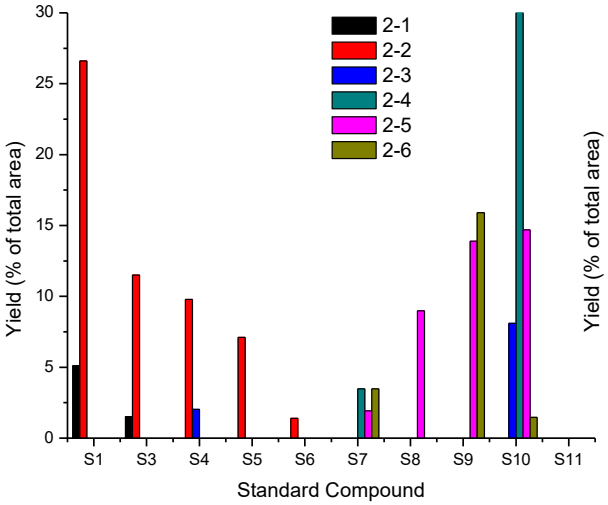
Amberlyst A21 free amine resin, which can selectively separate phenol.

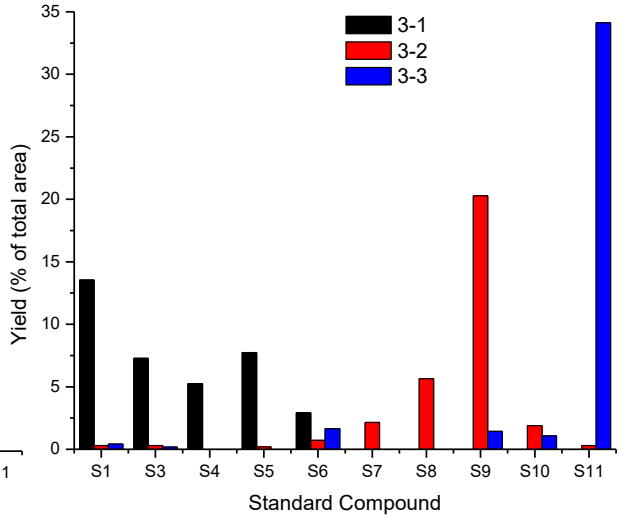


Column Purification

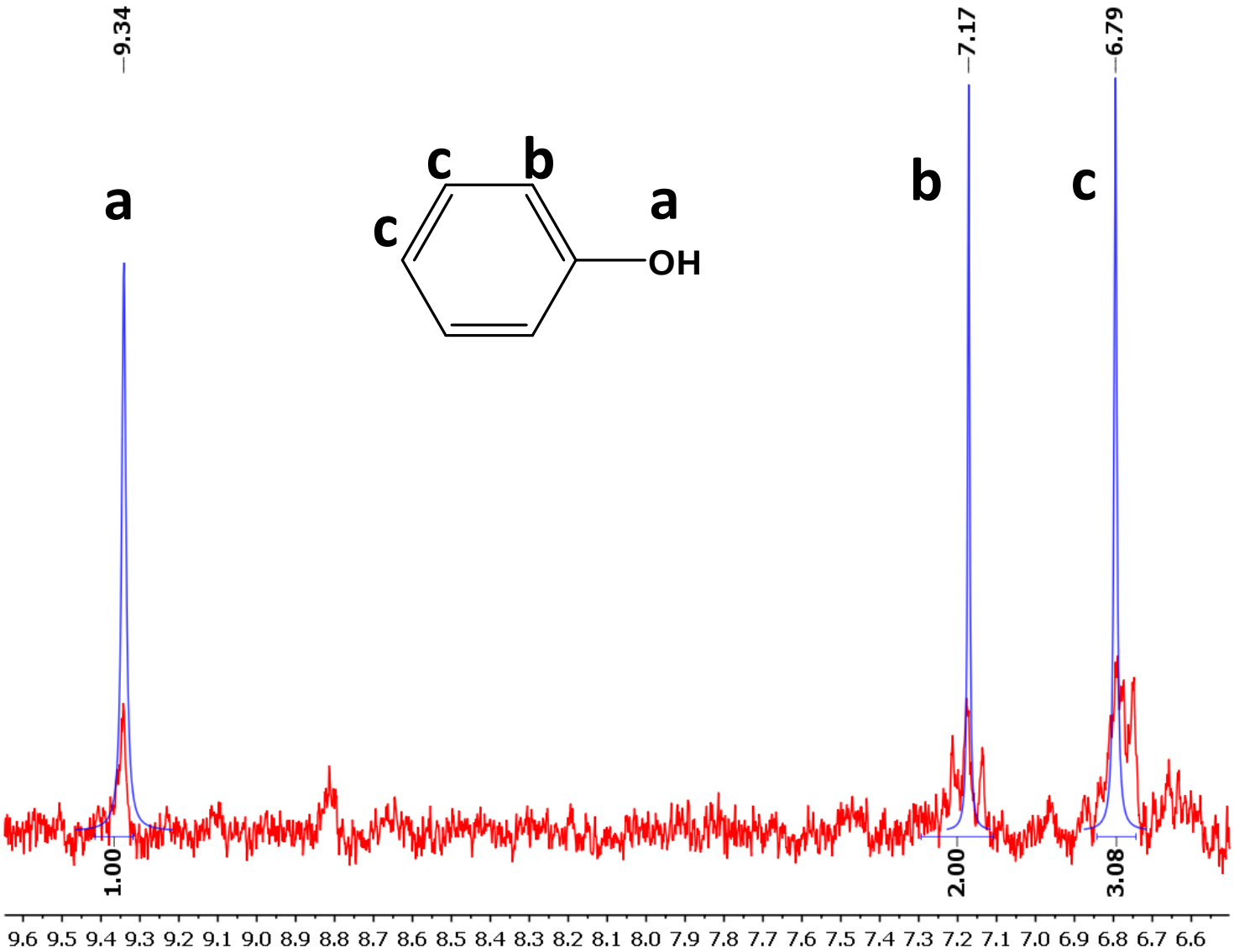








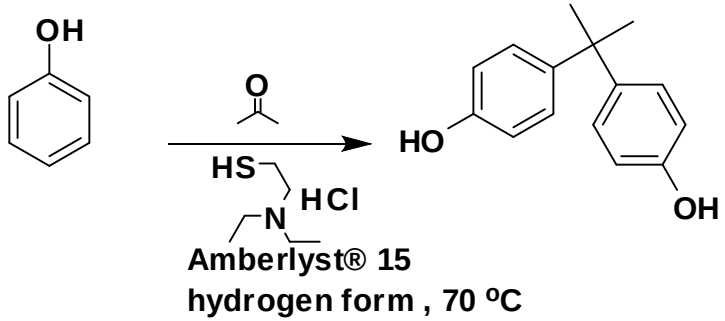
^{1}H NMR of the Green Phenol

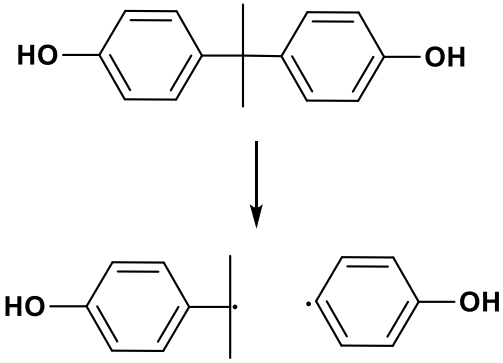


Synthesis of BPA

Problem:

- In stoichiometry high amount of phenol and very low amount of acetone is required.
- Higher the purity of the phenol, better will be conversion.
- The Green BPA will be delivered to the NRL.





Exact Mass: 135.08 Exact Mass: 93.03

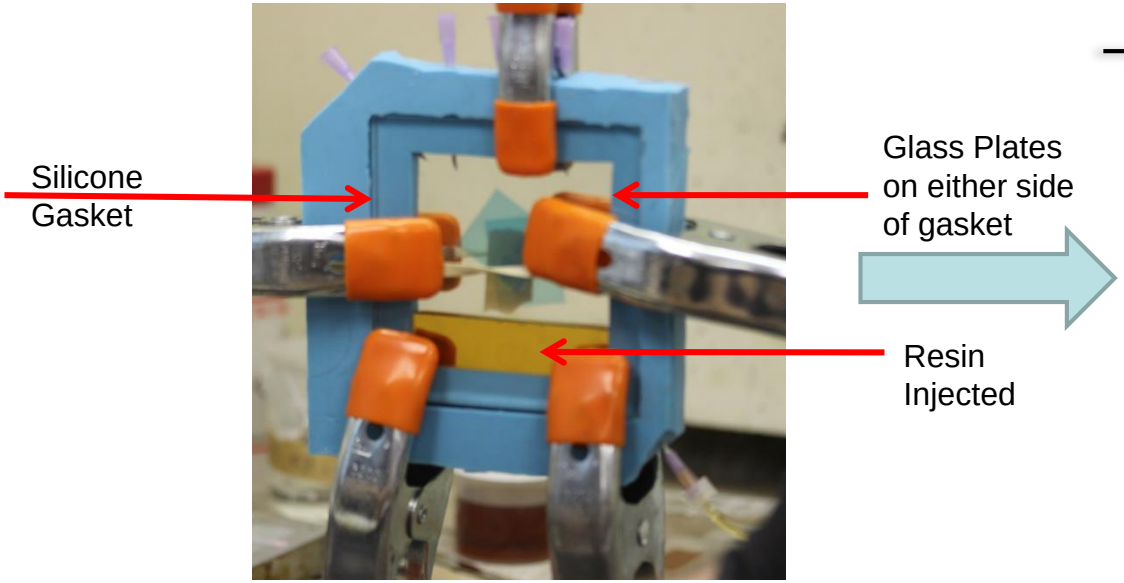
- The fragmented BPA peaks at 7.891 and 10.640 min were observed in GC spectra of green BPA.
- The mass spectra of peak at 7.885 and 10.663 confirmed presence of phenol and p-isopropyl phenol respectively.
- The GC-data confirmed that we have successfully synthesized BPA starting from lignin.

Scale-up and Coupon Fabrication of Green VER

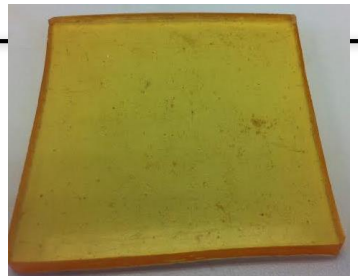
- Resin synthesis was scaled-up and coupons were fabricated by mixing green resin with Ashland's commercial resin in different compositions.

<u>Neat Resin Coupon Fabrication Procedure</u>.

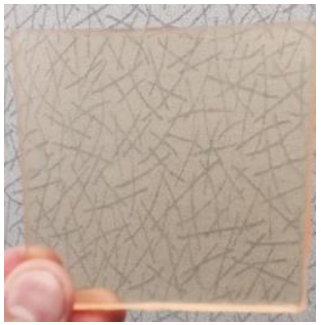
- Resin injected at one corner of the set up.
- Glass plates fit on either side of the gasket.
- Resin flows upwards while degassing concurrently.



20% Green Nonbrominated Resin Coupon



20% Green Brominated Resin Coupon



10% Green Brominated Resin Coupon

Action Items-1 (Bromination of BPA)

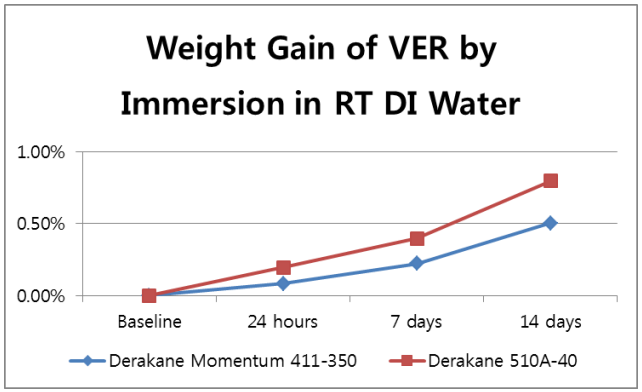
Action Item 1: provide justification for bromination of bisphenol-A.

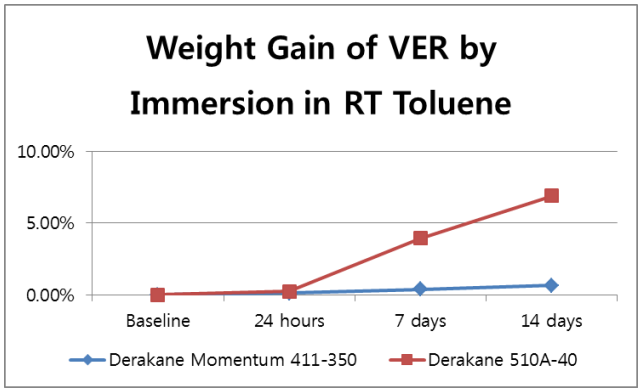
- Bromination of BPA was performed to demonstrate feasibility of the synthetic route.
- Currently available brominated DERAKANE 510A-40 is highly economical resin having good anti-flammability properties.
- Bromination of BPA was performed using potassium bromide and bromine in acetonitrile for a short reaction time of only 5-10 min at room temperature. The TBBPA was isolated with 99 % yields and high purity.
- The reaction conditions and personal protective equipment's were approved by environmental and health safety (EHS) person-in-charge at Umass Lowell.
- In year II and III of the project, we will focus more on the BPA based VER and will not perform bromination of BPA in laboratory.

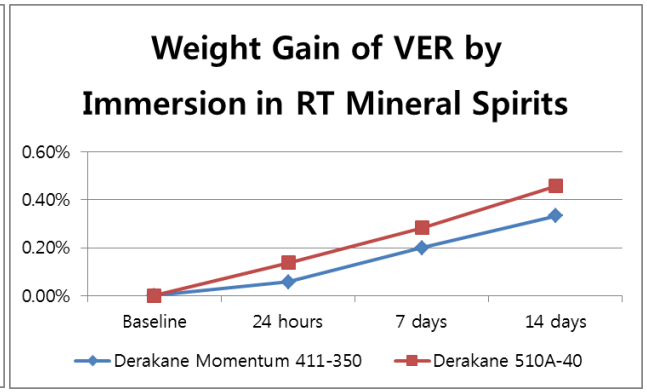
"Instantaneous, Facile and Selective Synthesis of Tetrabromobisphenol A using Potassium Tribromide: An Efficient and Renewable Brominating A gent" Kumar, L., Sharma, V., Mahajan, T., and Agarwal, D. D., Organic Process Research & Development 14, 174–179, (2010)

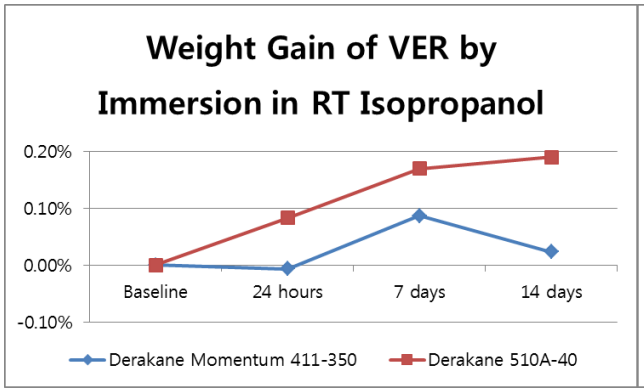
Action Items-2 (Water Uptake Studies)

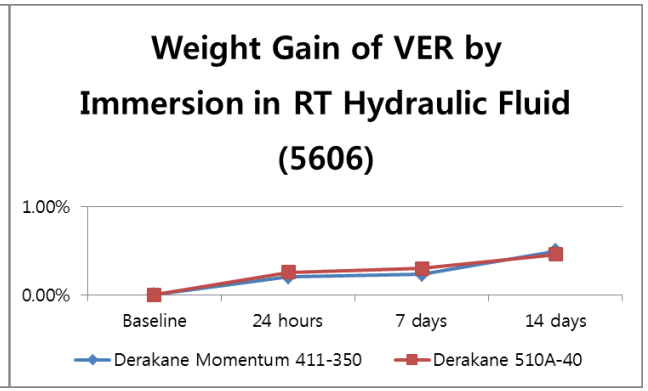
Action Item 2: Uptake of water, hydraulic fluids, or hydrocarbon fuels by Green Vinyl Ester Resins

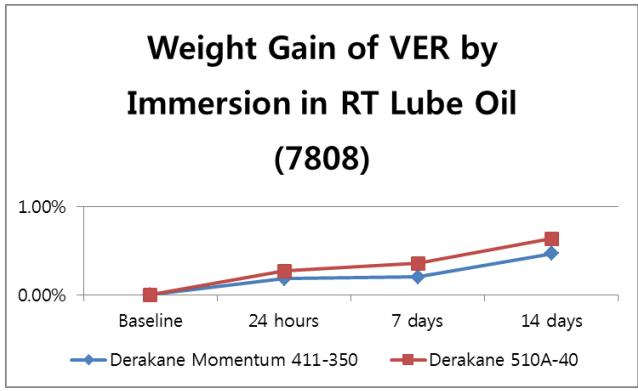






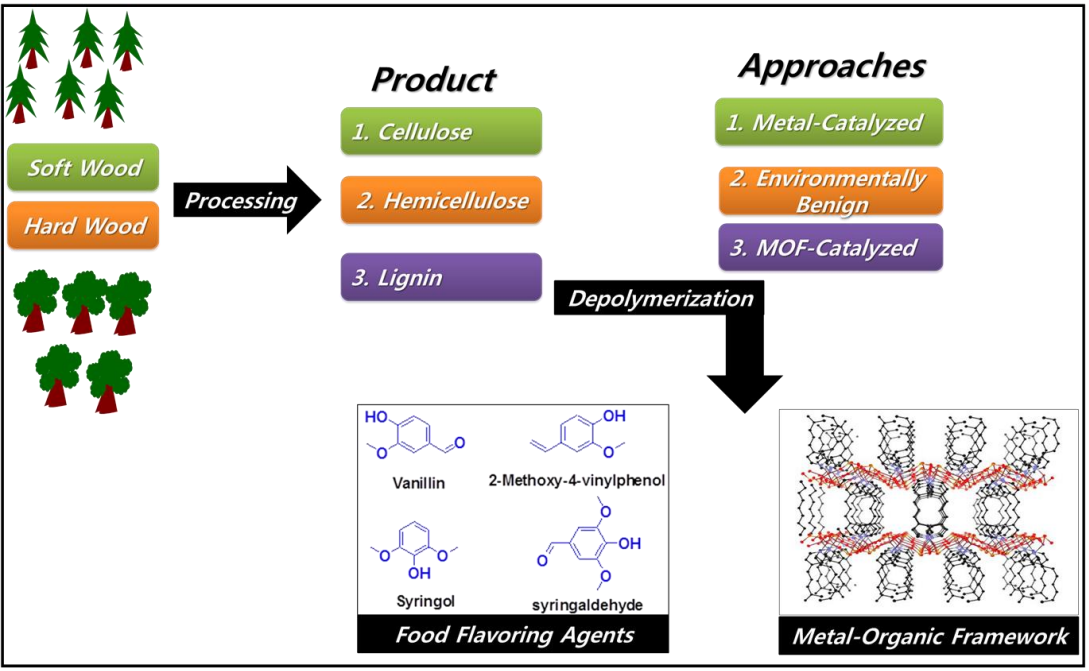






Action Items-3 (New Approaches for Improving Yields of Phenolics)

Action Item 3: submission of a white paper for additional approaches for optimization of the yield of phenol and other valuable phenolic



Background: A very high activation energy is required to depolymerize ligni The activation energy can be reduced significantly using different catalytic systems.

Energy Sources: Various energy sources available.

Thermal Energy (Pyrolysis)
Sound Energy (Sonication Based Depolymerization)
Electromagnetic Radiation (Microwave Based Depolymerization)

Prior Work

No	Lignin	Catalyst	Temperature (°C)	Products
1	Kraft lignin	Si-Al catalyst ZrO_2-Al_2O_3-FeO_x	200–350	phenols, methoxyphenol
2	Lignosulfonate	Ni/C, NiLa/C, NiPt/C, NiCu/C, NiPd/C, and NiCe/C	200	methoxyphenols
3	Corn stalk lignin	Pt/C, Pd/C, Ru/C	200–250	4-ethylphenol 4-ethylguaicol

No	Lignin	Approach	Catalyst	Products
4	Organosolv olive tree lignin	Microwave catalyzed (140 °C)	Ni, Pd, Pt, or Ru supported by Mesoporous Al-SBA-15	syringaldehyde, vanillin
5	Pinus radiata lignin	Ionic liquid catalyzed (250 °C)	1-butyl-3-methylimidazolium acesulfamate	methoxyphenols
6	Organosolv beech lignin	Ionic liquid catalyzed (100 °C)	1-ethyl-3-methylimidazolium-trifluoromethansulfonate with $Mn(NO_3)_2$	2,6-dimethoxy-1,4-benzoquinone

[i] T.Yoshikawa,T.Yagi, S. Shinohara et al., "Production of phenols from lignin via depolymerization and catalytic cracking," *Fuel Processing Technology*, 108, 69–75, **(2012)**

[ii] Q. Song, F.Wang, and J. Xu, "Hydrogenolysis of lignosulfonate into phenols over heterogeneous nickel catalysts," *Chemical Communications*, 48, 7019–77021, **(2012)**

[iii] Y. Ye, Y. Zhang, J. Fan, and J. Chang, "Selective production of 4-ethylphenolics from lignin via mild hydrolysis," *Bioresource Technology*, 118, 648–651, **(2012)**

[IV] X. Gu, K. Cheng, M. He, Y. Shi, Z. Li, "La-Modified SBA-15/H_2O_2 system for the microwave assisted oxidation of organosolv beech wood lignin" *Maderas.Ciencia y tecnología*, 14(1): 31-42 **(2012)**

[V] A. Pinkert, D. F. Goeke, K. N. Marsh, and S. Pang, "Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids," *Green Chemistry*, 13, 3124–3136, **(2011)**

[Vi] K. St¨ark, N. Taccardi, A. B¨osmann, and P. Wasserscheid, "Oxidative depolymerization of lignin in ionic liquids," *Chem-SusChem*, 3, 719–723, **(2010)**

Applications of Green Phenolics

- **Various Resin Materials**. The isolated phenolic can be used as a building block for synthesis of different types of resin materials, which can be used for defense purposes. Such as cyanate esters can be made from vanillin, and other resins can be made from bisphenol A.

- **Food Flavoring Agents**. Several phenolics have large number of applications as food flavoring agents; such as, vanillin, syringol, syringadehyde, 2-methoxy-4-vinylphenol, etc.

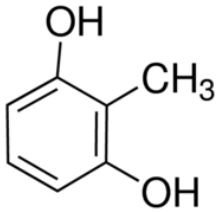
- **Precursor for Pharma Industries**. Many phenolics can be used as an important precursor in many pharma industry. Such as, Guaifenesin (Robitussin®) from guaiacol and many more. So, by several simple organic reactions one pyrolyzed material can be easily converted to more economical products.

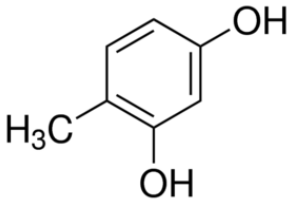
C. F. H. Allen and G. W. Leubner, "Syringic aldehyde", *Org. Synth.; Coll.* 4: 866 **(1963)**

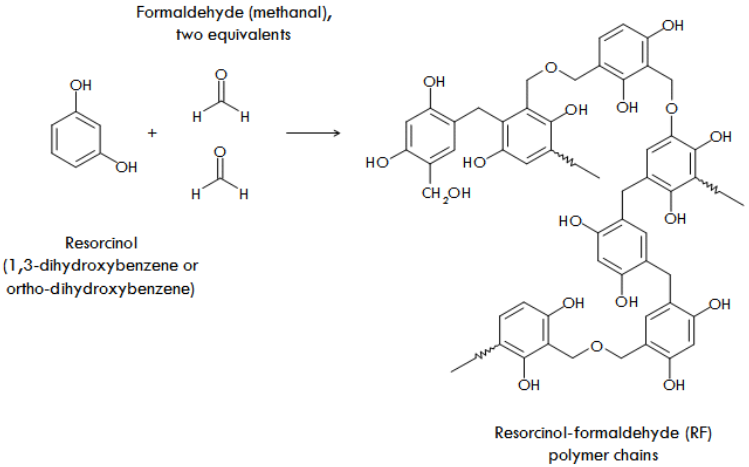
Green Resorcinol – Formaldehyde Resins and Aerogels

2-methylresorcinol and 4-methylresorcinol

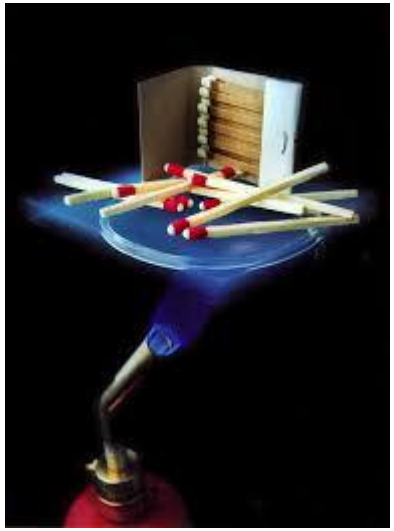
Obtained from microwave pyrolysis of lignin







Resorcinol-Formaldehyde (RF) aerogels

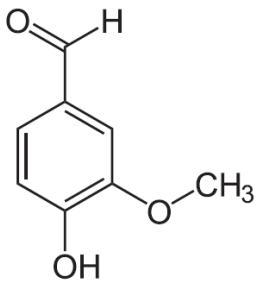


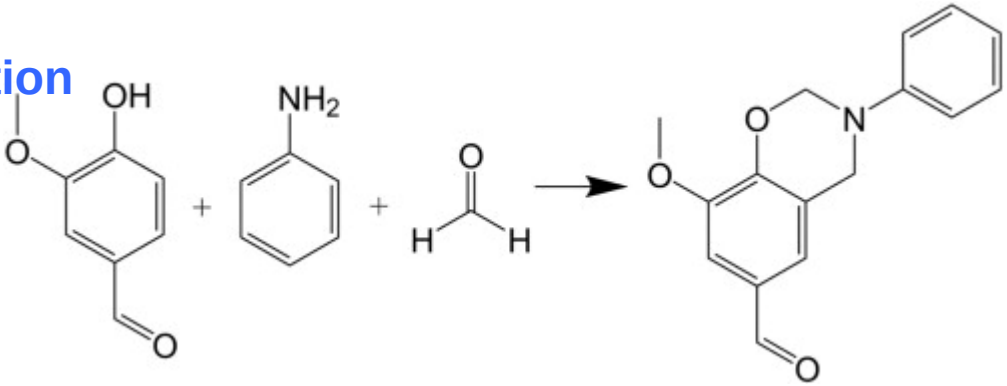
Collaborations with NASA, ARL and NRL

Green Vanillin based Benzoxazine Resins

Vanillin

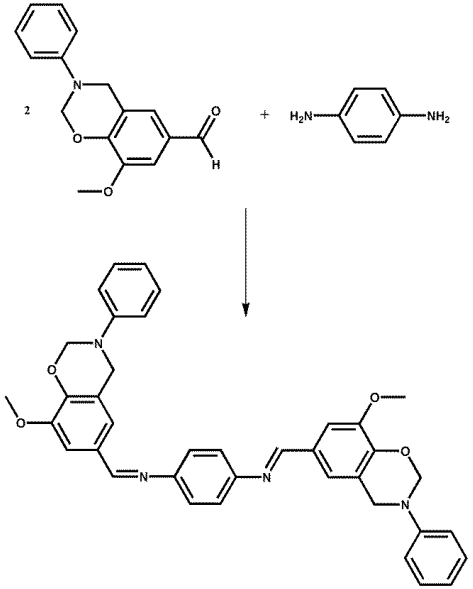
Obtained from base catalyzed sonication assisted degradation of of lignin





Ishida, H. et al. *Polymer* **2014**, *55*, 1443 - 1451

Can be dimerized using p-phenylenediamine



Composites
products for manufacturing fiber reinforced structural components

Assembly
materials for bonding, surface preparation and protection

MRO
repair solutions for composite and metal structures to support your commitment to the aircraft lifecycle

Collaborations with AFRL, NRL and NASA

Project Funding

	FY13*	FY14*	FY15*	FY16	Total
Proposal Requested ($K)	380	289	433	150	1252
Funds Received ($K)	380	289	433		1102
% Expended	100	77.5	0.0		54.7
Projected Out-Year Funds Required ($K)					1252

***NOTES:**

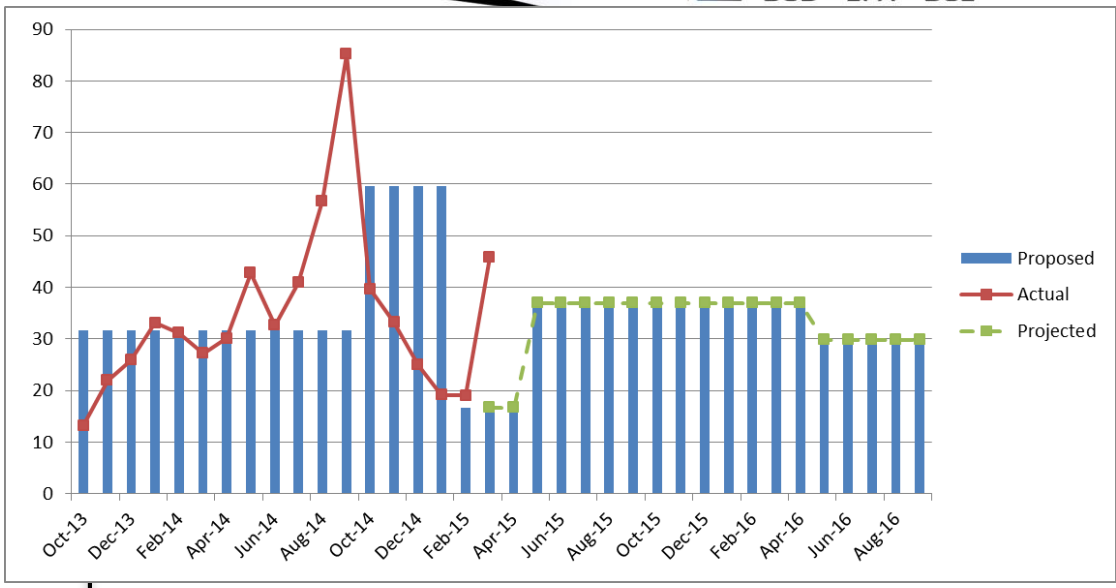
This table reflect SERDP funds sent to all directly funded and second tier performers working on the project.

Include columns for all fiscal years for which funding has been received, is budgeted to be received, or is proposed to be received in the Revised Funding Profile. Add columns as needed.

Based on your spend rates for funding already received and any discussion with your program manager, identify your proposed out-year funding requirements. Total should not exceed current total project value.

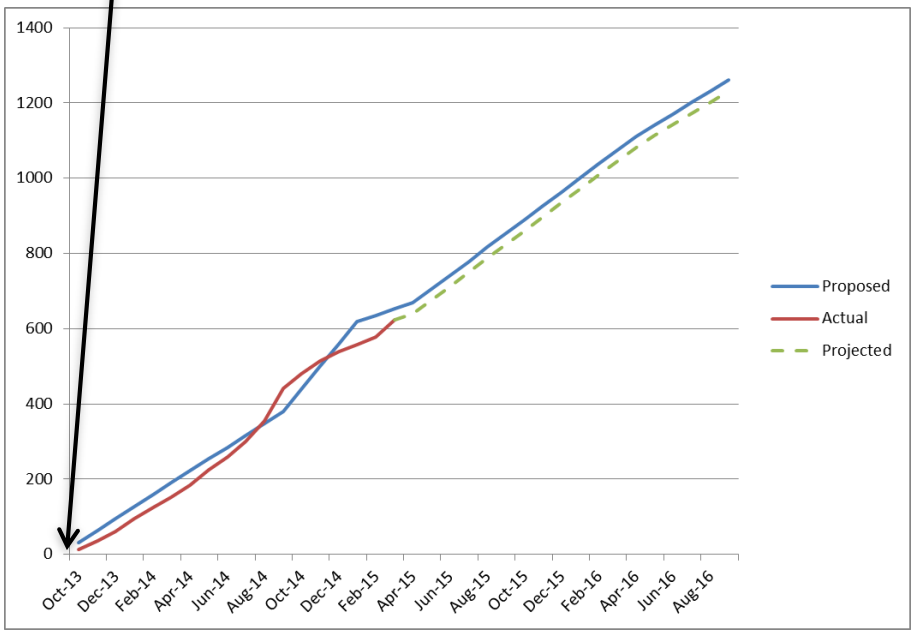
Financial Execution

- Proposed Start: *October 2013*
- Contract Award/MIPR Receipt:
- *October 2013*
- Proposed v. Actual Execution Delta:
- Contract End Date: *September 30, 2016*
- Additional Funds Needed in Next Calendar Year:
  - ♦Lead Org:
  - ♦Co-Performer(s):
- Execution Outlook:
  - ♦ *Discuss future project execution*

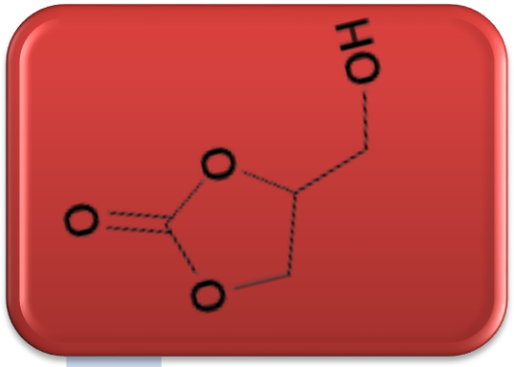


Contract Award or Receipt of MIPR

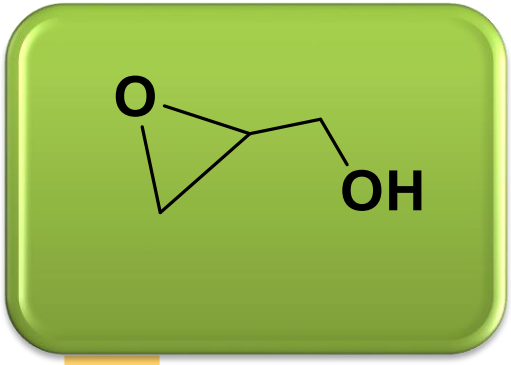
Values in k($)



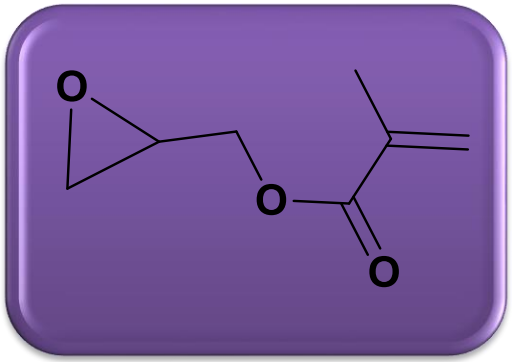
Transition Plan



- Solvent
- Batteries
- Cement
- Cosmetics
- Gas separation



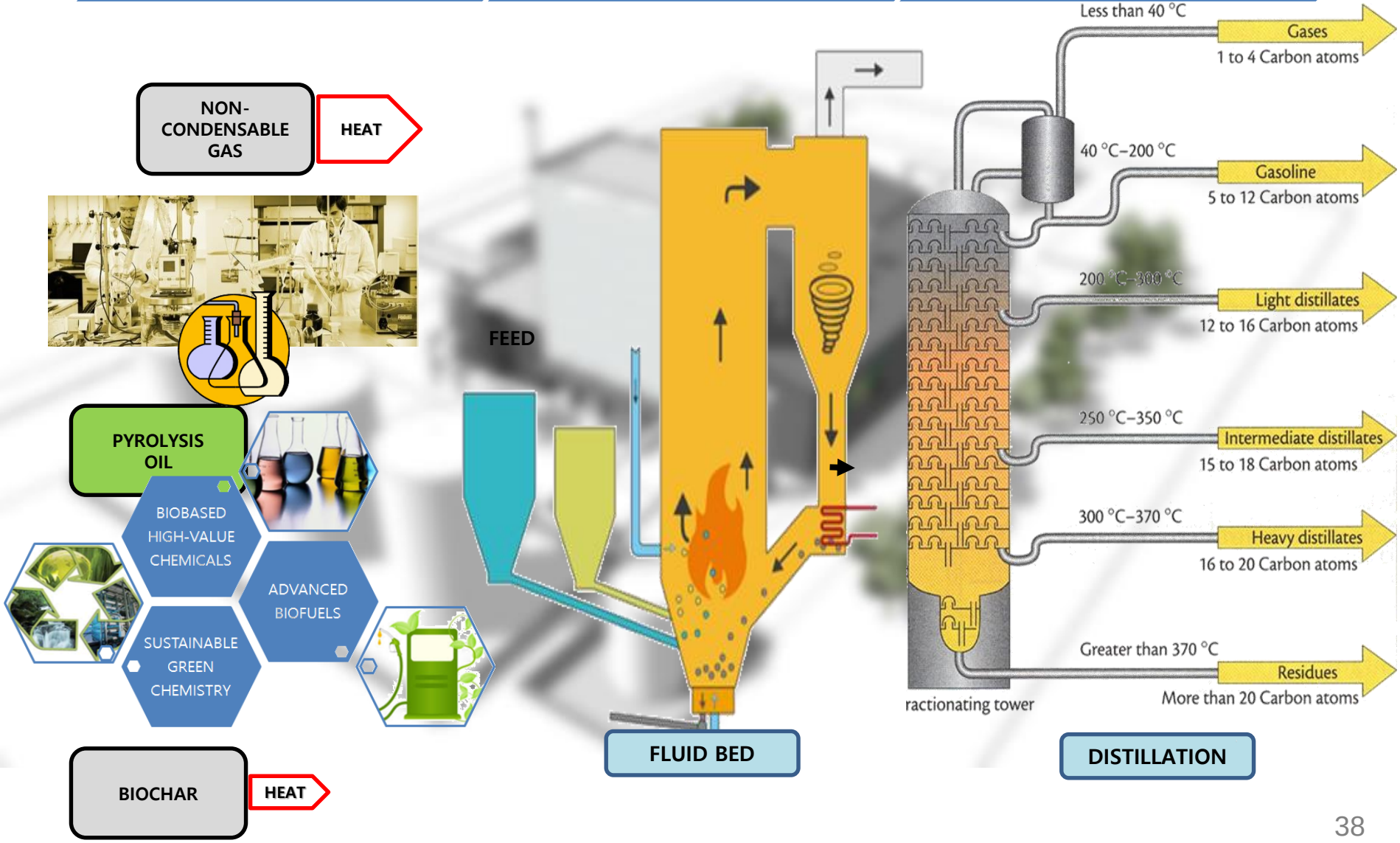
- Stabilizer
- Intermediate for many products
- Surface Coatings



- Dual functionality: epoxy and vinyl group
- Various applications

Ready to use materials synthesized from biodiesel glycerin

LAB-SCALE > SCALE-UP > REFINEMENT

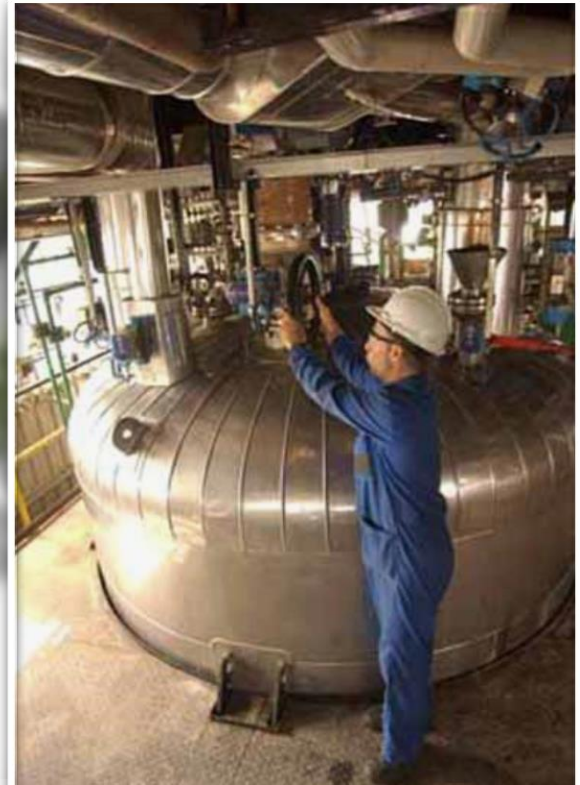


Transition Plan

Pilot scale

Reactor

Lab scale



BACKUP MATERIAL

Publications

Publications and Manuscripts in preparation:

- P. N. Shah, N. Kim, Z. Huang, M. Jayamanna, A. Kokil, A. Pine, J. Kaltsas, E. Jahngen, D. K. Ryan, S. Yoon, R. F. Kovar, Y. Lee, Environmentally Benign Synthesis of Vinyl Ester Resin from Biowaste Glycerin. *RSC Advances*, *In revision*.
- P. N. Shah, A. Kokil, M. Jayamanna, D. K. Ryan, R. F. Kovar, Y. Lee, Novel Pyrolysis Assembly with Optimized Conditions for Improved Phenolic yields from Lignin. *Biomass Conversion and Biorefinary*, *Submitted*.
- P. N. Shah, A. Kokil, R. F. Kovar, Y. Lee, Flame-Retardant Vinyl Ester Resin from Renewable Biowaste. *In preparation*.
- A. Kokil, P. N. Shah, M. Jayamanna, D. K. Ryan, R. F. Kovar, Y. Lee, Synthesis of Green Bisphenol A from Biowaste Lignin. *In preparation.*

Invention Disclosure to UML:

- High Value Phenol Enriched Phenolics by Cost-Effective Pyrolysis of Biowaste Lignin: Yongwoo Lee, Robert F. Kovar, Priyank N. Shah, Namjoon Kim, Akshay Kokil, Edwin Jahngen, David K. Ryan; *Invention Disclosure*, UML- 2015-007.
- Sustainable “Green” Vinyl Ester Resin (VER) from Renewable Resources, Name: Yongwoo Lee, Robert F. Kovar, Priyank N. Shah, Namjoon Kim, Akshay Kokil, Edwin Jahngen; *Invention Disclosure*, UML- 2015-008.

Appendix S

Sustainable "Green" Vinyl Ester Resin (GVER) from Renewable Resources

WP 2317

Yongwoo Lee
University of Massachusetts Lowell

In-Progress Review Meeting
April 29th, 2016

SERDP
DOD ▪ EPA ▪ DOE

WP-2317: Sustainable "Green" Vinyl Ester Resin (GVER) from Renewable Resources

Performers:

Y. Lee, P. Shah, N.Kim, R. F. Kovar, and A. Kokil

Technology Focus

- *Synthetic protocol for GVER and its processing into VARTM composites, pyrolysis of lignin, extraction of phenol*

Research Objectives

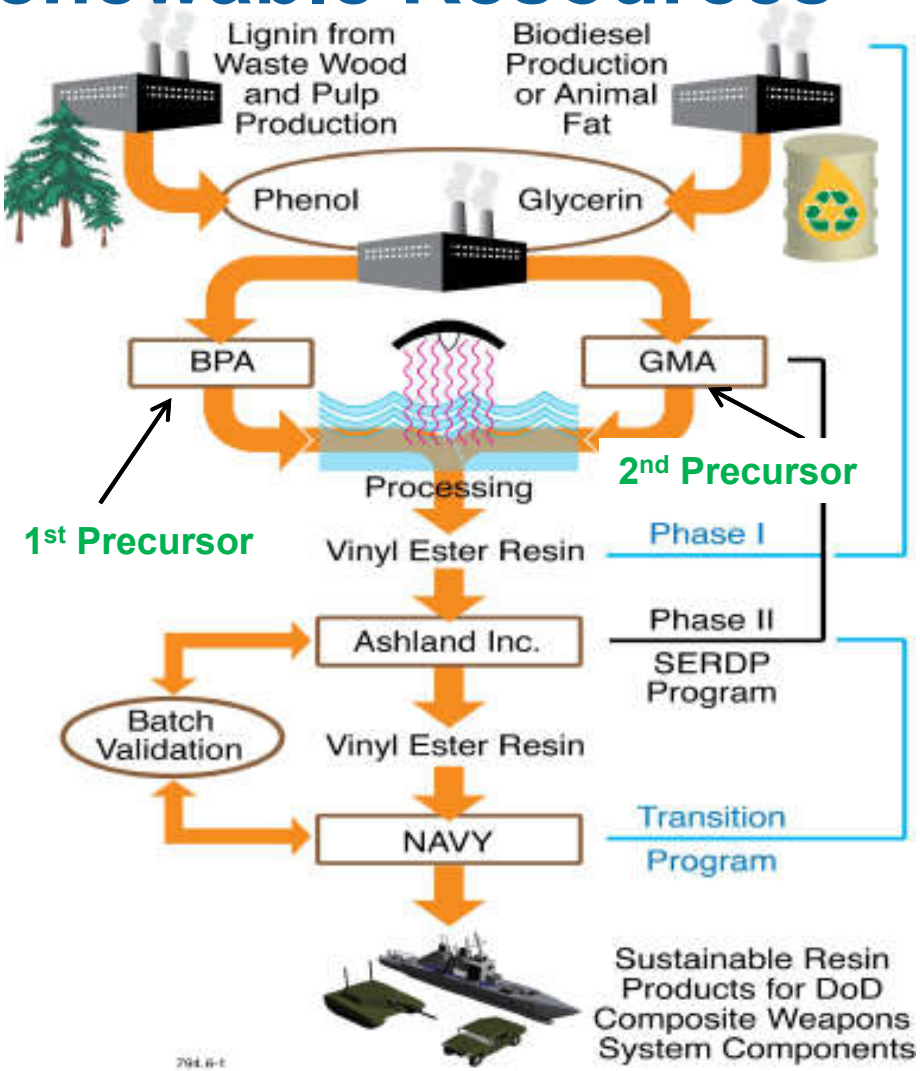
- *Demonstrate synthesis of GMA from glycerin.*
- *Isolation of phenol from lignin to get BPA and TBBPA.*
- *Demonstrate synthesis of GVER and VARTM processing.*

Project Progress and Results

- *Successfully scaled up synthesis of GMA and GVER from biowaste glycerin.*
- *Fabricated neat coupons using GVER and Br-GVER synthesized from bio-waste glycerin .*
- *Synthesized Green BPA using lignin pyrolysate.*
- *Developed alternate lignin depolymerization protocols for selective yield of constituent chemicals.*

Technology Transition

- *Working with Ashland Inc. to understand industrial demands.*
- *Working with paper and biodiesel company for procuring lignin and glycerin.*



Teaming Partners

Team	Person In-Charge (Point of Contact)	Role
UMass Lowell	Dr. Yongwoo Lee (PI) Dr. Priyank Shah (Co-PI) Dr. Namjoon Kim Dr. Akshay Kokil	Developing GVER from biowaste and coordinating research teams
UMass Lowell	Prof. Hansen/Mr. Sid Dev	Developing GVER composites using VARTM
UMass Lowell	Prof. David Ryan	Developing analytical technique for characterization of pyrolysates
UMaine Orono	Prof. W. DeSisto	Fluidized fast pyrolysis to generate bio-oils: New Partnership
UMass Lowell	Prof. H. Wong	GC-MS analysis prior to LC-MS analyses for separation
Bentley University	Prof. Ryan Bouldin	Business development
NAVAIR	Dr. John Brennan	Developing composites with flame retardant ability
NAVSEA	Mr. Usman Sorathia	Examine flame retardant properties of the composites
R.F. Kovar & Associates	Dr. Robert F. Kovar	Provide technical expertise to UML team.
Ashland Inc.	Dr. Stevens, Dr. Joe Fox	Industrial teaming partner
Maine Standard Biofuels	Mr. Jarmin Kaltsas	Provide unrefined glycerin obtained during biodiesel manufacturing
Flambeau River Paper LLC	Mr. Bill Tomczak	Provide lignin from paper industry waste stream
Maine Seed Company	Mr. Tate McPherson	Provide lignin from different plant source
Dixie Chemical Co.	Mr. Alexander T. Grous (Dr. John La Scala-ARL)	MFAs as Styrene replacements-New Partnership
TPI Composite, Inc.	Mr. Stephen C.Nolet	New Partnership

Technical Objective

- Refine Phenol from Lignin
- Refine GMA from Glycerin
- Scale up VER resin

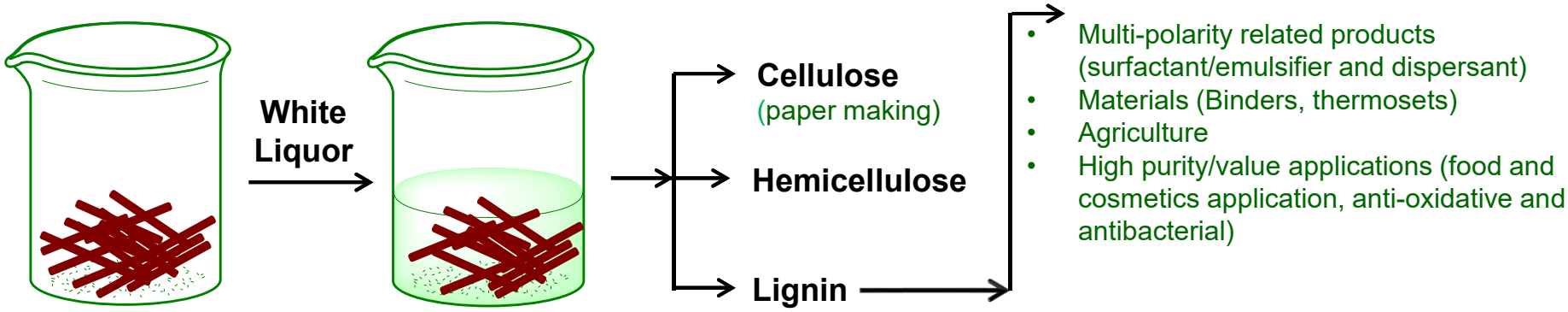
Year I

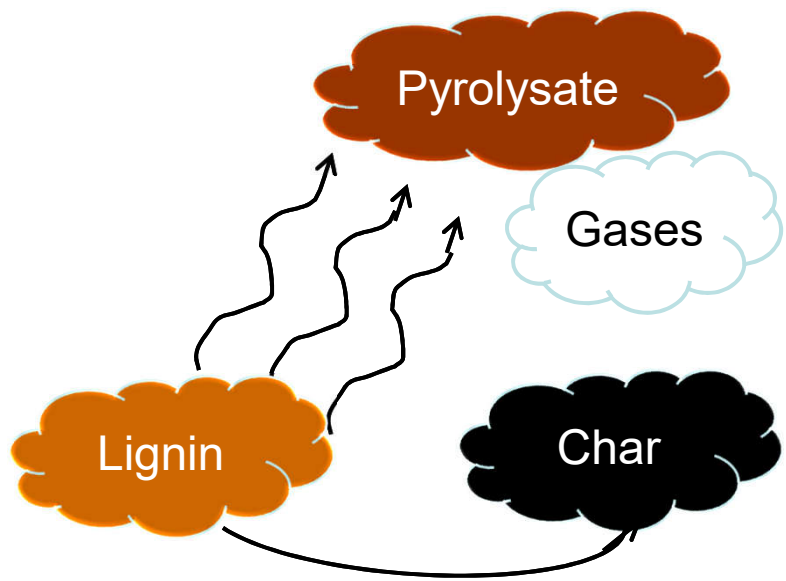
- Formulation with Derakane Vinyl Ester
- Fabricate composites with VARTM
- Conduct structural testing for equivalence

Year II & Year III

Technical Approach-1A

Pyrolysis of Lignin





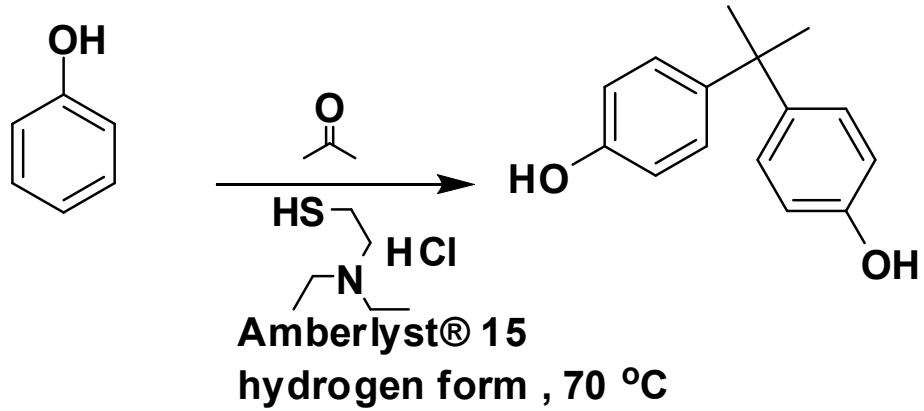
Pyrolysis Concept

Samples of lignin provided by Flambeau River Papers LLC (Park Falls, WI) and Maine Seed Company (Mapleton, ME)

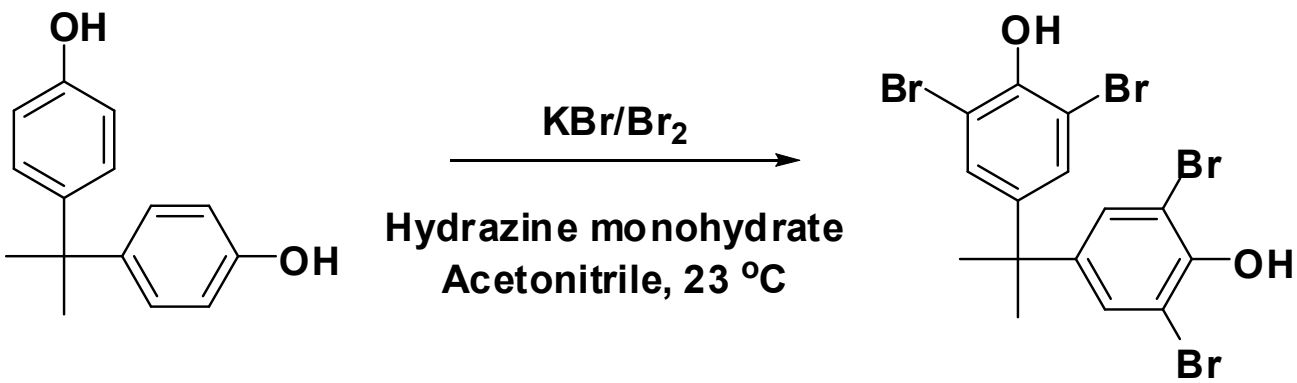
http://www.ili-lignin.com/

Technical Approach-IB

Synthesis of BPA



Synthesis of TBBPA



Purification by precipitation in water

Technical Approach-2A

Introduction to Glycerin

Vegetable Oil, Animal Fat (Triglycerides)[1] →

- **Water, NaOH (Hydrolysis, Saponification)** → **long-chain carboxylate salts used as soaps**
- **Alcohol, NaOH Transesterification** → **esters of fatty acids used as biodiesel**

+ glycerin

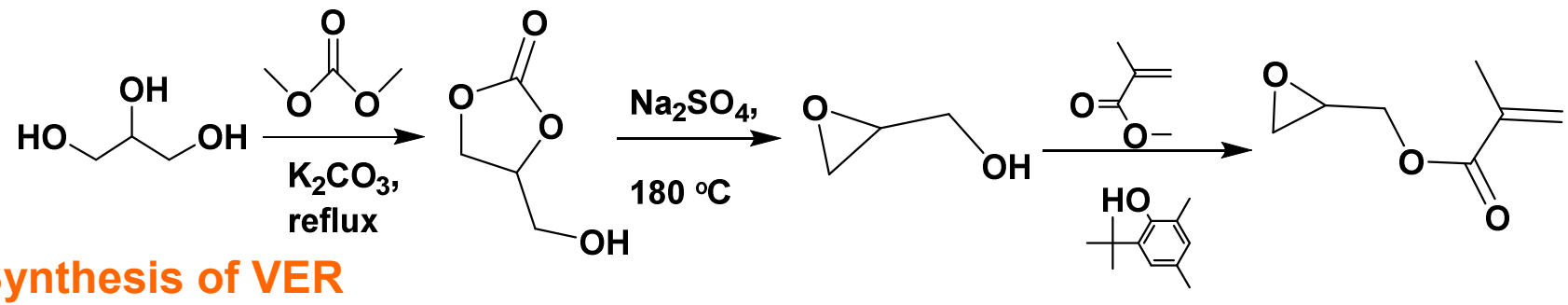
- By 2020, the production of glycerin will be six times higher than its demand.[2]
- Disposal of glycerin in the waste stream would require increasing expenditures for biodiesel industry

We are using crude glycerin from bio-diesel waster stream provided by Maine Standard Biofuels (Portland, Maine)

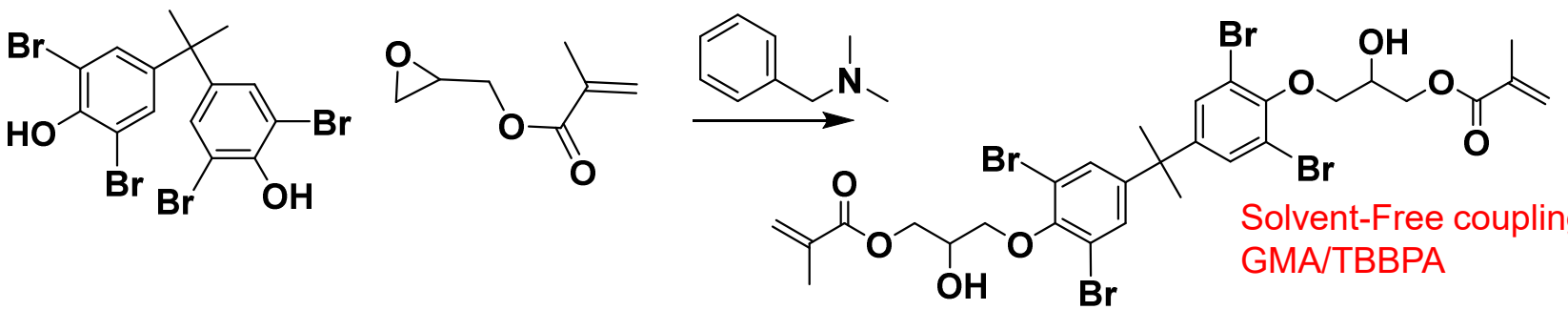
1. Sims, Bryan (2011-10-25). "Clearing the Way for Byproduct Quality: Why quality for glycerin is just as important for biodiesel". Biodiesel Magazine
2. Christoph, Ralf; Schmidt, Bernd; Steinberner, Udo; Dilla, Wolfgang; Karinen, Reetta (2006). "Glycerol". Ullmann's Encyclopedia of Industrial Chemistry. doi:10.1002/14356007.a12_477.pub2. ISBN 3527306730.

Technical Approach-III

Synthesis of GMA

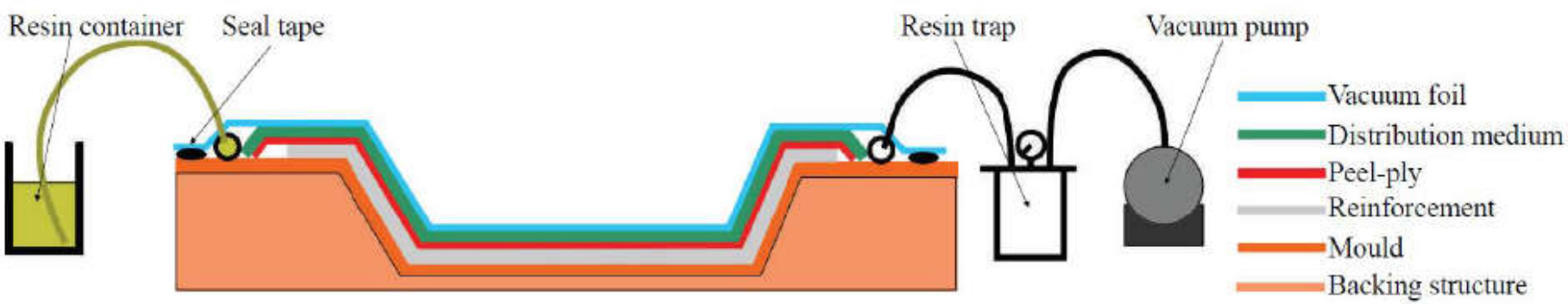


Synthesis of VER



Solvent-Free coupling of GMA/TBBPA

Carbon fabric reinforced panel fabrication by VARTM



Significance

Environmental Advantages

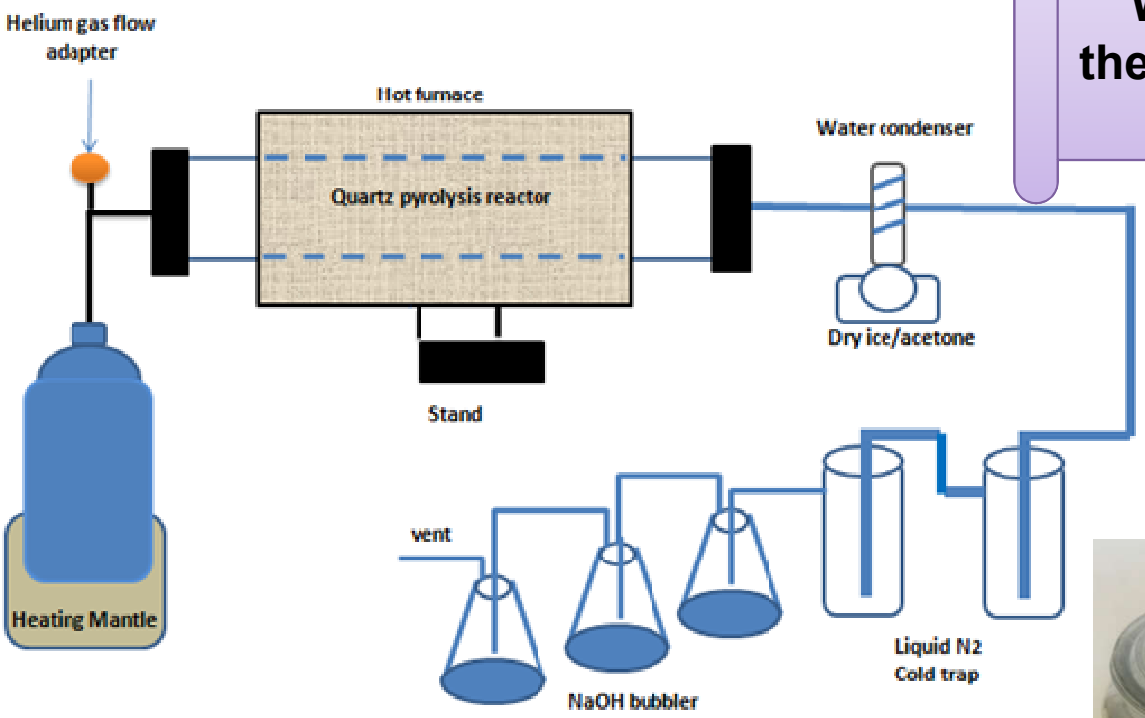
- **Elimination of US dependence upon foreign oil** in manufacturing critical military composites.
- **Replacement of epichlorohydrin** with GMA yields an environmentally benign synthesis.
- Production of green BPA and GMA will provide raw materials **for other high-value chemical products**.
- Finally, the proposed use of biomass waste **will not affect the nation's food supply**.
- Pyrolysis of lignin produces **many other valuable phenolic derivatives**.

Technical Advantages

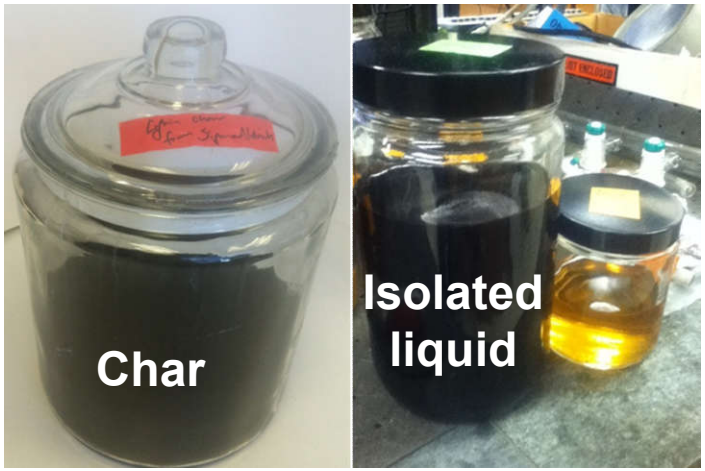
- **Solvent-free** synthesis of vinyl ester resin monomer.
- GVER from TBBPA and GMA forms only **pure, low molecular weight product**,
  - Good for VARTM processing
  - Reduces usage of reactive diluent (styrene)
  - Increases wetting of resins and decrease voids/bubbles in composites

Overview

Inspiration: Coal had been pyrolyzed to isolate phenol before WW-I and during WW-II, when there was a shortage of petroleum feed-stock

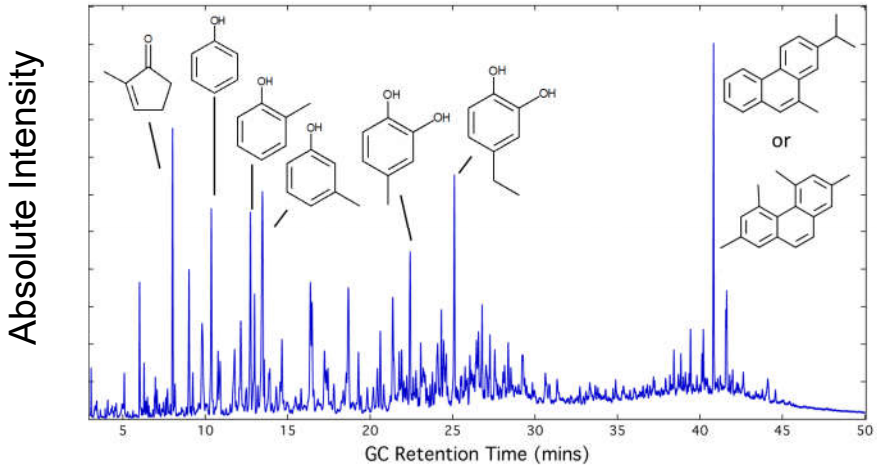


Purified product after solvent extraction

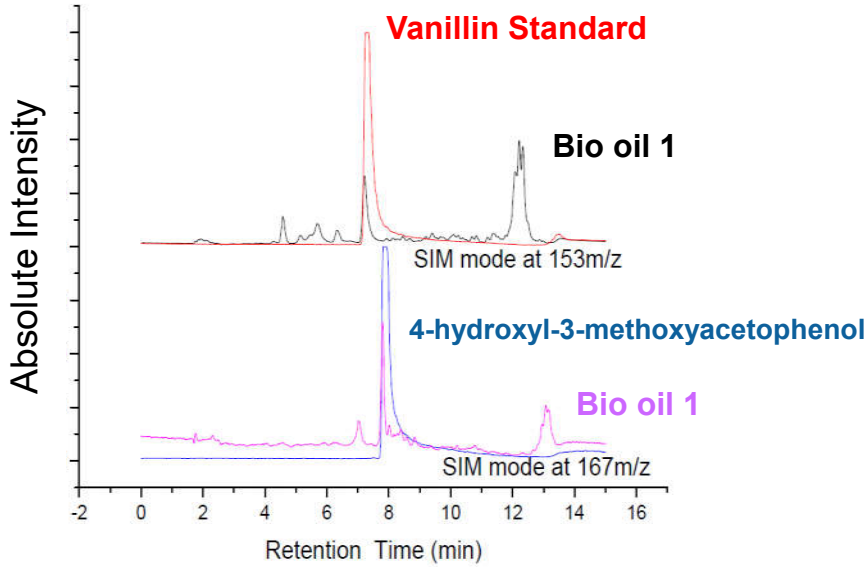


"Advanced Organic Chemistry"; Louis F. Fieser and Mary Fieser, New York, Reinhold Publishing Corporation, Chapman & Hall, Ltd., London, 1961, pp.640-645.

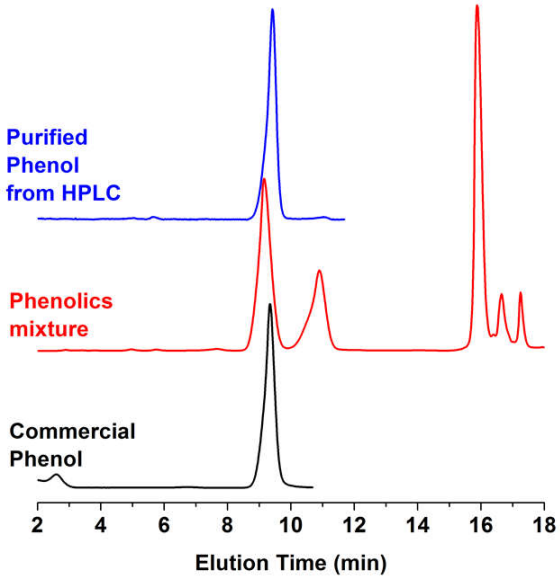
GC-MS Analysis

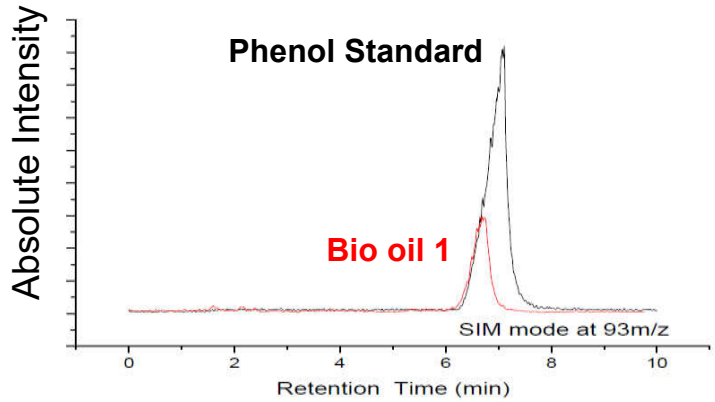


LC-MS Analysis/purification



HPLC purification





Phenols from lignin pyrolyzed bio-oil

Compound	wt %
phenol	3.90%
1,2-benzenediol	2.60%
2-methyl phenol	1.60%
3-methyl phenol	2.60%
4-methyl phenol	2.60%
3-methylbenzene-1,2-diol	3.20%
4-methylbenzene-1,2-diol	0.00%
2-ethylphenol	0.10%
2,5-dimethylphenol	0.80%
2,4-dimethylphenol	0.50%
3,5-dimethylphenol	0.40%
2,6-dimethylphenol	0.20%
3,4-dimethylphenol	0.40%
4-ethylbenzene-1,2-diol	1.80%
4-ethylphenol	0.90%
2,3,5-trimethyl phenol	0.10%
Total	21.70%

Current Interest

No	Lignin	Catalyst	Temperature (°C)	Products
1	Kraft lignin	Si-Al catalyst ZrO_2-Al_2O_3-FeO_x	200–350	phenols, methoxyphenol
2	Lignosulfonate	Ni/C, NiLa/C, NiPt/C, NiCu/C, NiPd/C, and NiCe/C	200	methoxyphenols
3	Corn stalk lignin	Pt/C, Pd/C, Ru/C	200–250	4-ethylphenol 4-ethylguaicol

No	Lignin	Approach	Catalyst	Products
4	Organosolv olive tree lignin	Microwave catalyzed (140 °C)	Ni, Pd, Pt, or Ru supported by Mesoporous Al-SBA-15	syringaldehyde, vanillin
5	Pinus radiata lignin	Ionic liquid catalyzed (250 °C)	1-butyl-3-methylimidazolium acesulfamate	methoxyphenols
6	Organosolv beech lignin	Ionic liquid catalyzed (100 °C)	1-ethyl-3-methylimidazolium-trifluoromethansulfonate with $Mn(NO_3)_2$	2,6-dimethoxy-1,4-benzoquinone

[i] T.Yoshikawa,T.Yagi, S. Shinohara et al., "Production of phenols from lignin via depolymerization and catalytic cracking," *Fuel Processing Technology*, 108, 69–75, **(2012)**

[ii] Q. Song, F.Wang, and J. Xu, "Hydrogenolysis of lignosulfonate into phenols over heterogeneous nickel catalysts," *Chemical Communications*, 48, 7019–77021, **(2012)**

[iii] Y. Ye, Y. Zhang, J. Fan, and J. Chang, "Selective production of 4-ethylphenolics from lignin via mild hydrolysis," *Bioresource Technology*, 118, 648–651, **(2012)**

[IV] X. Gu, K. Cheng, M. He, Y. Shi, Z. Li, "La-Modified SBA-15/H_2O_2 system for the microwave assisted oxidation of organosolv beech wood lignin" *Maderas.Ciencia y tecnología*, 14(1): 31-42 **(2012)**

[V] A. Pinkert, D. F. Goeke, K. N. Marsh, and S. Pang, "Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids," *Green Chemistry*, 13, 3124–3136, **(2011)**

[Vi] K. St¨ark, N. Taccardi, A. B¨osmann, and P. Wasserscheid, "Oxidative depolymerization of lignin in ionic liquids," *Chem-SusChem*, 3, 719–723, **(2010)**

Pyrolysis of Lignin from Various Sources

Mass balance between different phases	*Label*	*Vacuum Setup (SA)*	*Helium Setup*					
			SA	**TCI (alk)**	**TCI (dealk)**	**FRP-LLC**	**MSC-SL***	**MSC-BL***
Char (Solid) (wt %)		55.0	54.9	62.6	54.9	52.7	-	-
Phenolics (Liquid) (wt %)		7.1	12.6	11.5	3.2	17.9	-	-
(Gases)		37.9	32.5	25.9	41.9	29.4	-	-
Main phenolics identified								
Guaiacol	S1	31.4	10.3	9.48	2.84	4.35	5.13	6.59
2-methoxy-4-methylphenol	S3	9.40	1.95	1.34	0.45	0.65	0.46	0.64
Phenol	S4	6.30	9.41	20.2	4.59	3.97	13.4	10.7
4-ethyl-2-methoxyphenol	S5	6.83	1.85	0.91	0.40	0.58	0.68	0.71
2-methoxy-4-vinylphenol	S6	3.70	0.66	1.44	0.00	0.22	0.22	0.62
2,6-dimethoxyphenol	S7	0.53	0.57	0.25	0.15	0.64	1.50	0
vanillin	S8	0.87	0.03	0.92	0.89	0.83	2.07	0
4-hydroxy-3-methoxyacetaphenone	S9	0.63	0.55	0.61	0.46	0.37	2.71	0.39
catechol	S10	0.10	11.7	2.27	2.02	4.15	4.93	4.82
Homovanillic acid	S11	1.40	0.50	0.43	0.22	0.18	5.36	0

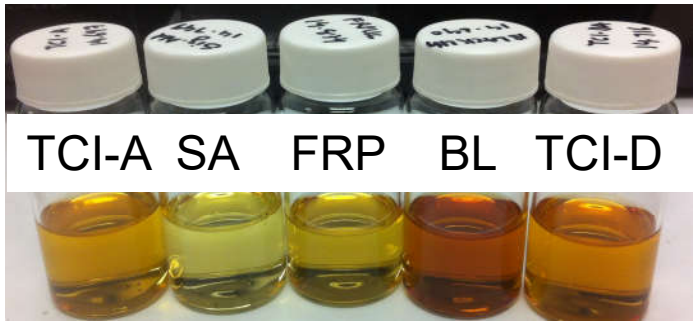
Lignin (left vial) strong liquor, (center vial) weak liquor and (right vial) black liquor obtained from Maine Seed Company

* *Waiting for Mass Balance Data*

Pyrolysis of Lignin Using Microwave Irradiation

Phenolics	*Lignin Materials*				
	SA	**TCI (alk)**	**TCI (dealk)**	**FRP-LLC**	**MSC-BL***
Guaiacol	11.4	5.12	8.88	1.18	3.58
2-methoxy-4-methylphenol	4.74	1.42	2.88	0.00	0.81
Phenol	1.08	1.47	1.58	3.95	0.83
4-ethyl-2-methoxyphenol	8.27	2.55	3.87	1.35	2.83
2-methoxy-4-vinylphenol	0.00	0.00	0.00	0.00	0.00
2,6-dimethoxyphenol	0.00	0.69	1.61	3.52	8.43
vanillin	0.00	0.00	0.00	0.00	0.00
4-hydroxy-3-methoxyacetaphenone	0.00	0.00	0.00	0.00	0.00
catechol	1.69	4.44	3.76	0.00	1.46
Homovanillic acid	5.93	0.00	0.00	0.00	0.00

Microwave Reactor



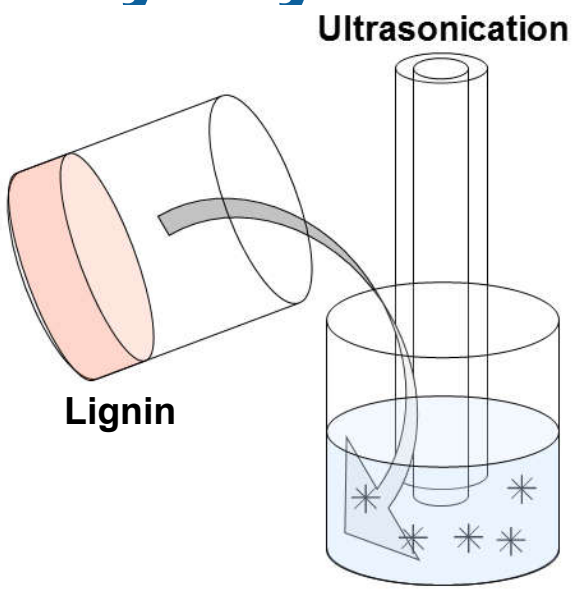
Microwave based depolymerization produced significant amount of 2-methyl resorcinol and 4-methyl resorcinol.

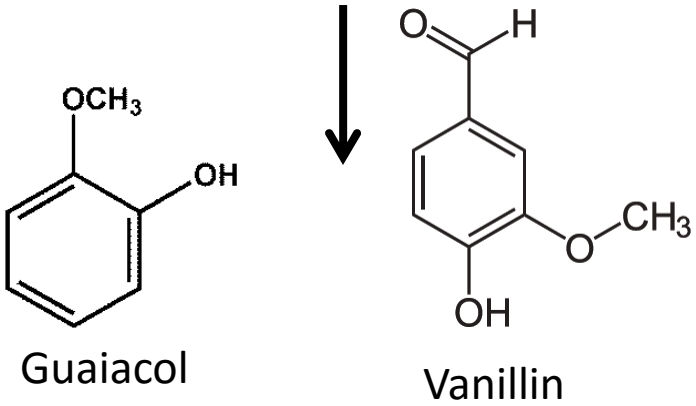
Pyrolysis of Lignin in presence of MOF

Phenolics	*Sigma-Aldrich lignin*			
	Without Catalyst	GO-Cu MOF	Ca-Al MOF	Iron Oxide NP
Guaiacol	10.3	2.82	4.81	12.7
2-methoxy-4-methylphenol	1.95	0.63	0.35	4.91
Phenol	9.41	10.7	3.83	5.16
4-ethyl-2-methoxyphenol	1.85	0.39	1.31	5.52
2-methoxy-4-vinylphenol	0.66	0.14	0.18	1.74
2,6-dimethoxyphenol	0.57	0	0	0.76
vanillin	0.03	0	0	0.80
4-hydroxy-3-methoxyacetaphenone	0.55	0.18	0.34	1.01
catechol	11.7	10.2	8.64	8.21
Homovanillic acid	0.50	0	0.28	2.47

- MOFs and Nanoparticles are considered excellent heterogeneous catalyst due to their unique properties.
- Graphene-Oxide based MOF has exhibited great selectivity towards cleaving of methoxy and converting it to hydroxy group as a result, high amount of phenol and catechol observed compared with guaiacol.

Pyrolysis of Lignin using Sonication





Compound name	Retention time (min)	% from the total
Guaiacol	27.917	5.65
2-methoxy-4-methylphenol	Not Detected	0.00
Phenol + Methylphenol	Not Detected	0.00
4-ethyl-2-methoxyphenol	Not Detected	0.00
2-methoxy-4-vinylphenol	Not Detected	0.00
2,6-dimethoxyphenol	Not Detected	0.00
Vanillin	39.149	17.1
4-hydroxy-3-methoxyacetaphenone	Not Detected	0.00
Catechol	Not Detected	0.00
Homovanillic acid	Not Detected	0.00

- Base catalyzed depolymerization of lignin can be assisted through ultrasonication.
- The temperature of the lignin dispersion was maintained at 23 °C using a water bath.

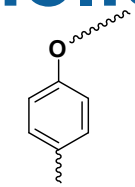
Oxidation of Lignin Using Potassium Permanganate

Phenolics	Types of lignin		
	Sigma-Aldrich	TCI (Alkaline)	TCI (Dealkaline)
Guaiacol	6.81	0.00	0.00
2-methoxy-4-methylphenol	0.00	0.00	0.00
Phenol	0.00	0.00	0.00
4-ethyl-2-methoxyphenol	0.44	0.00	0.00
2-methoxy-4-vinylphenol	1.40	0.00	0.00
2,6-dimethoxyphenol	0.00	0.00	0.00
Vanillin	10.4	32.0	17.7
4-hydroxy-3-methoxyacetaphenone	3.09	8.03	2.90
Catechol	0.00	0.00	0.00
Homovanillic acid	5.18	0.00	10.9

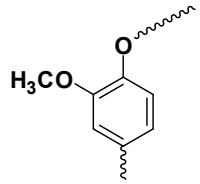
The oxidation of lignin using potassium permanganate produced vanillin dominantly.

Various Phenolics Identified

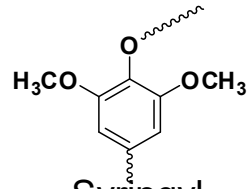
Monomeric Units of Lignin



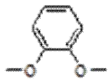
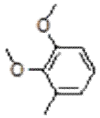
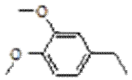
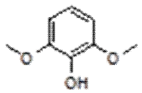
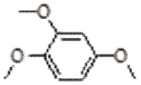
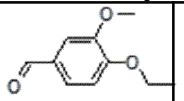
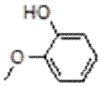
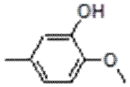
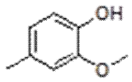
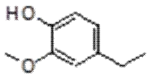
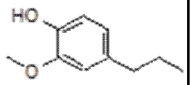
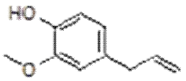
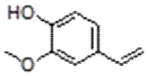
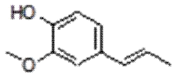
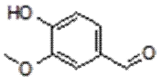
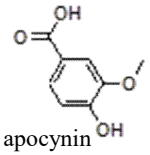
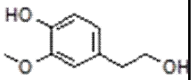
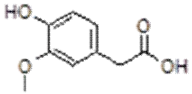
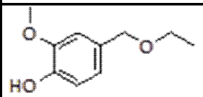
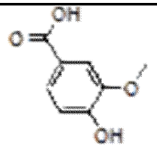
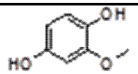
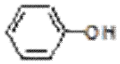
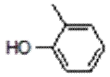
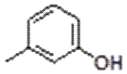
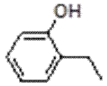
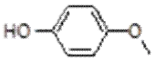
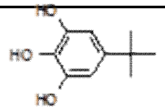
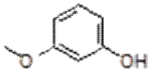
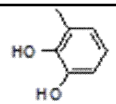
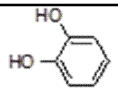
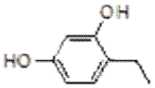
p-hydroxyphenyl



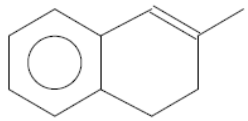
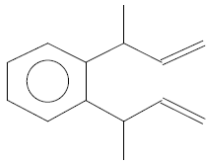
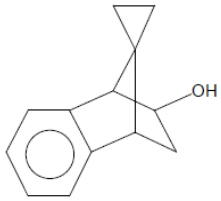
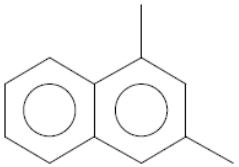
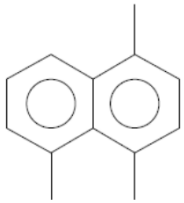
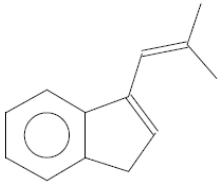
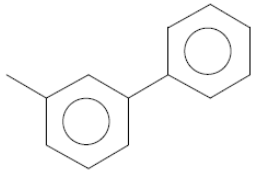
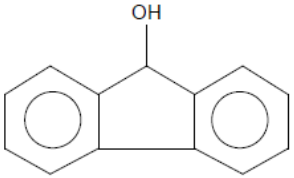
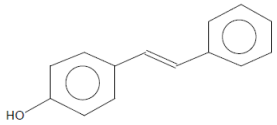
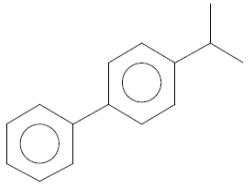
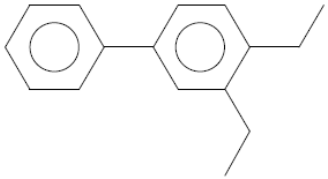
Guaiacyl



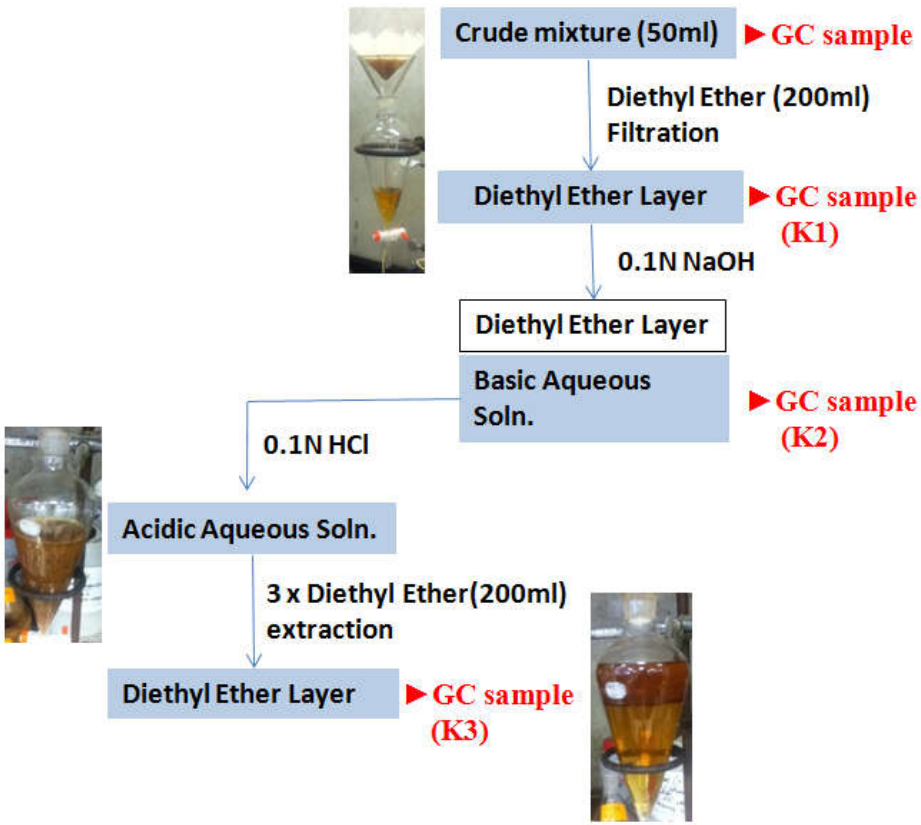
Syringyl

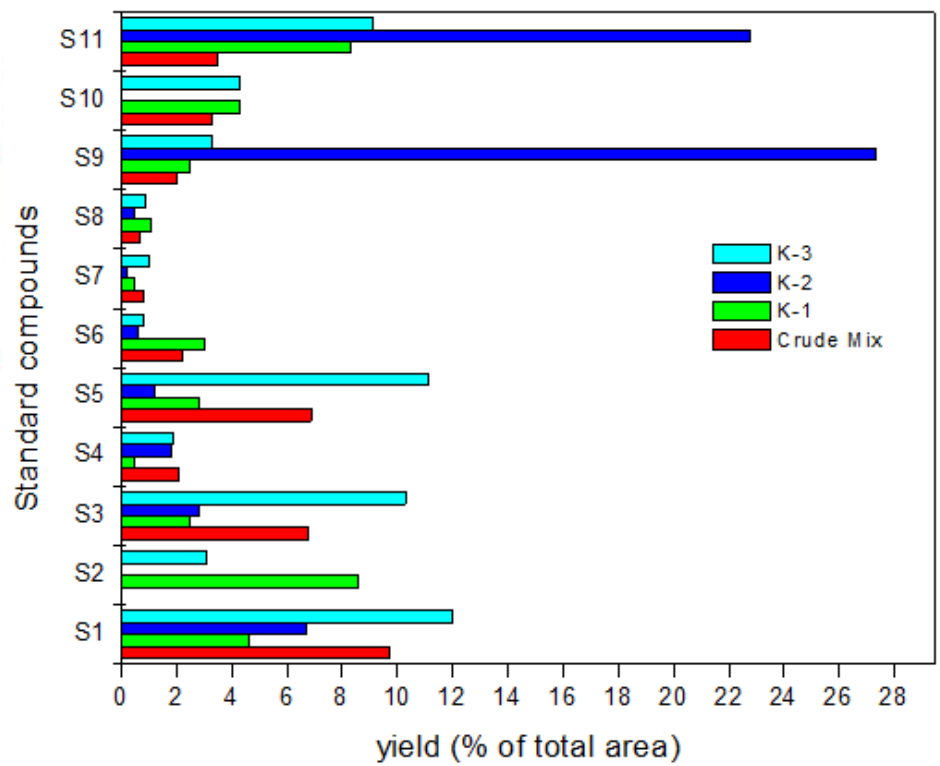
Syringol and Methoxy Containing Aromatics	 1,2-dimethoxy benzene (Veratrole) *25.380*	 2,3-Dimethoxy-toluene *27.416*	 1,2-dimethoxy, 4-ethyl benzene *32.104*	 2,6-dimethoxy-phenol *35.477*	 1,2,4-trimethoxy benzene *36.757*	 4-ethoxy-3-anisaldehyde *41.433*		
Guaiacol Derivatives	 Guaiacol *28.471*	2-methoxy-3-methylphenol *28.654*	 2-methoxy-5-methylphenol *30.032*	 2-methoxy-4-methylphenol *30.289*	 4-ethyl guaiacol *31.376*	 4-propyl guaiacol *33.023*	 4-allyl guaiacol *33.965*	 4-vinyl guaiacol *34.388*
	 4-propenyl-guaiacol *35.325*	 Vanillin *39.559*	 apocynin *40.569*	 Homovanilyl alcohol *43.228*	 Homovanillic acid *44.853*	 Phenol, 4-(ethoxymethyl)-2-methoxy *45.016*	 p-vanilic acid *52.182*	 2-Methoxyhydro quinone *27.253*
Phenol Derivatives	 Phenol *30.834*	 2 methyl phenol *32.563*	 3 methyl phenol *32.693*	 2-ethyl phenol *34.110*	 Mequinol *37.421*	 5-tert-butylpyrogallol *37.602*	 3-methoxy phenol *38.038*	 1,2-dihydroxy, 3-methyl benz-ene(*40.956*)
	 Catechol *41.523*	 1,3-dihydroxy,4-ethylbenzene *43.469*						

Possible Other Aromatic Compounds Identified During GC-MS

 Naphthalene, 1,2-dihydro-3-methyl- *24.129*	 Benzene, 1,2-bis(1-buten-3-yl)- *25.440*	 Spiro(tricyclo[6.2.1.0(2,7)]undeca -2,4,6-triene)-7,1'-cyclopropane *27.392*	 Naphthalene, 1,3-dimethyl- *29.706*	 Naphthalene, 1,4,5-trimethyl- *32.376*
 3-(2-Methyl-propenyl)-1H-indene *32.956*	 1,1'-Biphenyl, 3-methyl- *34.721*	 9H-Fluoren-9-ol *36.014*	 Phenol, 4-(2-phenylethenyl)- *37.814*	 1,1'-Biphenyl, 4-(1-methylethyl)- *37.893*
 1,1'-Biphenyl, 3,4-diethyl- *39.621*				

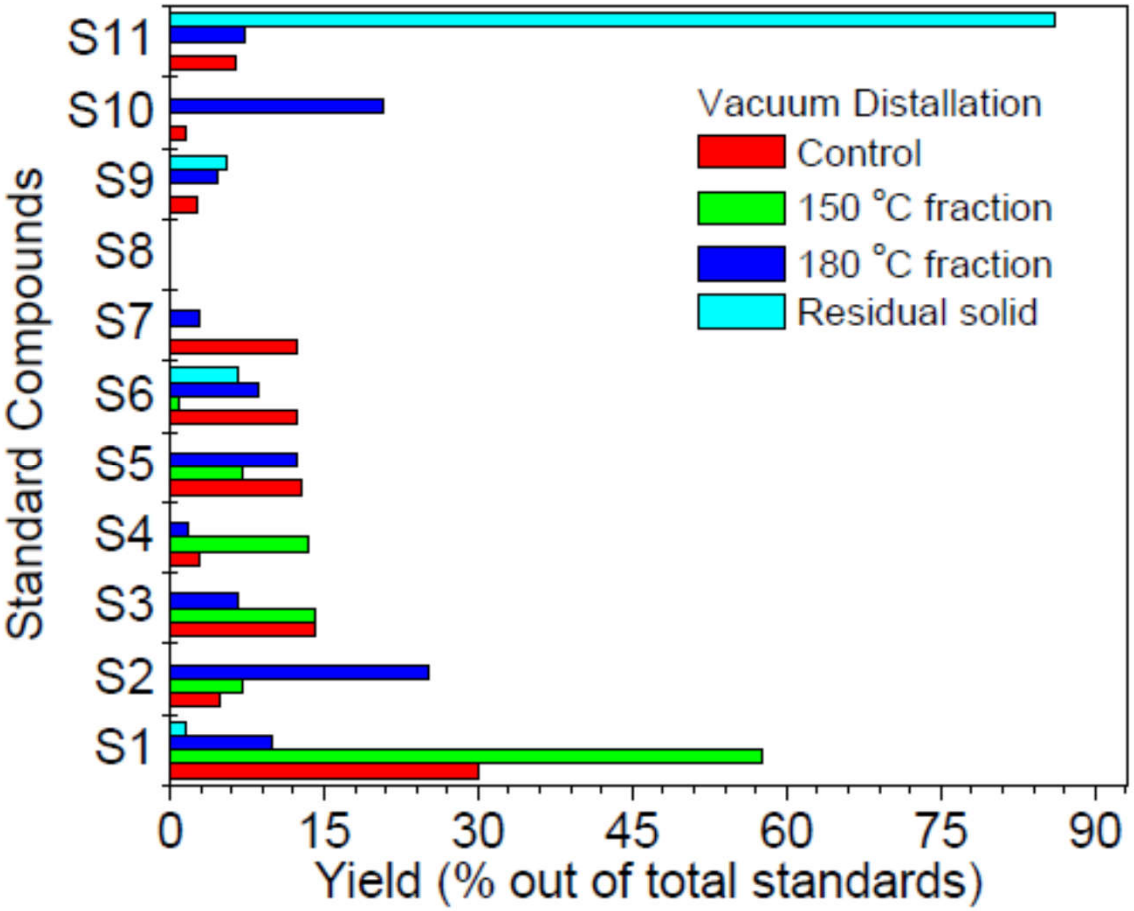
Purification of Pyrolysate-I Using Solvent Extraction



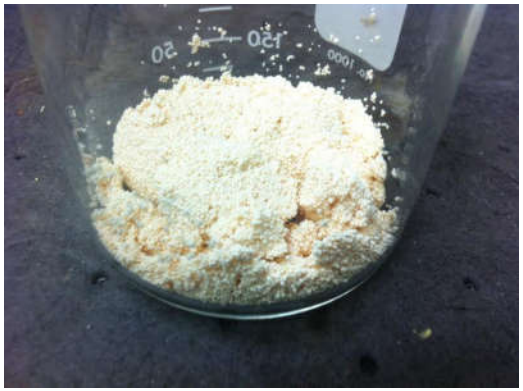


Purification of Pyrolysate-II by Fractional Vacuum Distillation

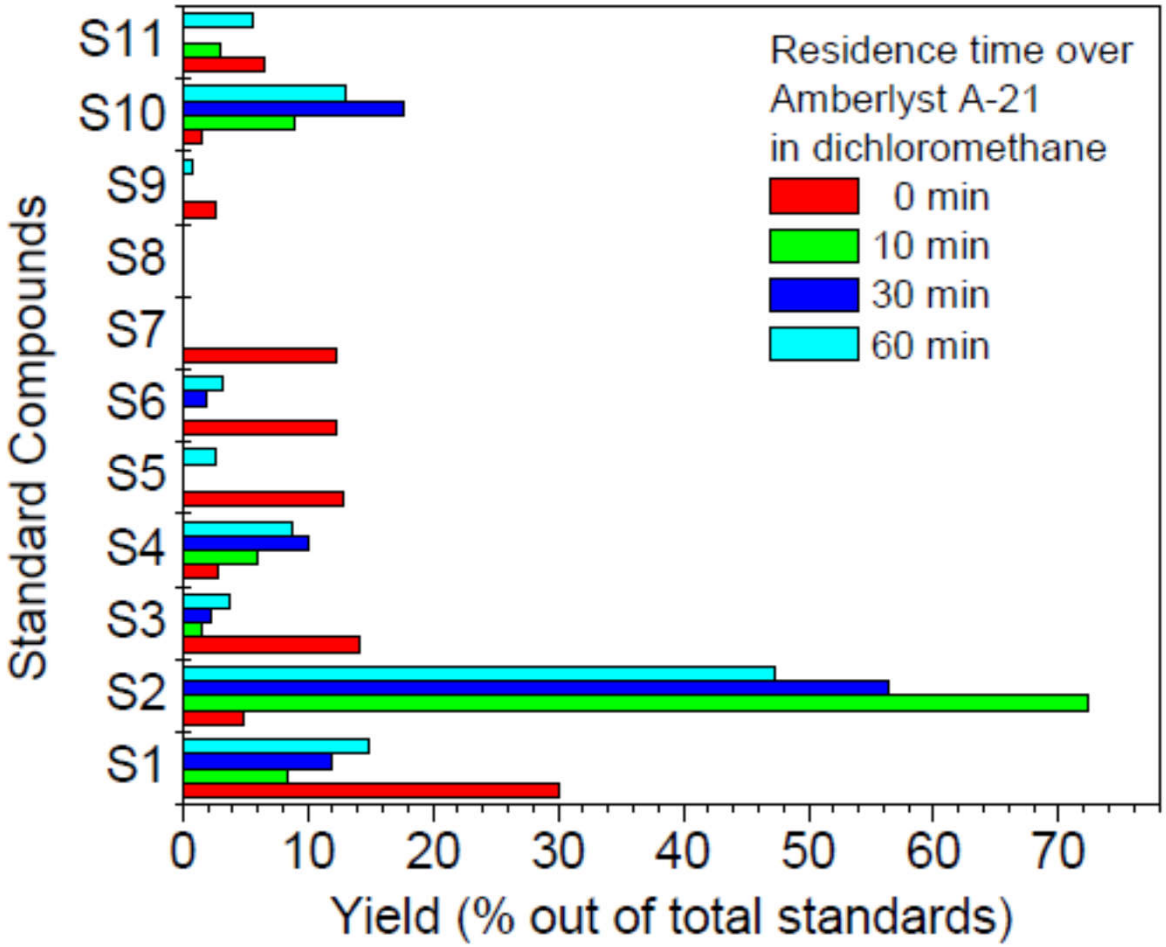
Typical Distillation Setup



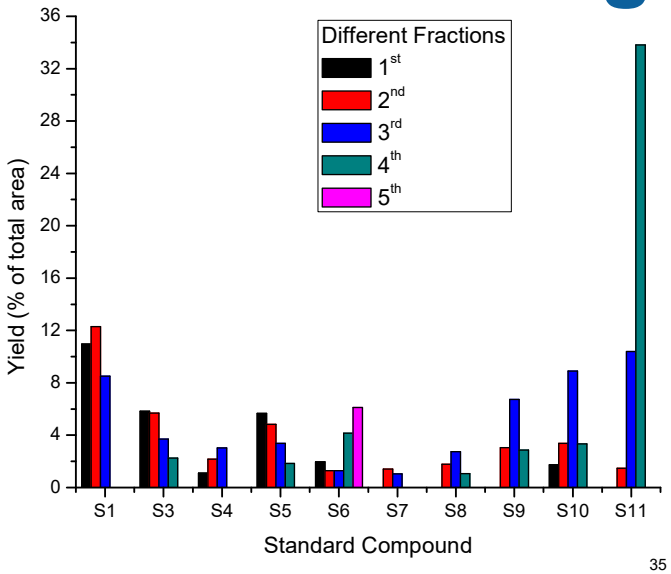
Purification of Pyrolysate III by Resin Treatment

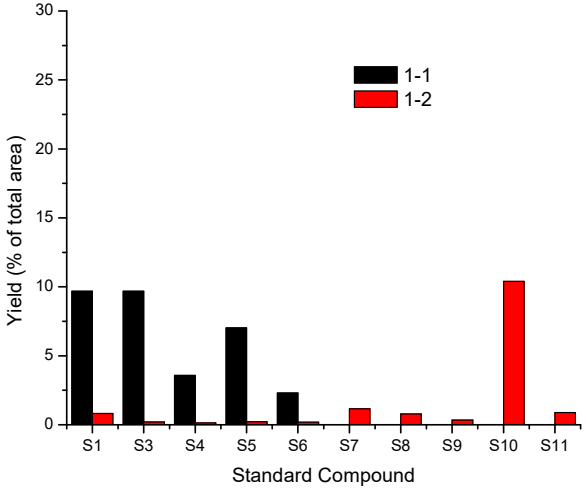


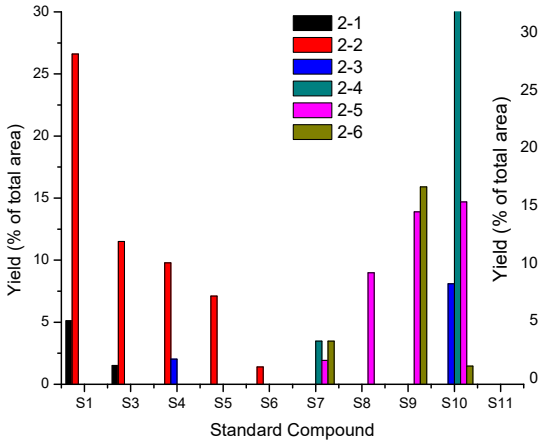
Amberlyst A21 free amine resin, which can selectively separate phenol.

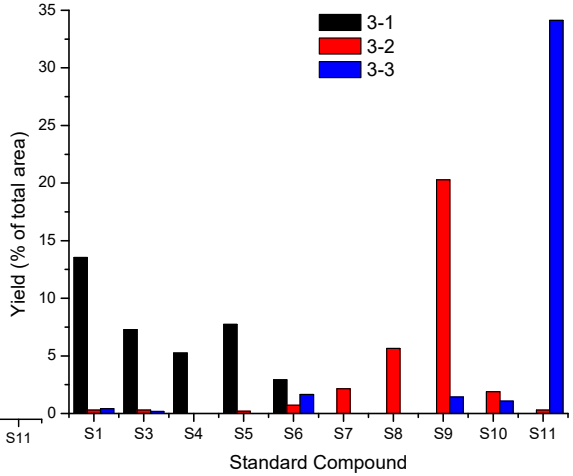


Purification of Pyrolysate IV by Column Chromatography

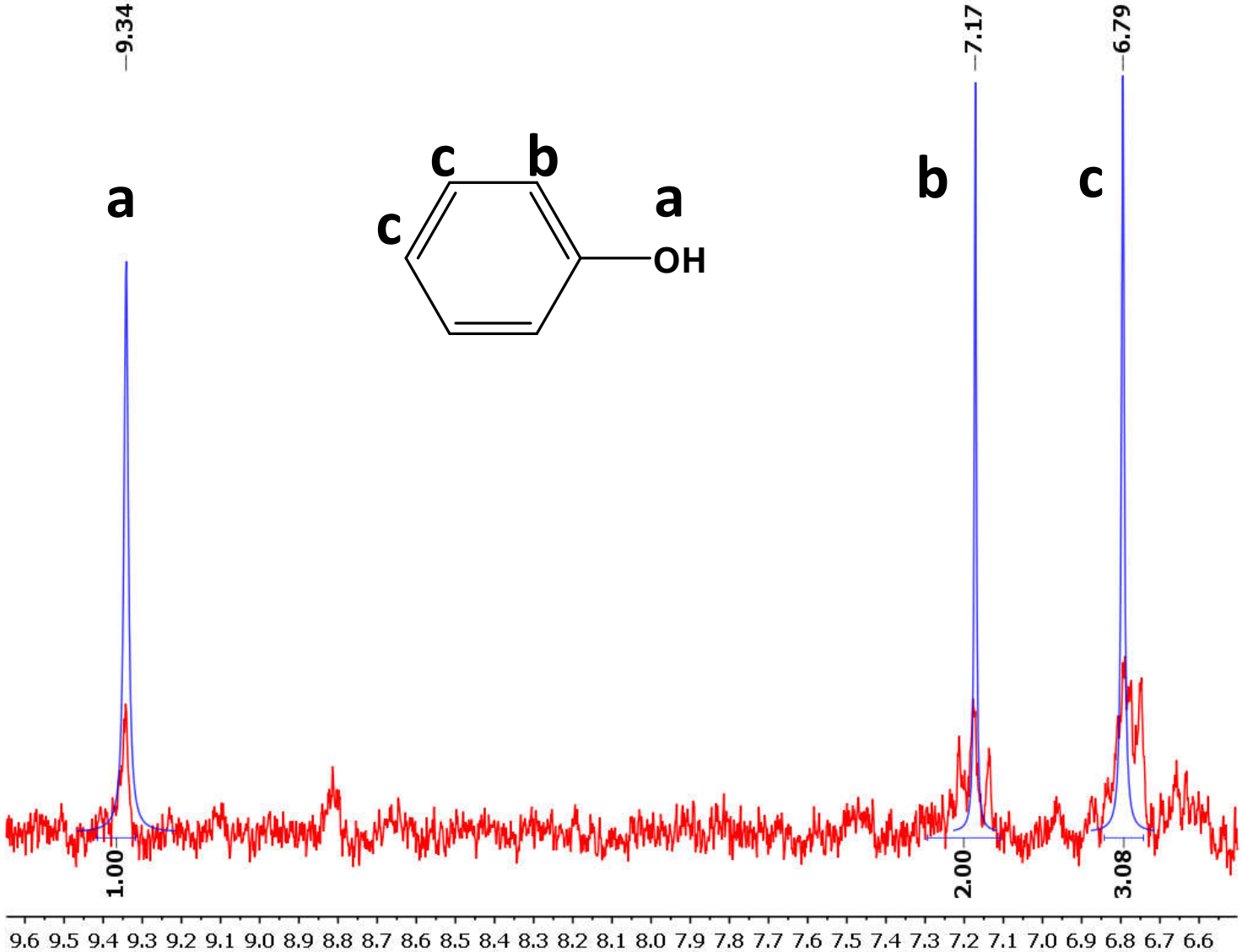






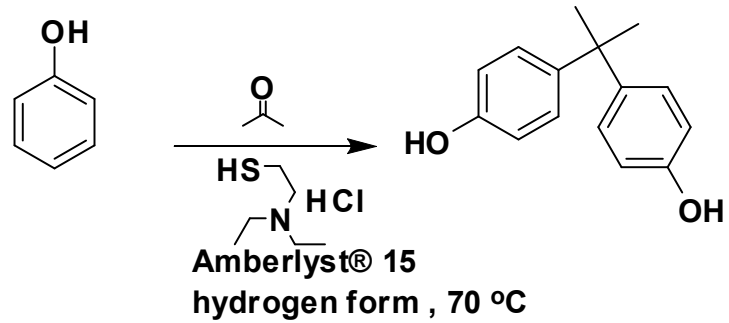


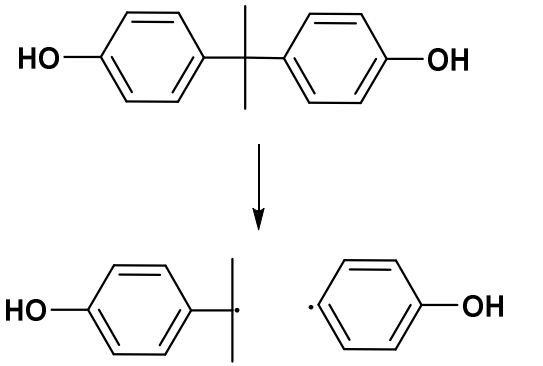
^{1}H NMR: Identification of the Green Phenol



Synthesis of BPA

- In stoichiometry high amount of phenol and very low amount of acetone is required.
- Higher the purity of the phenol, better will be conversion.





Exact Mass: 135.08 Exact Mass: 93.03

- The mass spectra of peak at 7.885 and 10.663 confirmed presence of phenol and p-isopropyl phenol respectively.
- The GC-data confirmed that we have successfully synthesized BPA starting from lignin.

- **Submitted to ACS Sustainable Chem.& Eng. Shah et al. Green Bisphenol A: A high valued Building Block Isolated from Lignin Biowaste.**

Applications of Green Phenolics

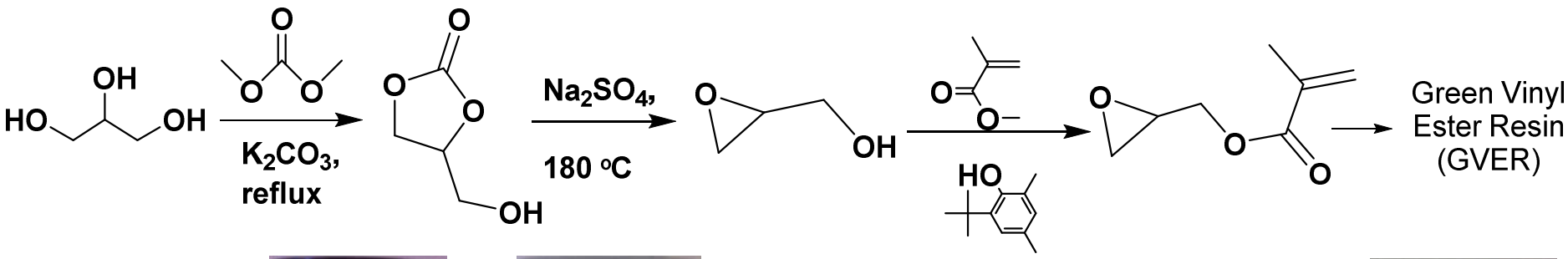
- **Various Resin Materials**. The isolated phenolic can be used as a building block for synthesis of different types of resin materials, which can be used for defense purposes. Such as benzoxazine resin can be made from vanillin, and other resins can be made from bisphenol A.

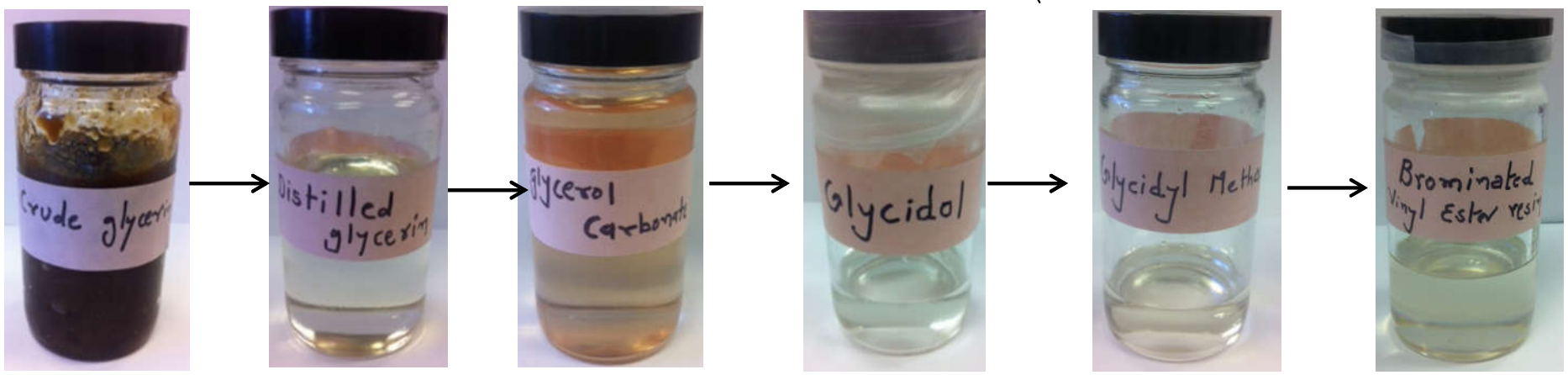
- **Food Flavoring Agents**. Several phenolics have large number of applications as food flavoring agents; such as, vanillin, syringol, syringadehyde, 2-methoxy-4-vinylphenol, etc.

- **Precursor for Pharma Industries**. Many phenolics can be used as an important precursor in many pharma industry. Such as, Guaifenesin (Robitussin®) from guaiacol and many more. So, by several simple organic reactions one pyrolyzed material can be easily converted to more economical products.

C. F. H. Allen and G. W. Leubner, "Syringic aldehyde", *Org. Synth.; Coll.* 4: 866 **(1963)**

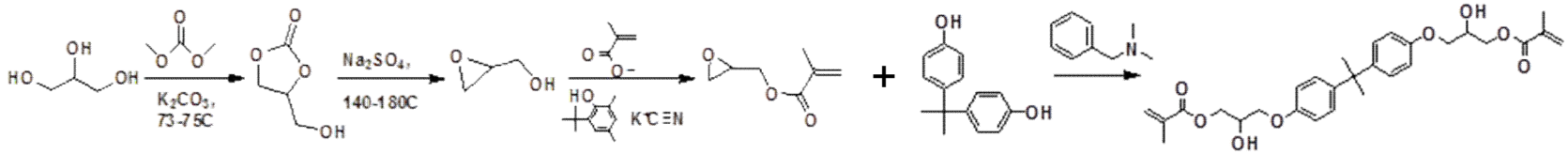
Green Vinyl Ester Resin from Biodiesel Glycerin



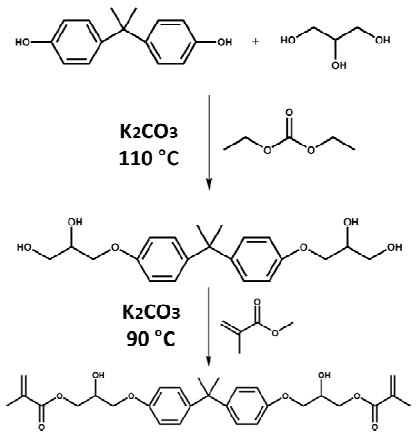


Crude Glycerin → *Distilled Glycerin* → *Glycerol Carbonate* → *Glycidol* → *Glycidyl Methacrylate* → *Green Vinyl Ester Resin*

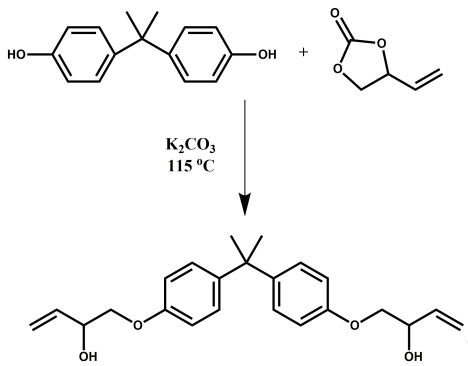
Results-IP



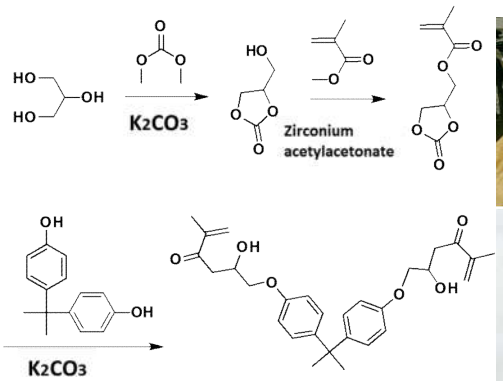
Y. Lee, Vinyl Ester Resin (VER) from Renewable Resources, FMI ID 2076, Nov. 2012
Shah and Lee "Environmentally benign synthesis of VER from biowaste glycerin" RSC AdvancesMay 2015



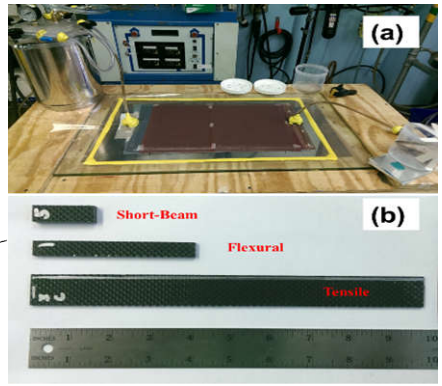
Y. Lee , Methods of making BHDE & VER UML 2015-038-01 (atty.Ref.no.4724.005PRV), US Application no.62/387,443



Y. Lee, Resins of VHER,UML # 2015-041(atty.Ref.no.4724.007PRV) US Application no.62/303,724



Y. Lee and P. N. Shah, GVER from GCMA and Bisphenol A, UML # 2016-020.



Y.Lee, P.N.Shah, C.Hensen, S.Dev Green Composites UML # 2016-008

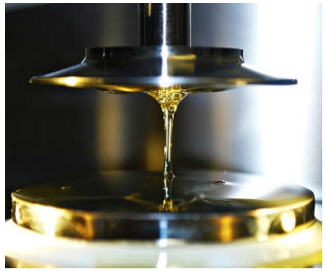
Resin compositions (Non-Brominated & Brominated)

Composition			Non-Brominated	Brominated
%CVER	%GVER	%Styrene		
100	0	40	CVER	CVER
80	20	40	FVER 1	FVER 1
50	50	40	FVER 2	FVER 2
20	80	40	FVER 3	FVER 3
0	100	40	GVER 1	GVER 1
0	100	30	GVER 2	GVER 2
0	100	20	GVER 3	GVER 3

Characterization tests were conducted on neat resin specimens

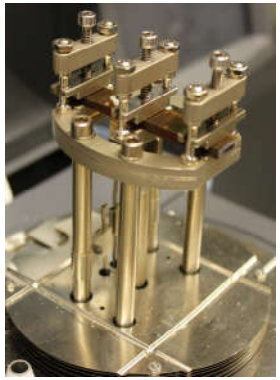
- Resin synthesis was scaled-up and coupons were fabricated by mixing green resin with Ashland's commercial resin in different compositions.

Rheology



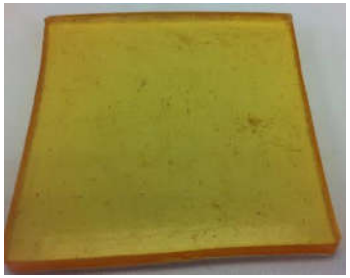
1) Gel Time
2) Zero Shear Viscosity

Dynamic Mechanical Analysis



1) Storage Modulus
2) Glass Transition temperature (T_g)

Flammability



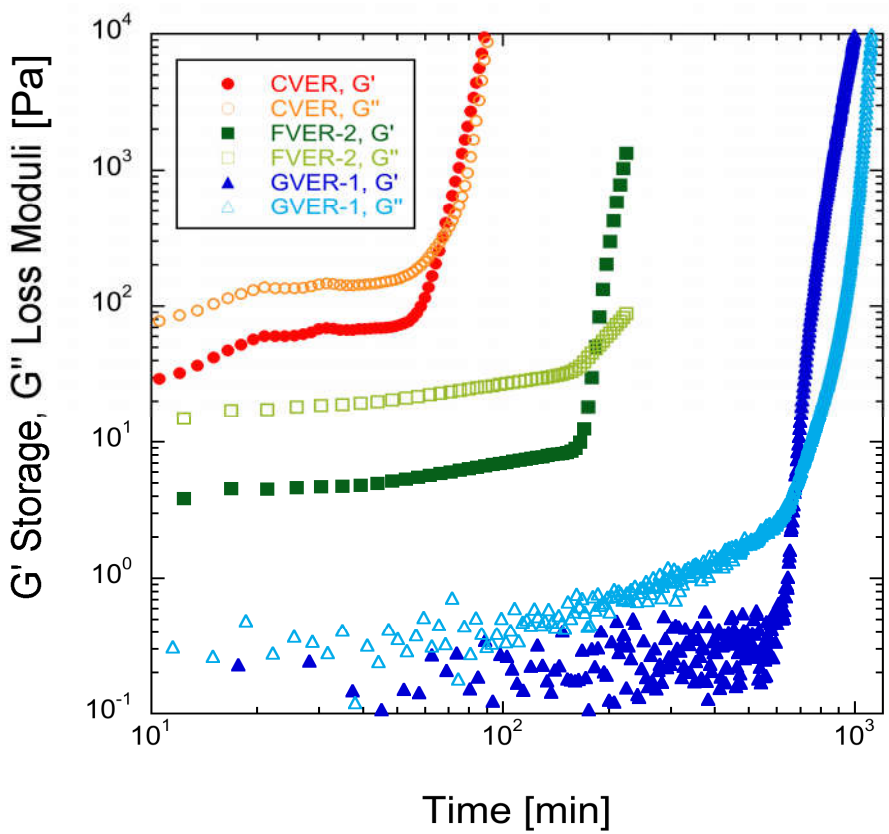
1) Heat Release Rate
2) Smoke Density

Rheology Image Source: www.sheffield.ac.uk

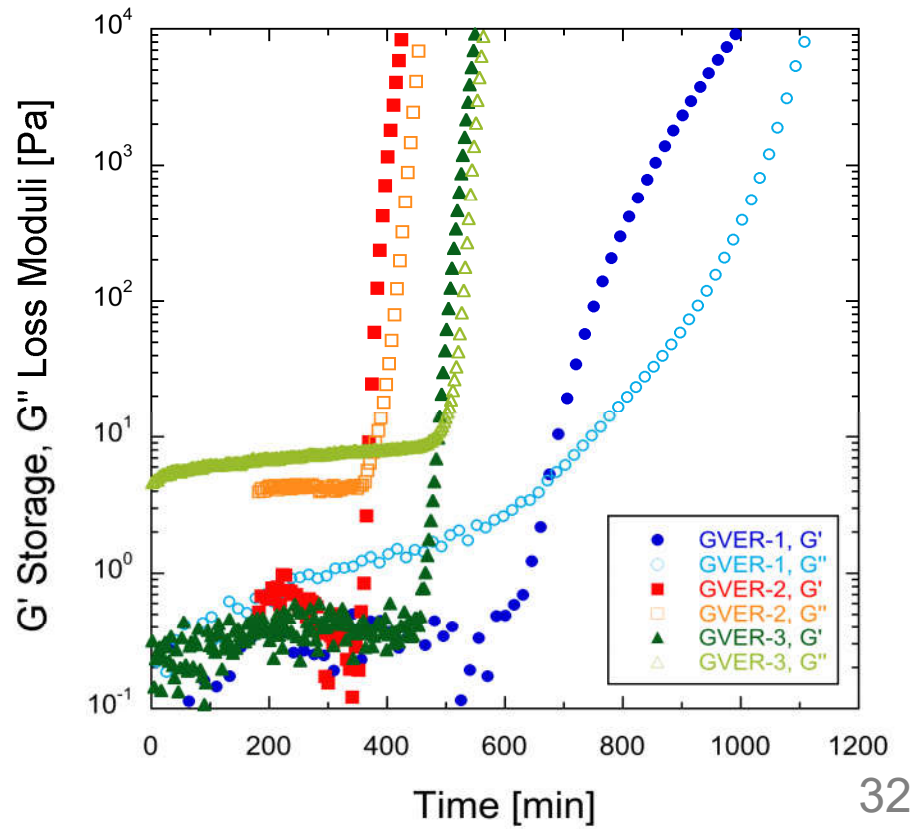
Chemo-Rheological Studies

- Gel time is defined as the crossover point between the storage and loss moduli
- Longer gel time leads to improved permeability of resin through fabric preform and a higher fiber volume fraction which in turn improves mechanical properties
- 3 resins(CVER,FVER-2 & GVER-1) were characterized for their processing time before gelation
- Zero shear viscosities: CVER → 458 cP, FVER-2 → 245 cP, GVER-1 → 65 cP

Impact of varying GVER content



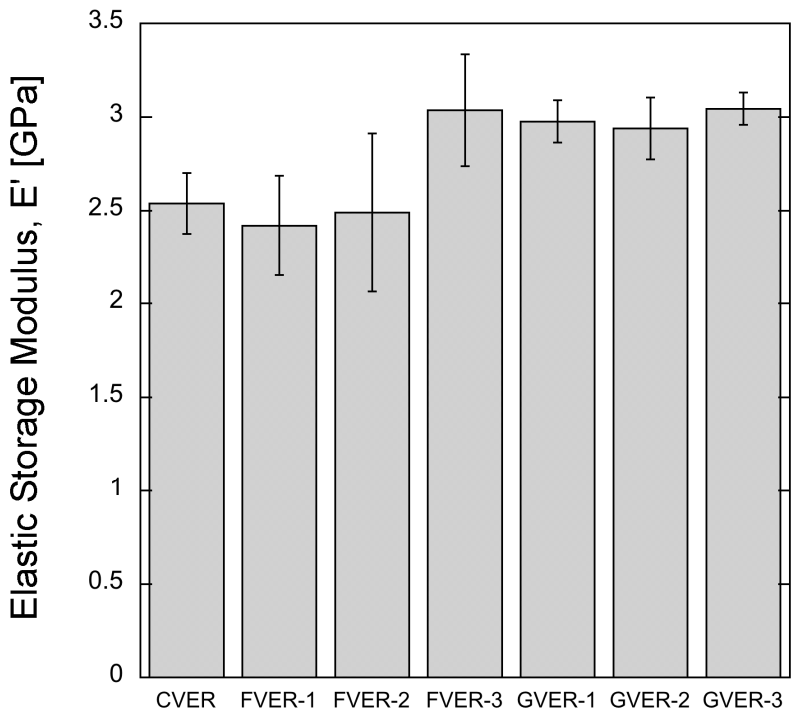
Impact of varying styrene content in GVER formulations



DMA (Non-Brominated)

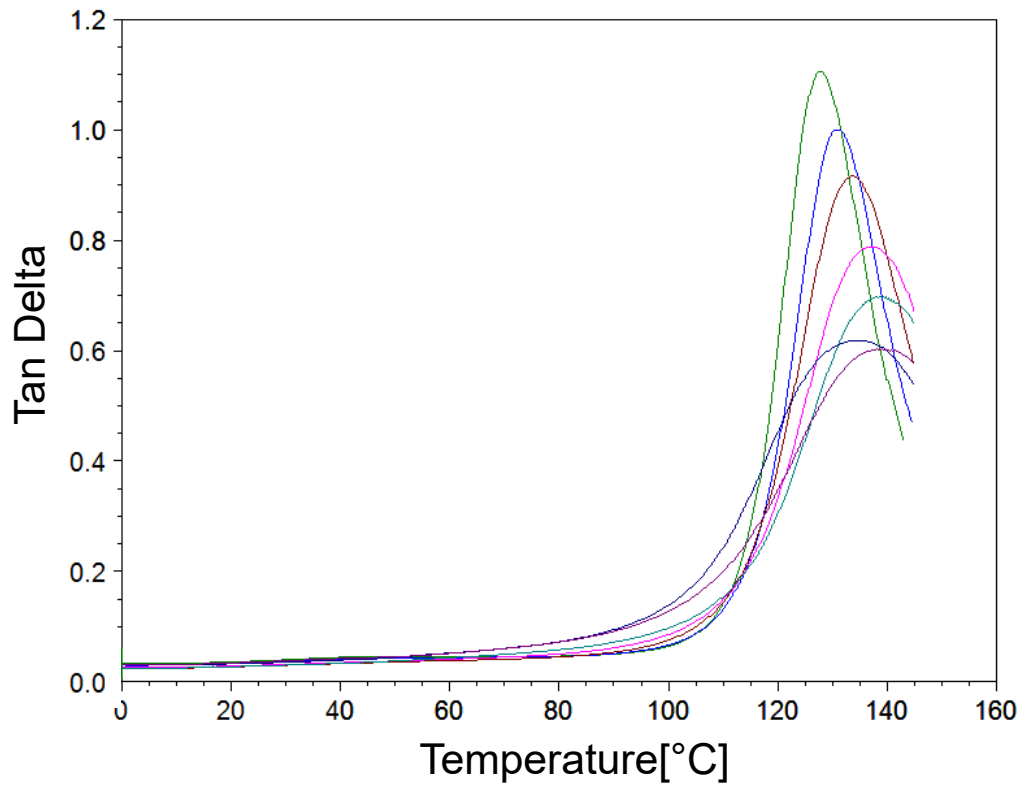
- Two key parameters of interest
  - **Storage Modulus –** Higher value indicates better resistance to deformation
  - **Glass Transition Temperature (T_g)** – Indicates higher cross link density

Storage modulus at room temperature



Increasing the content of bio-derived GVER leads to a higher storage modulus

Tan delta peaks representative of [T_g]



Increasing the content of bio-derived GVER increases the T_g

DMA (Brominated)

- Two key parameters of interest
  - **Storage Modulus –** Higher value indicates better resistance to deformation
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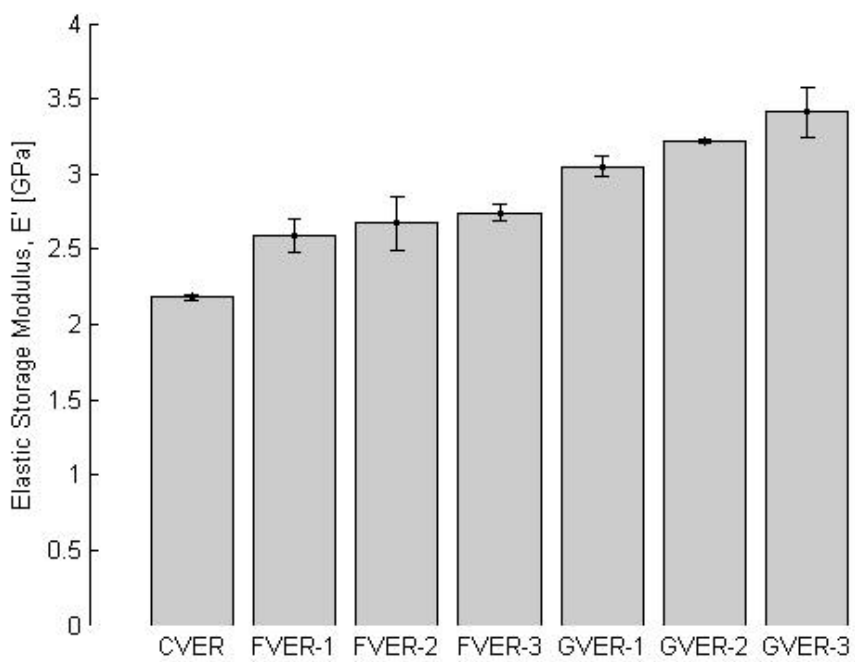
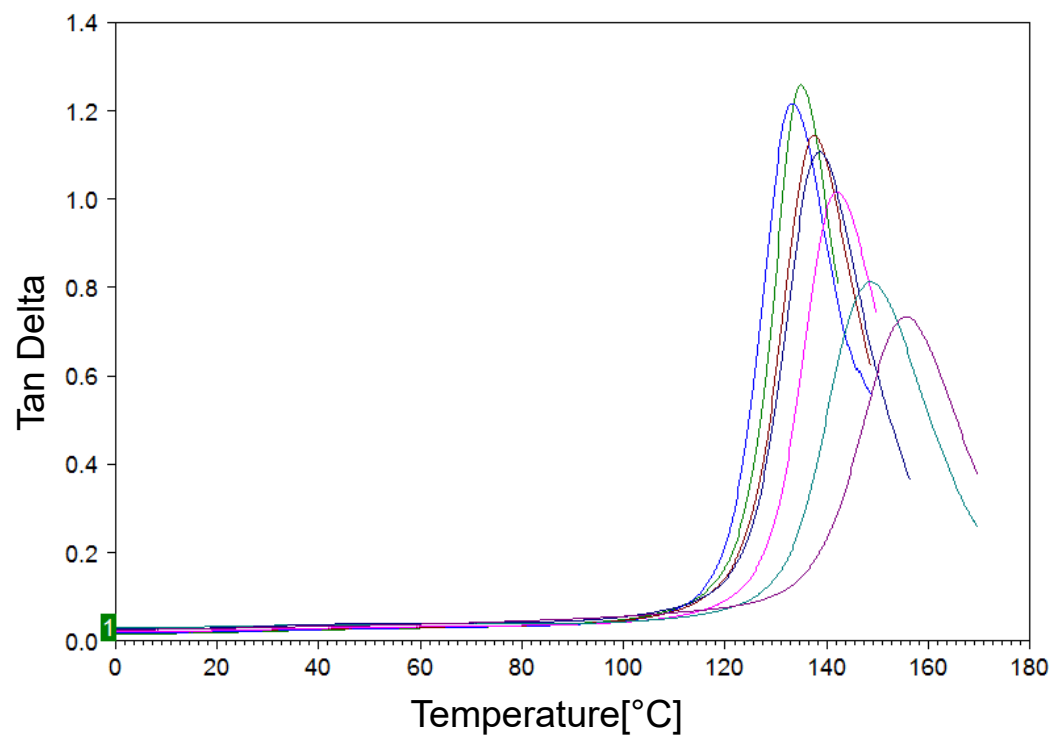
Storage modulus at room temperature



Tan delta peaks representative of [T_g]

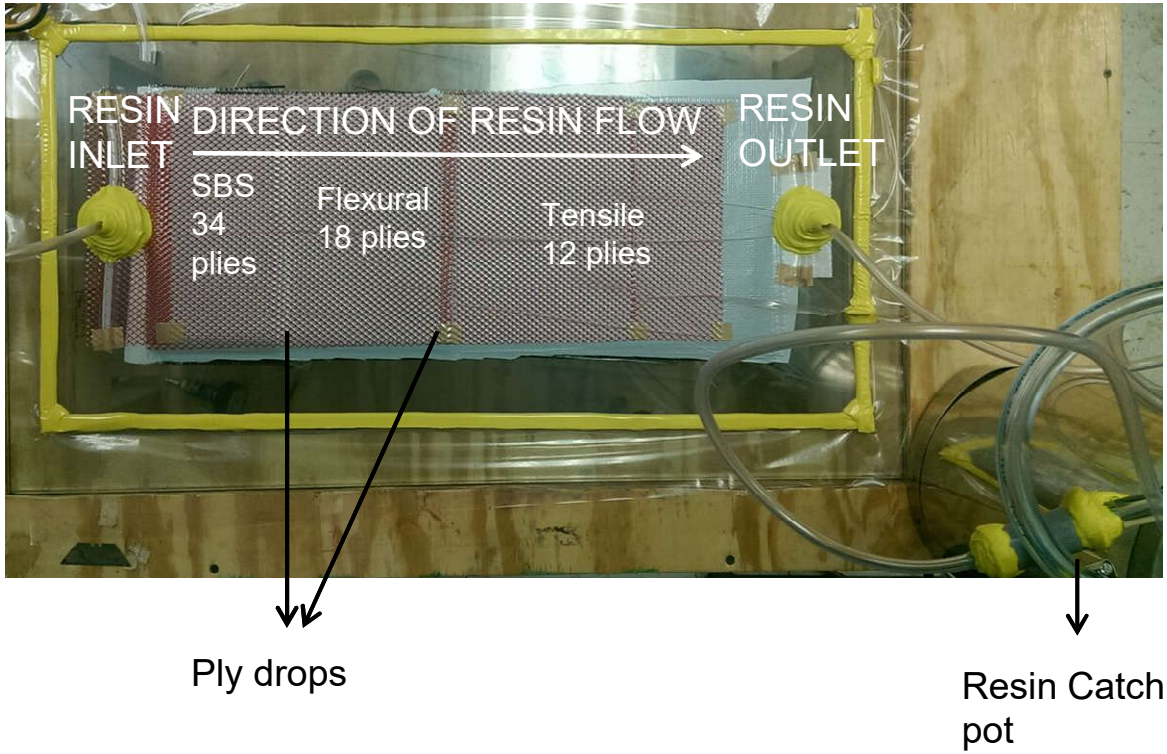


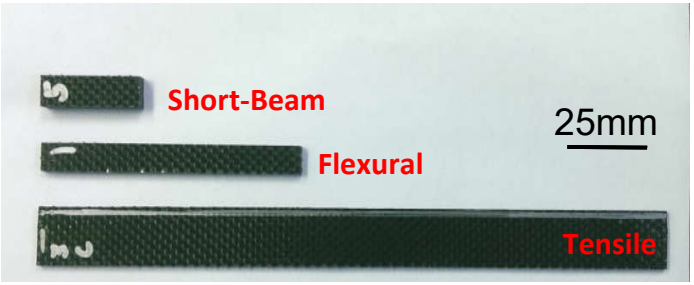
Increasing the content of bio-derived GVER leads to a higher storage modulus

Increasing the content of bio-derived GVER increases the T_g

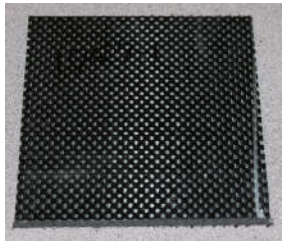
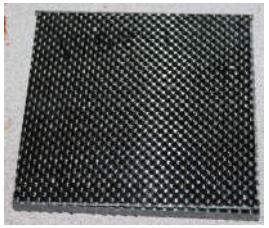
Fabrication of composite specimens

- Composites manufactured using 7 non brominated and 7 brominated GVER compositions
- Samples manufactured to ASTM standards (D3039, D7264, D2344) for tensile, flexural and short beam shear strength, respectively

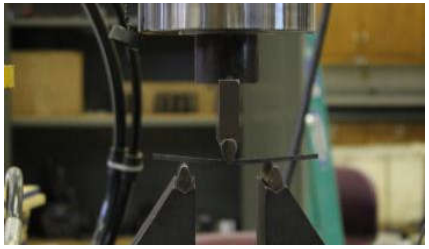




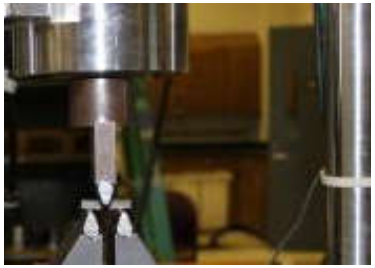
Mechanical and Flammability Testing

Material ID Material Description	UMass Lowell				NAVAIR	
	1742 Brominated VER	1750 VER	1757 'C' Fabric Reinforced / Brominated VER	1758 'C' Fabric Reinforced VER	1760 'C' Fabric Reinforced VER	1763 'C' Fabric Reinforced Brominated VER
Photo						

Setup for tensile testing of VER and Br-VER composite.

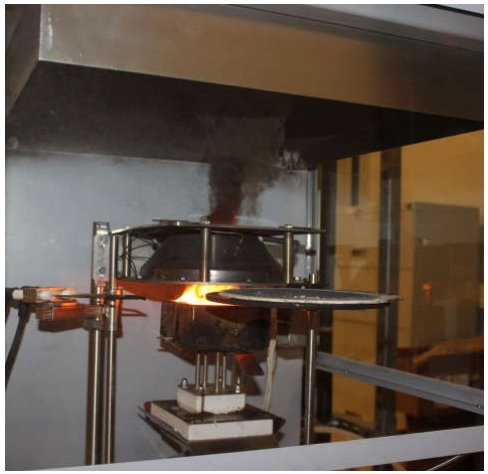


Setup for flexure testing of VER and Br-VER specimens.



Short Beam Strength Testing

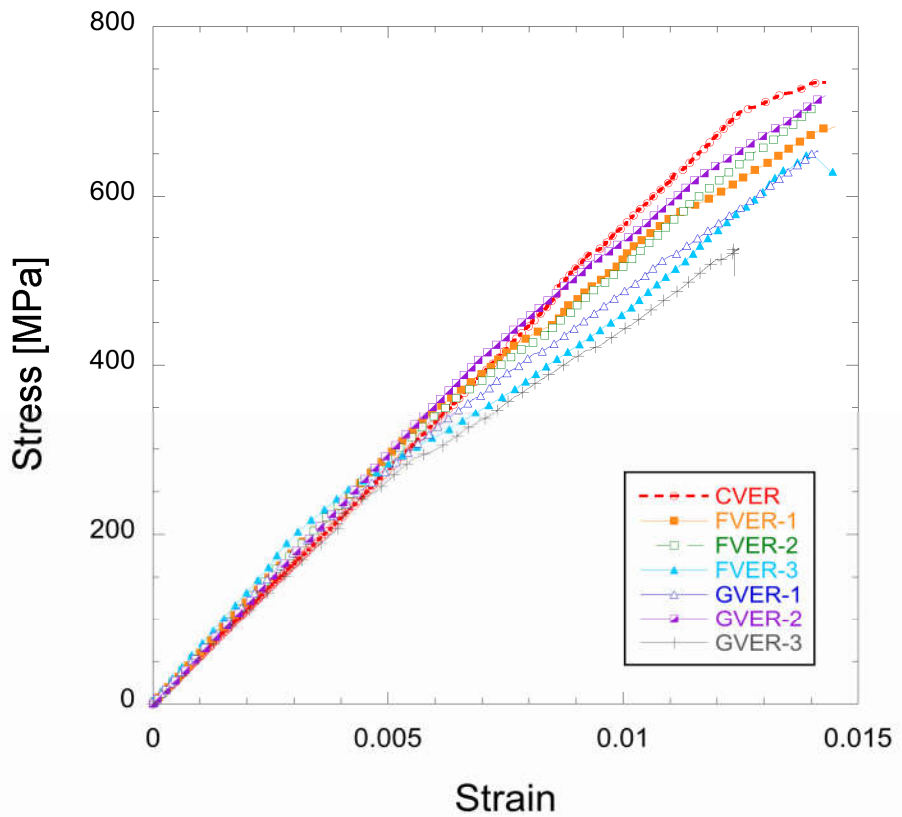
Maximum burning of the sample during cone calorimetry testing



Maximum generation of smoke during cone calorimetry testing

Tensile Testing (Non-Brominated)

- Tensile strength and Modulus are fiber dominated properties

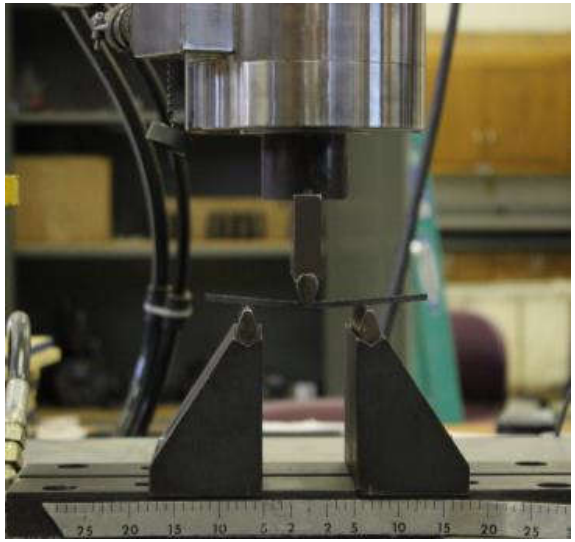


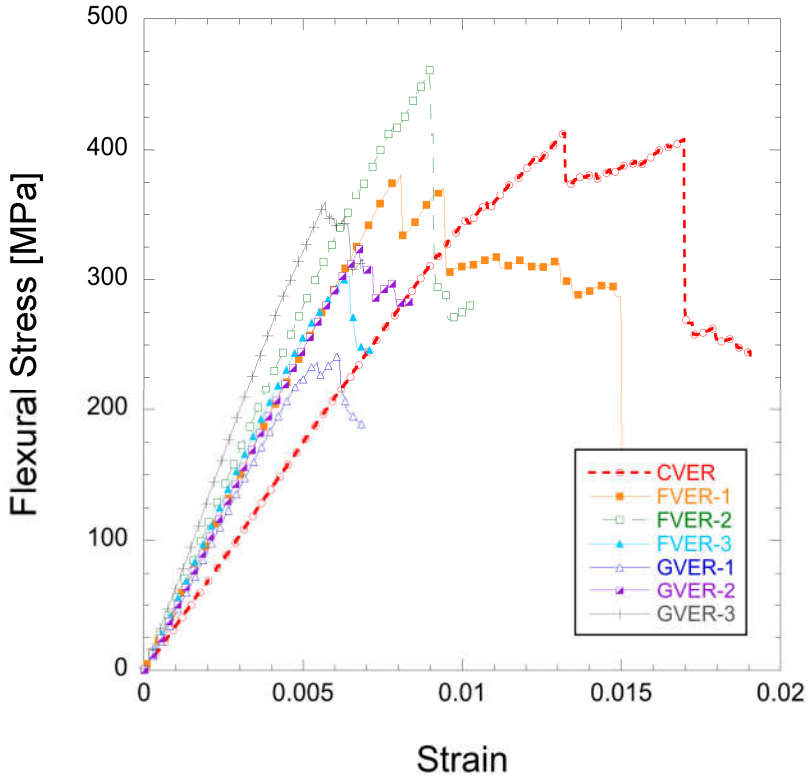
Specimen (sample size)	Fiber Volume Fraction	Tensile modulus (GPa)	Ultimate tensile strength (MPa)
CVER (n = 4)	0.41	53.0 ± 1.2	691 ± 41
FVER-1 (n = 3)	0.56	61.4 ± 2.9	669 ± 14
FVER-2 (n = 3)	0.59	60.5 ± 1.4	683 ± 22
FVER-3 (n = 3)	0.55	59.7 ± 2.8	684 ± 26
GVER-1 (n = 3)	0.55	59.0 ± 1.2	681 ± 35
GVER-2 (n = 3)	0.50	57.9 ± 1.4	692 ± 19
GVER-3 (n = 3)	0.48	52.3 ± 1.8	558 ± 14

All resins show good performance in this orientation. Low fiber volume fraction and shorter pot life explain low modulus for CVER

Flexural Testing (Non-Brominated)

- Flexural Strength and modulus are mixed mode dependent





Specimen (sample size)	Fiber Volume Fraction	Flexural strength (MPa)	Flexural modulus (GPa)
CVER (n = 5)	0.42	422 ± 8	34.1 ± 1.3
FVER-1 (n = 3)	0.54	398 ± 15	49.7 ± 0.5
FVER-2 (n = 3)	0.56	446 ± 18	49.5 ± 2.5
FVER-3 (n = 3)	0.56	263 ± 9	46.4 ± 0.9
GVER-1 (n = 3)	0.56	190 ± 9	44.6 ± 2.0
GVER-2 (n = 3)	0.57	363 ± 34	49.8 ± 2.0
GVER-3 (n = 3)	0.59	373 ± 17	63.3 ± 1.9

All 6 of the bio-derived resins show excellent modulus. 4 of the 6 FVER/GVERs show excellent flexural strength. Low fiber volume fraction explains low modulus for CVER

Short Beam Strength Testing (Non-Brominated)

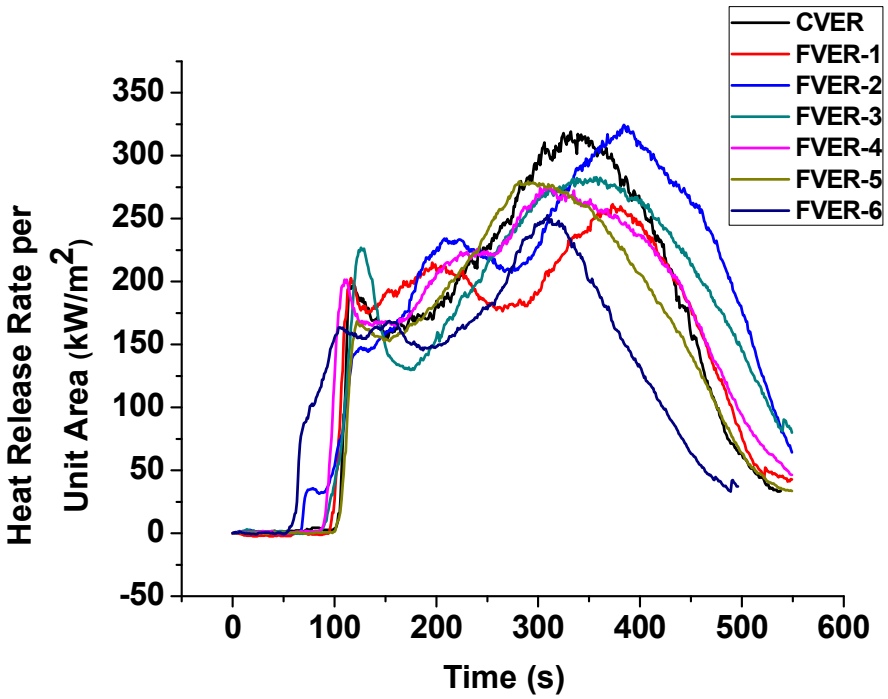
- Short beam strength is resin dominated

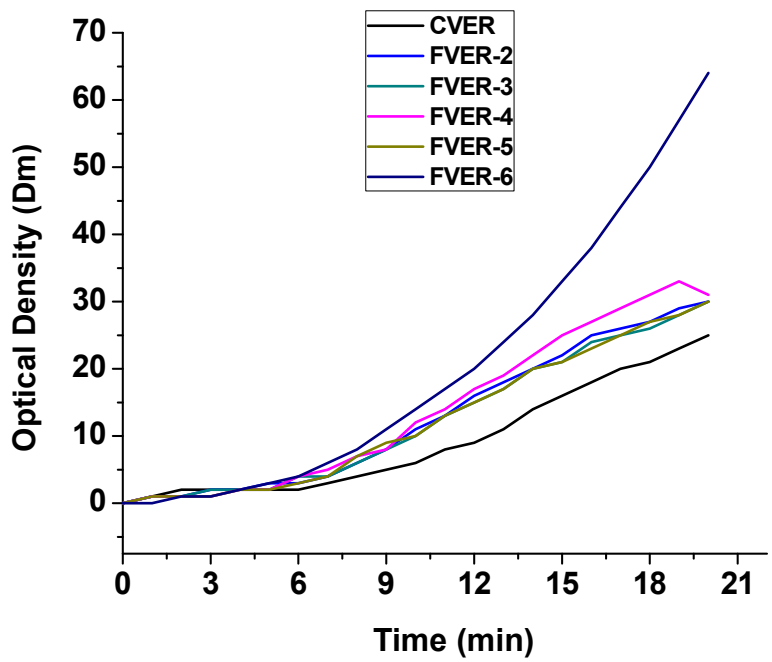
Specimen (sample size)	Short beam strength (MPa)
CVER (n = 5)	32 ± 3.0
FVER-1 (n = 5)	31.6 ± 2.0
FVER-2 (n = 3)	35 ± 0.6
FVER-3 (n = 3)	23.7 ± 1.5
GVER-1 (n = 3)	18.5 ± 0.4
GVER-2 (n = 3)	30.8 ± 2.1
GVER-3 (n = 3)	31.4 ± 0.9

Short beam strength values are consistent with the flexural strength values

Flammability Testing

- ASTM E1354
- 2 key parameters are typically of most interest
  - Avg. Heat Release Rate
  - Smoke Density





Peak HRR and Avg. eff. heat of combustion is lower for all bio-derived resins indicating better flammability performance. All 6 samples have comparable time to ignition values except FVER-6.

Conclusions

- Most of the bio-derived resins show similar if not better mechanical properties than the commercially available resin
- All bio-derived resins have a significantly longer pot life than the commercial resin (CVER)
- Ease of processing for manufacturing composites using VARTM becomes easier as the GVER content increases.
- Most of the bio-derived resins show improved flammability properties in comparison with the commerical resin
- Order of Resin Performance→ FVER 2 > FVER 1 > GVER 2 > GVER 3 (This is only one perspective as there are multiple determining factors)

Specimen (sample size)	Flexural modulus (GPa)	Flexural strength (MPa)
CVER (n = 5)	34.1 ± 1.3	422 ± 8
FVER-2 (n = 3)	49.5 ± 2.5	446 ± 18

FVER-2 shows a 6% increase in flexural strength over CVER

Specimen (sample size)	Short beam strength (MPa)
CVER (n = 5)	32 ± 3.0
FVER-2 (n = 3)	35 ± 0.6

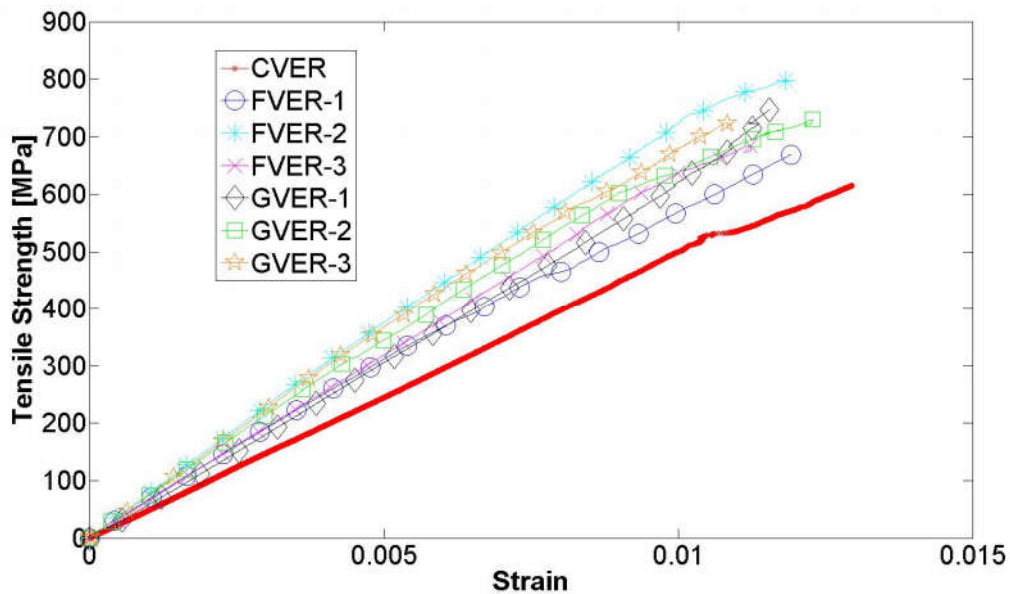
FVER-2 shows a 9% increase in short beam shear strength over CVER

Sample ID	Average Effective Heat of Combustion (MJ/kg)	Peak HRR (kW/m^2)
CVER (n = 3)	30	317
FVER-2 (n=3)	27	333

FVER-2 shows a lower heat of combustion and a similar peak HRR

Tensile Testing (Brominated)

- Tensile strength and Modulus are fiber dominated properties

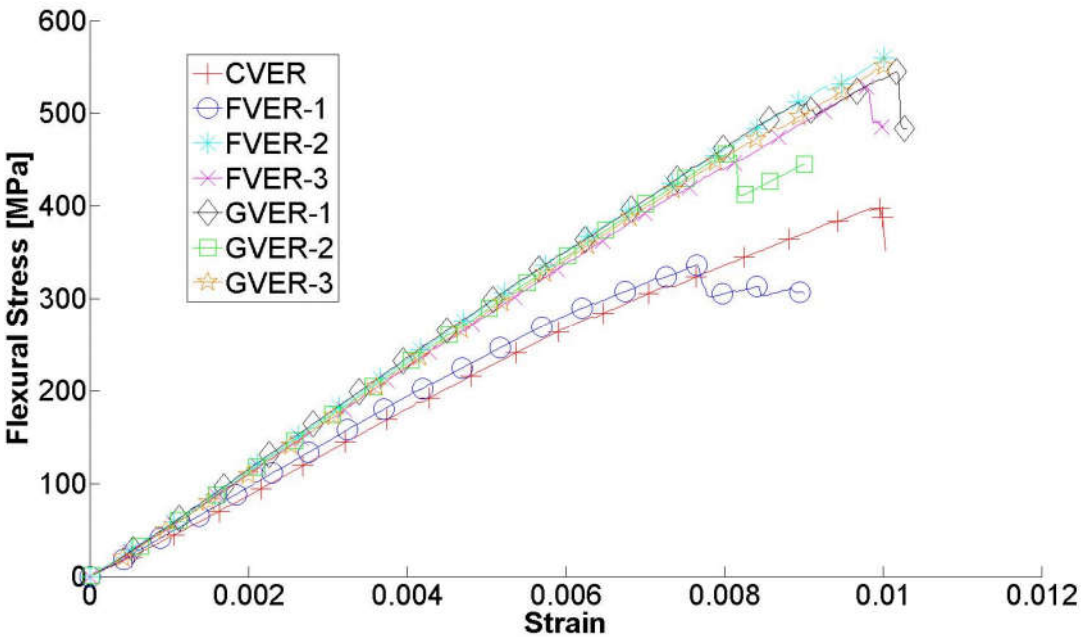


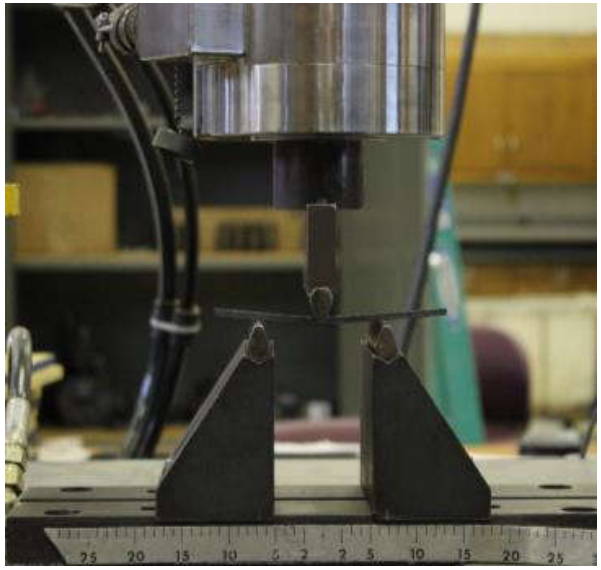
Specimen (sample size)	Tensile modulus (GPa)	Ultimate tensile strength (MPa)
CVER (n = 4)	51.2 ± 1.5	687 ± 66
FVER-1 (n = 3)	59.1 ± 3.9	649 ± 18
FVER-2 (n = 3)	75.2 ± 4.1	804 ± 19
FVER-3 (n = 3)	64.9 ± 5.6	706 ± 54
GVER-1 (n = 3)	60.3 ± 3.2	732 ± 46
GVER-2 (n = 3)	74 ± 9.0	731 ± 2.2
GVER-3 (n = 3)	75.4 ± 4.2	714 ± 7.3

All resins show good performance in this orientation. Low fiber volume fraction and shorter pot life explain low modulus for CVER

Flexural Testing (Brominated)

- Flexural Strength and modulus are mixed mode dependent





Specimen (sample size)	Flexural modulus (GPa)	Flexural strength (MPa)
CVER (n = 5)	48.9 ± 5	402 ± 27
FVER-1 (n = 3)	47.9 ± 2	339 ± 12
FVER-2 (n = 3)	58.5 ± 1.4	572 ± 39
FVER-3 (n = 3)	56.3 ± .46	533 ± 26
GVER-1 (n = 3)	58.1 ± 1.7	562 ± 42
GVER-2 (n = 3)	56.4 ± 1.4	461 ± 25
GVER-3 (n = 3)	61.3 ± 2.9	599 ± 32

All 6 of the bio-derived resins show excellent modulus and flexural strength. Low fiber volume fraction explains low modulus for CVER

Short Beam Strength Testing (Brominated)

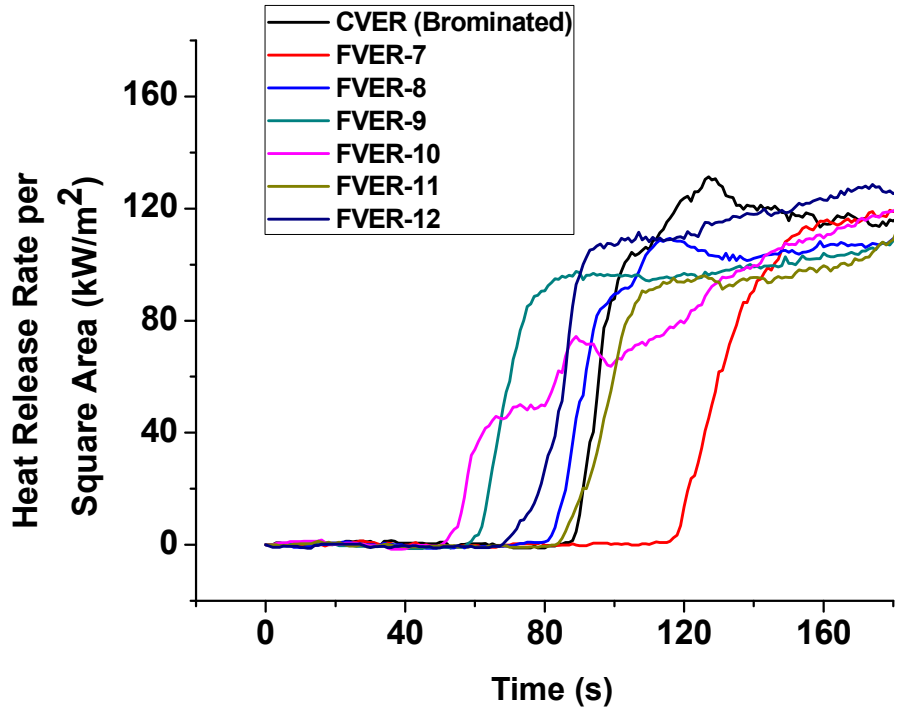
- Short beam strength is resin dominated

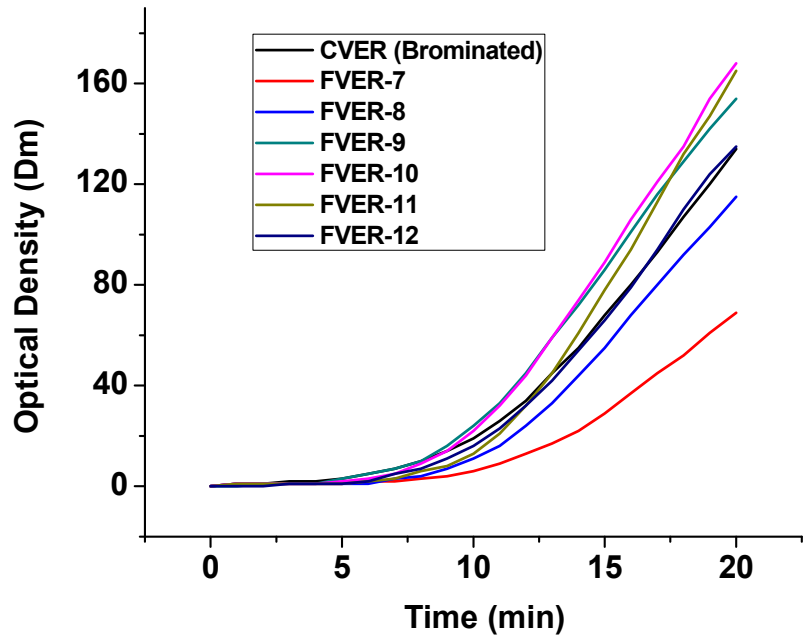
Specimen (sample size)	Short beam strength (MPa)
CVER (n = 5)	32 ± 2.6
FVER-1 (n = 5)	29.2 ± 2.2
FVER-2 (n = 3)	44 ± 1.2
FVER-3 (n = 3)	39.5 ± 2.6
GVER-1 (n = 3)	45.2 ± 1.1
GVER-2 (n = 3)	43.5 ± 2.3
GVER-3 (n = 3)	50.3 ± 1.9

Short beam strength values are consistent with the flexural strength values

Flammability Testing (Brominated)

- ASTM E1354
- 2 key parameters are typically of most interest
  - Avg. Heat Release Rate
  - Smoke Density





Peak HRR and Avg. eff. heat of combustion is lower for all bio-derived resins indicating better flammability performance. All 6 samples have comparable time to ignition values except GVER-3.

Conclusions (Brominated Data)

- All 6 formulated resins show excellent mechanical properties in comparison to the commercial brominated resin
- Ease of processing for manufacturing composites using VARTM becomes easier as the GVER content increases.
- FVER 2 and GVER 3 show strongest mechanical performances. However, GVER 3 has a higher viscosity than CVER, making it more difficult to process via VARTM
- Order of Resin Performance→ FVER 2> GVER3 > GVER 1>GVER 2 (This is only one perspective as there are multiple determining factors)

Specimen (sample size)	Flexural modulus (GPa)	Flexural strength (MPa)
CVER (n = 5)	48.9 ± 5	402 ± 8
FVER-2 (n = 3)	58.5 ± 1.4	572 ± 18

FVER-2 shows a 40% increase in flexural strength over CVER

Specimen (sample size)	Short beam shear strength (MPa)
CVER (n = 5)	32 ± 2.6
FVER-2 (n = 3)	44 ± 1.2

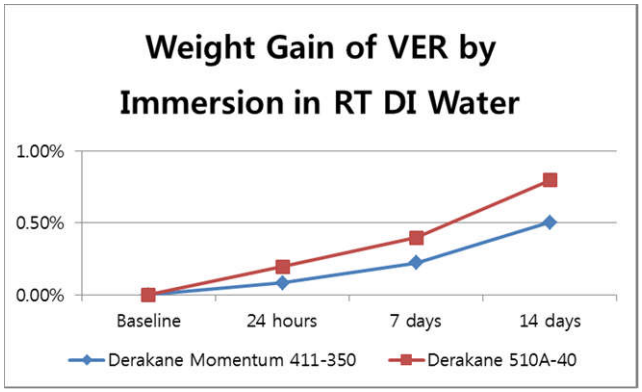
FVER-2 shows a 38% increase in short beam shear strength over CVER

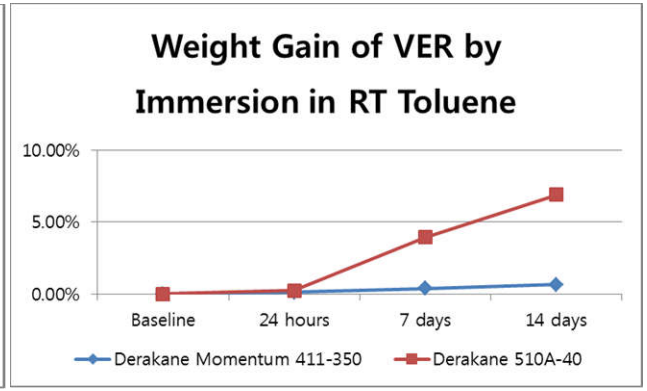
Sample ID	Average Effective Heat of Combustion (MJ/kg)	Peak HRR (kW/m^2)
CVER (n = 3)	13	159
FVER-2 (n=3)	12	142

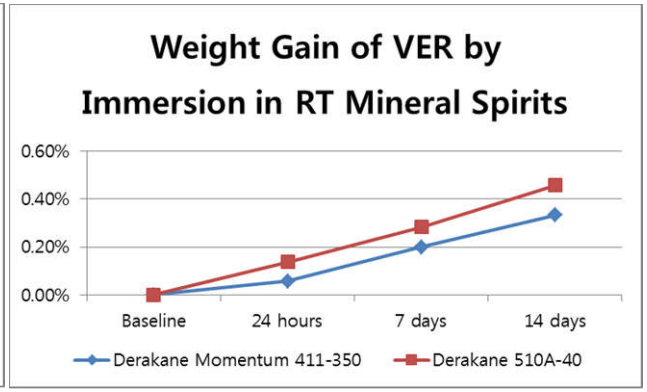
FVER-2 shows a significantly lower peak HRR

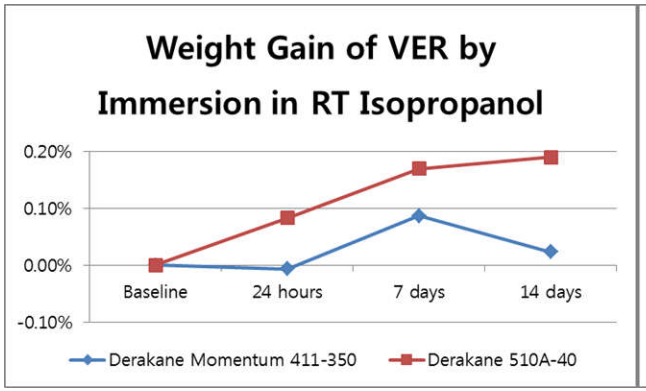
Fluid Uptake Studies (Ashland)

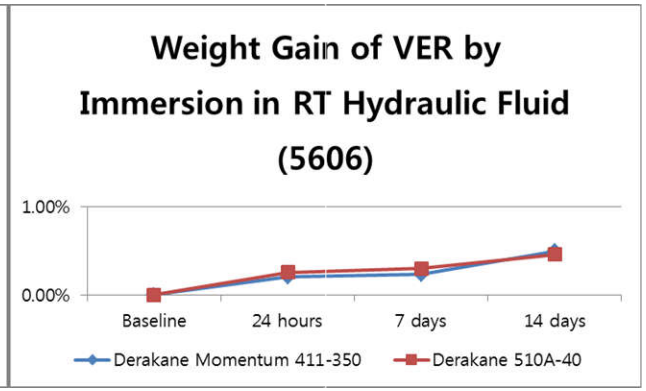
Uptake of water, hydraulic fluids, or hydrocarbon fuels by Green Vinyl Ester Resins

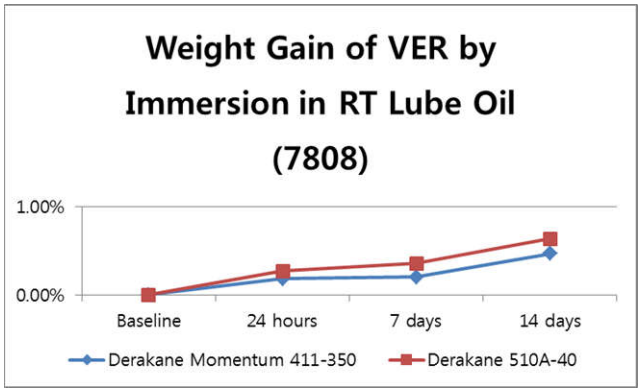




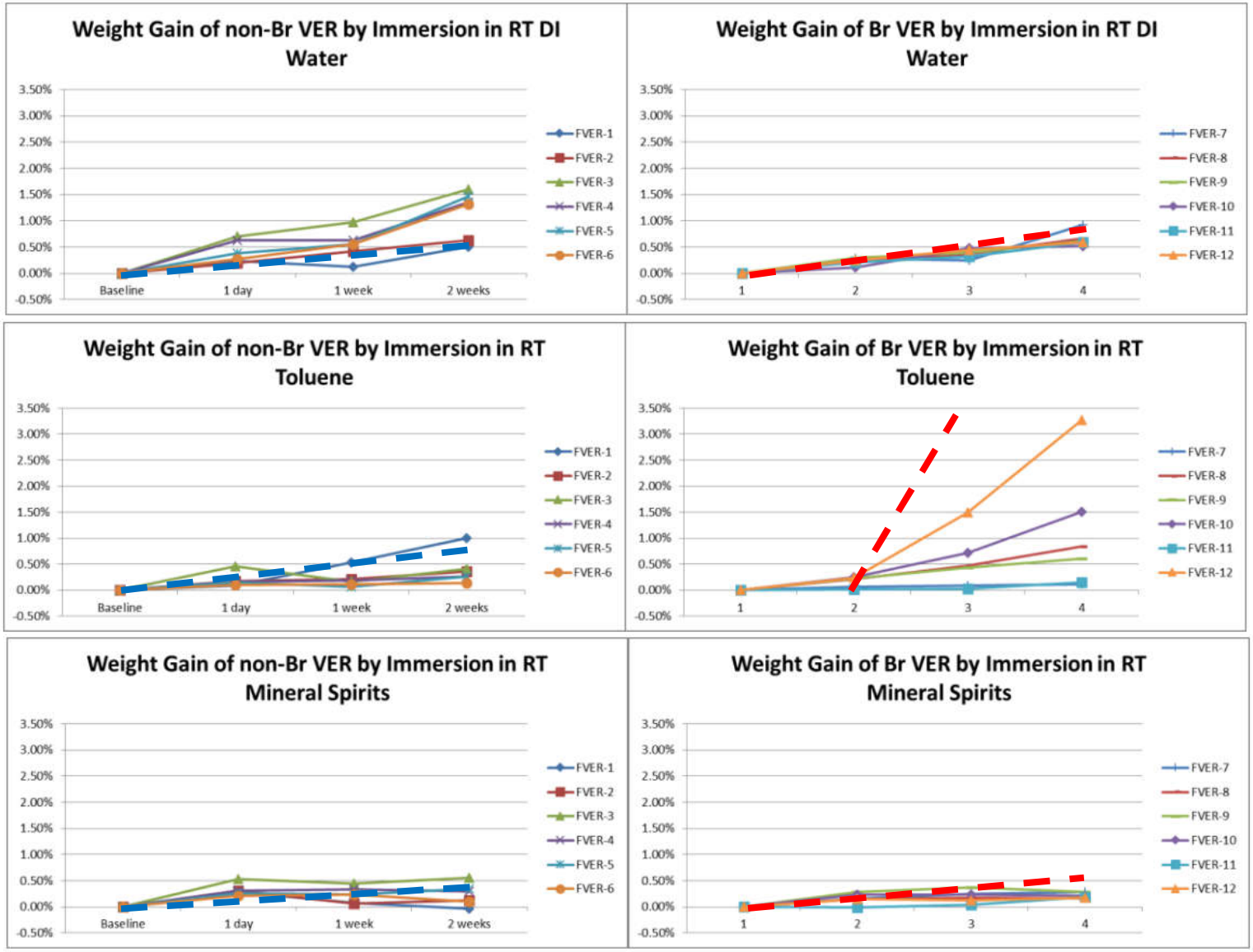




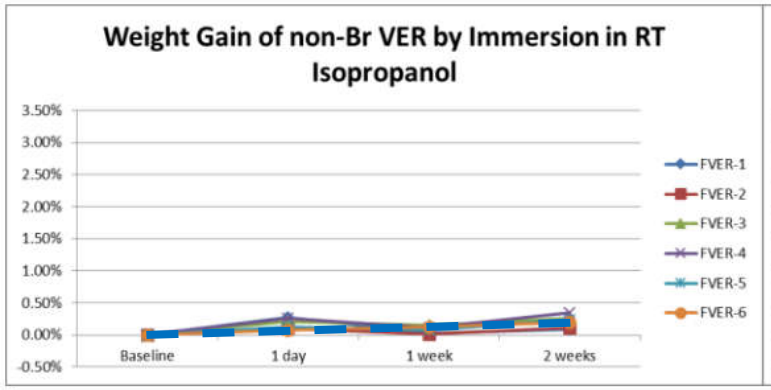


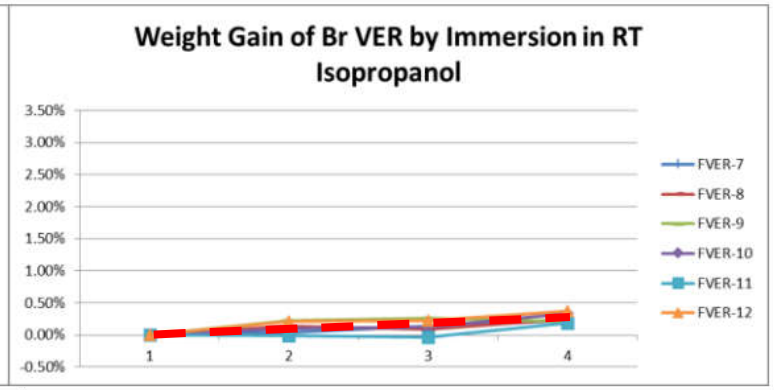


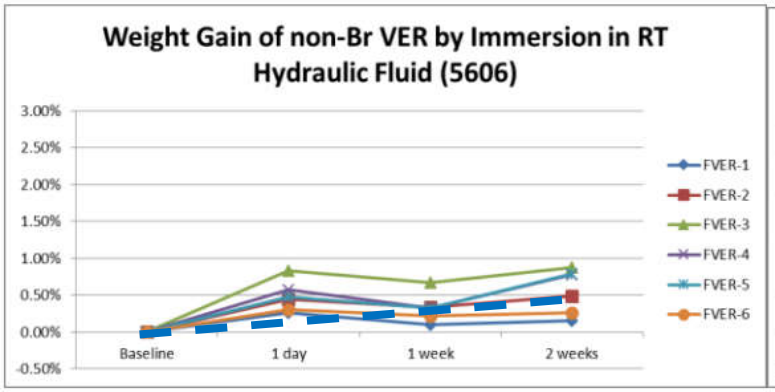
Fluid Uptake Studies (UML)

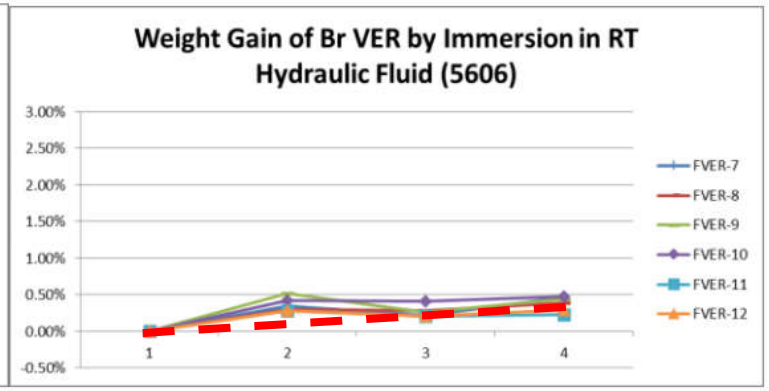


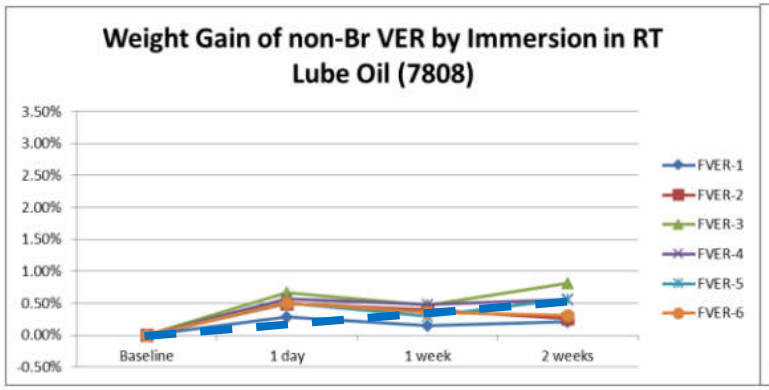
Fluid Uptake Studies (UML)

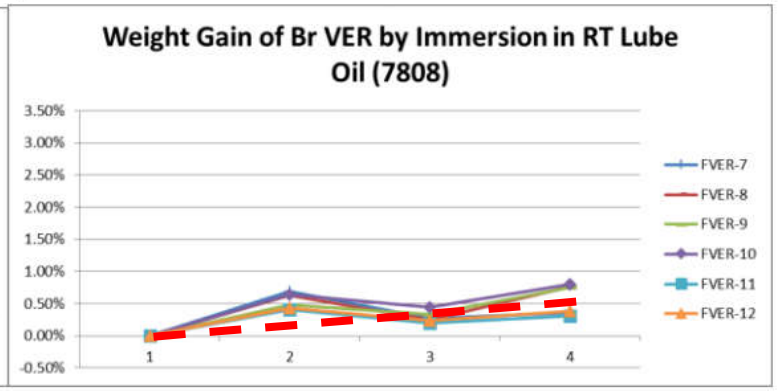












Action Items-1 (White paper)

Action Item 1: submit a white paper to Robin Nissan.

- Title: Potential Impact of Green Vinyl Ester Resin (GVER) on Military Applications and Environmental Issues

  - The low viscosity of VER for composite structures such as ship hulls and deck housings.

  - Demonstrate the significant positive impact of economically producing a cost sustainable, environmentally-compliant, Green Vinyl Ester Resin (GVER) recovered from biodiesel wastes.

  - Subject to SERDP approval, a follow-on program will be proposed to demonstrate and validate the positive impact of GVER technology upon DoD weapons platforms and the environment.

- Teaming Partners: Yongwoo Lee (UML), John La Scala (ARL), Stephen Nolet (TPI)

Action Items-2 (Funding /timeframe for spending)

Action Item 2: A brief summary of our funding situation and an overview of the timeframe for spending our remaining FY14 funds.

- **Action item 2:** In an email to Robin Nissan (robin.a.nissan.civ@mail.mil), Lisa Miller (lisamiller@hgl.com) and Sarah Barlow (sbarlow@hgl.com) by June 3, 2015, please provide a brief summary of your funding situation and an overview of the timeframe for spending your remaining FY14 funds. Include what your records indicate your current expenditures are at the time you submit the email. Please note that FY14 reimbursable funds expire on 9/30/15, and will need to be returned if they are not spent.

- **Response:** We received FY 14 funding of $288,658 in two instalments, first of $238,658 in 07/14, and second of $50,000 in 02/15. Originally we had proposed fund of $438,658 for year-II of the project. When we received the first installment of $238,658 of FY14, we had an impression that the remaining second part of FY14 $200,000k will be allotted during 01/15, which should be good enough for us till 09/15. So, we allotted entire year-II money as planned to NAVAIR and NAVSEA of $30,000 each out of $238,658, which should be good enough for them till 09/15.

Project Funding

	FY13*	FY14*	FY15*	FY16	Total
Proposal Requested ($K)	380	289	443	140	1252
Funds Received ($K)	380	289	443	110	1222
% Expended	100	100	97.7		90
Projected Out-Year Funds Required ($K)					1252

***NOTES:**

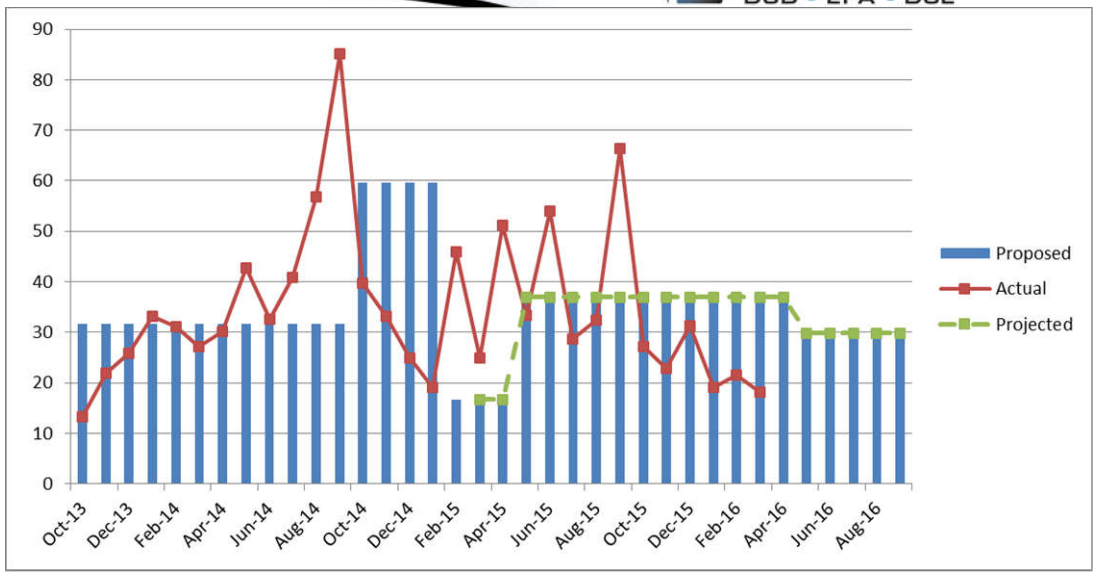
This table reflect SERDP funds sent to all directly funded and second tier performers working on the project.

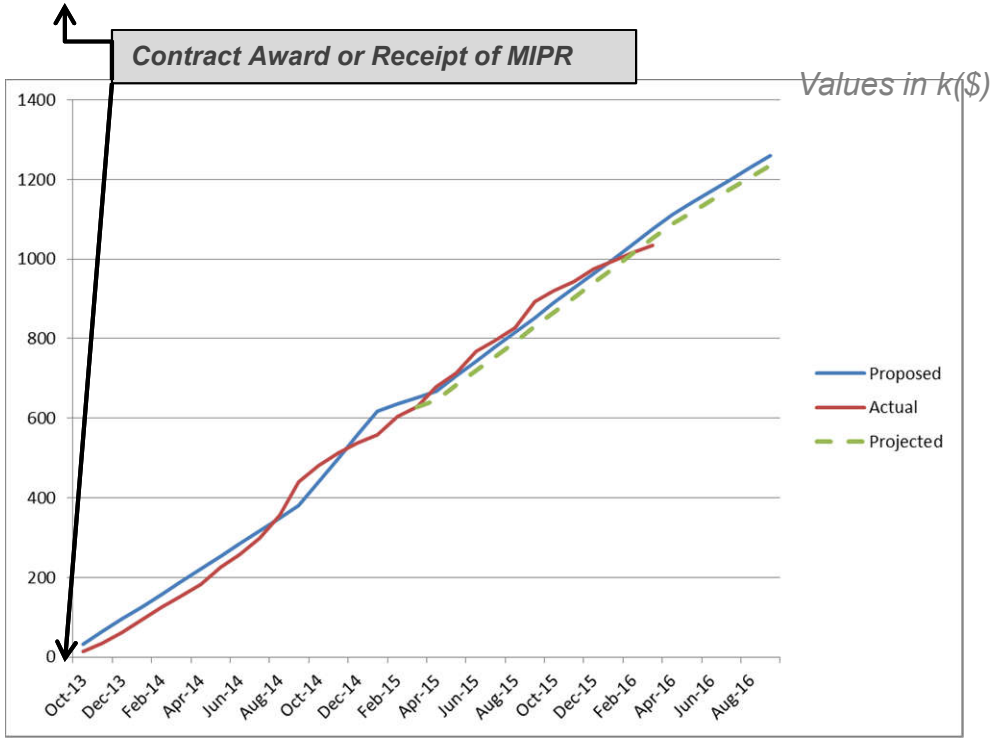
Include columns for all fiscal years for which funding has been received, is budgeted to be received, or is proposed to be received in the Revised Funding Profile. Add columns as needed.

Based on your spend rates for funding already received and any discussion with your program manager, identify your proposed out-year funding requirements. Total should not exceed current total project value.

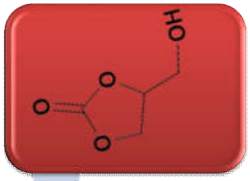
Financial Execution

- Proposed Start: *October 2013*
- Contract Award/MIPR Receipt:
- *October 2013*
- Proposed v. Actual Execution Delta:
- Contract End Date: *September 30, 2016*
- Additional Funds Needed in Next Calendar Year:
  - ♦Lead Org:
  - ♦Co-Performer(s):
- Execution Outlook:
  - ♦ *Discuss future project execution*

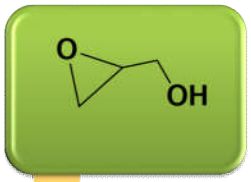




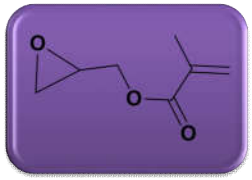
Transition Plan



- Solvent
- Batteries
- Cement
- Cosmetics
- Gas separation

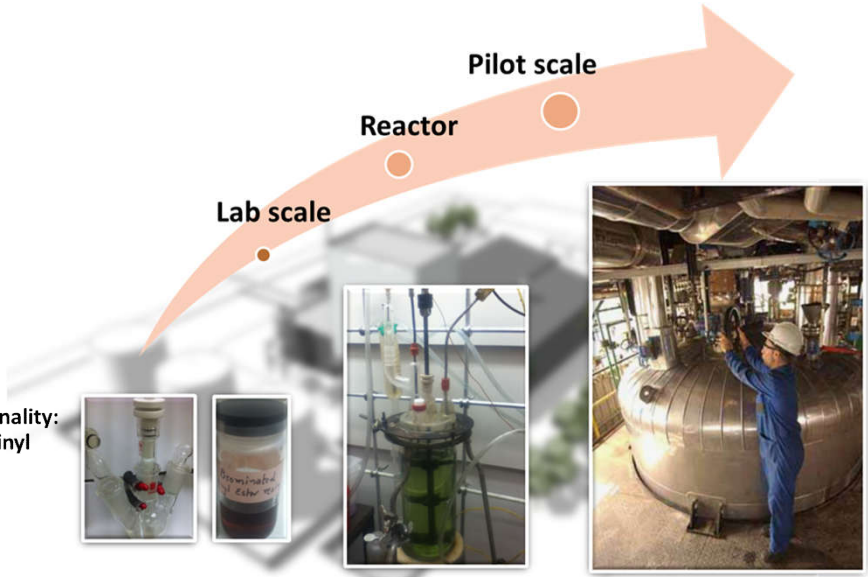


- Stabilizer
- Intermediate for many products
- Surface Coatings

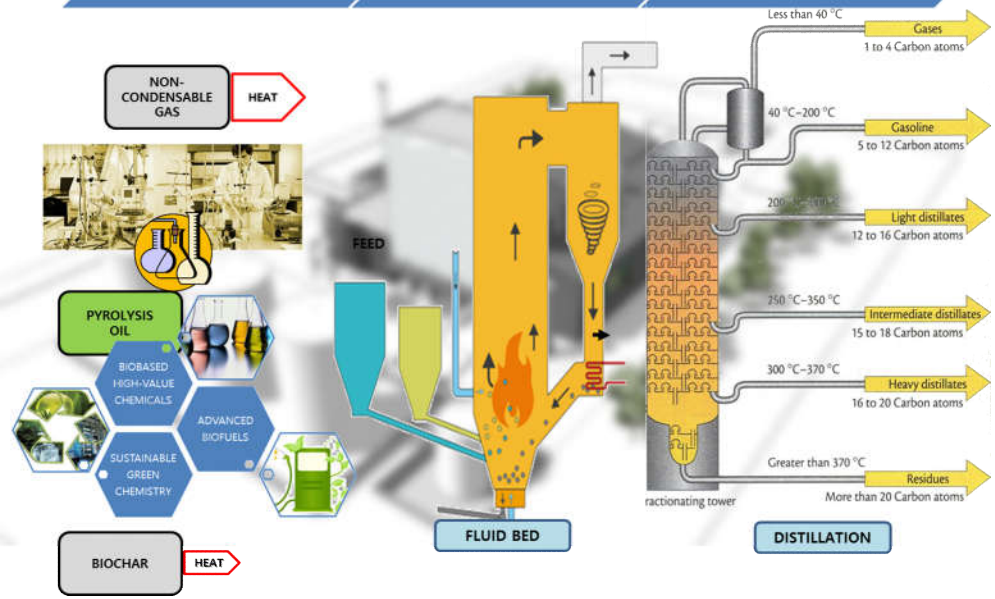


- Dual functionality: epoxy and vinyl group
- Various applications

Ready to use materials synthesized from biodiesel glycerin



LAB-SCALE > SCALE-UP > REFINEMENT



Transition Plan

NDA with Ashland, Inc.

University of Massachusetts Lowell and Ashland, Inc.
Agreement Ref. No.

CONFIDENTIAL DISCLOSURE AGREEMENT

This Agreement, effective as of January 27th, 2016 ("Effective Date"), is between the **University of Massachusetts,** as represented by its Lowell Campus ("UOM"), located at 1 University Avenue, Lowell, Massachusetts, 01854, and **Ashland Inc.** ("Ashland"), located at 5200 Blazer Parkway, Dublin, Ohio 43017.

*** VER manufacturer for Navy: Dr. Michael Stevenson / Dr. Joe Fox**

NDA with Dixie Chemical Co.

University of Massachusetts Lowell and Dixie Chemical Co.
Agreement Ref. No.

CONFIDENTIAL DISCLOSURE AGREEMENT

This Agreement, effective as of April 4, 2016 ("Effective Date"), is between the University of Massachusetts, as represented by its Lowell Campus, located at 1 University Avenue, Lowell, Massachusetts, 01854, and **Dixie Chemical Co.**, located at **10601 Bay Area Blvd. Pasadena TX, 77507**.

*** MFAs Inventor: Dr. John La Scala (Army Research Laboratory)**

Looking to the future -- if you can find someone who is upstream of Ashland in the value chain who feels they can economically scale up one (or more) of your processes to produce intermediates like GCMA, we could become a very important downstream customer for them.

Joe Fox Director, Emerging & External Technologies

NDA with TPI Composite, Inc.

TPI Composites Inc. would be interested in employing such formulations for fabrication of the fiberglass and carbon fiber reinforced polymer products we sell around the globe. Please do not hesitate to contact me directly if you have questions about the value of this research, the applications we support or the technologies that will benefit from the successful application of this technology.

Sincerely,

Stephen C. Nolet
Senior Director, Innovation & Technology

Phone: (401) 247-4009
Email: snolet@tpicomposites.com

*** VER composite: Mr. Nolet (Senior Director, Innovation & Technology)**

BACKUP MATERIAL

Publications

Publications and Manuscripts in preparation:

- P. N. Shah, N. Kim, Z. Huang, M. Jayamanna, A. Kokil, A. Pine, J. Kaltsas, E. Jahngen, D. K. Ryan, S. Yoon, R. F. Kovar, Y. Lee, Environmentally Benign Synthesis of Vinyl Ester Resin from Biowaste Glycerin. *RSC Advances*, *2015, 5, 38673*.
- P.N.Shah, S.Dev, U.Soranthia,Y.Lee,C.Hensen, Processing and Mechanical Properties of Green Vinyl Ester Resin-based composites (submitted to Journal "Composite A" on 032616)
- P.N.Shah, S.Dev, Y.Zhang, D.Ryan, N.Kim, C.Hensen, Y.Lee, Synthesis of Mechanical Properties of Flame Retardant Vinyl Ester Resin from Renewable Biowaste (in preparation)
- P.N.Shah, N.Kim, A.Kokil, M.Jayamanna, Y.Zhang, D.Ryan, R.Kovar, W.DeSisto, Y.Lee, Green Bisphenol A: A High Valued Building Block Isolated from Lignin Biowaste (in preparation)

Invention Disclosure to UML:

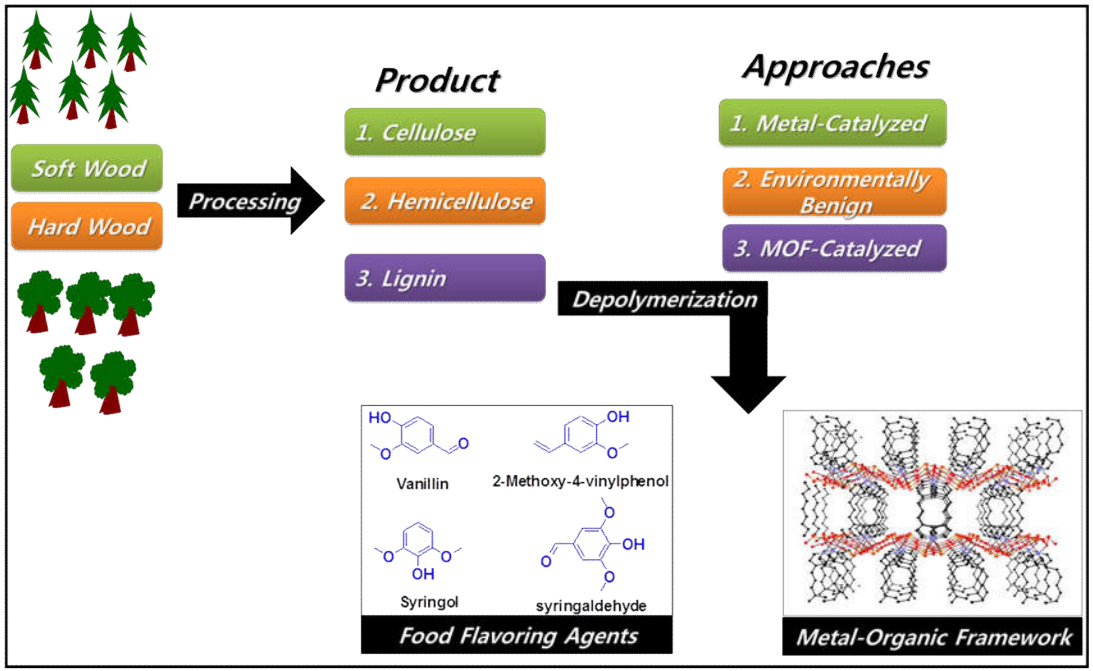
- High Value Phenol Enriched Phenolics by Cost-Effective Pyrolysis of Biowaste Lignin: Yongwoo Lee, Robert F. Kovar, Priyank N. Shah, Namjoon Kim, Akshay Kokil, Edwin Jahngen, David K. Ryan; *Invention Disclosure*, UML-2015-007.
- Sustainable "Green" Vinyl Ester Resin (VER) from Renewable Resources, Name: Yongwoo Lee, Robert F. Kovar, Priyank N. Shah, Namjoon Kim, Akshay Kokil, Edwin Jahngen; *Invention Disclosure*, UML- 2015-008.
- UML CVIP Invention Disclosure of Y.Lee, P.N.Shah, C.Hansen, S.Dev: Green Composites of Green Vinyl Ester Resin (GVER) Prepared from Biowaste. #UML 2016-008
- Y. Lee and P. N. Shah, Green" Vinyl Ester Resin (VER) from Glycerol Carbonate Methacrylate and Bisphenol A, UML # 2016-020

Provisional Patent Application

- A. Kokil, Y. Lee, P. N. Shah. Methods of making Bis(hydroxydrocarbyl)ether bisphenol and Vinyl Ester Resin.#UML2015-038-01 (atty.Ref.no.4724.005PRV), United States Application no.62/387,443
- A. Kokil, Y. Lee, Vinyl Hydroxyl Ether Resins.#UML 2015-041(atty.Ref.no.4724.007PRV) United States Application no.62/303,724

Action Items-3 (New Approaches for Improving Yields of Phenolics)

Action Item 3: submission of a white paper for additional approaches for optimization of the yield of phenol and other valuable phenolic

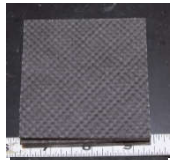
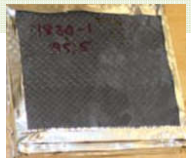


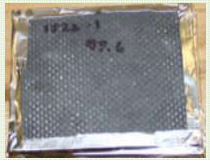
Background: A very high activation energy is required to depolymerize lignin. The activation energy can be reduced significantly using different catalytic systems.

Energy Sources: Various energy sources available.

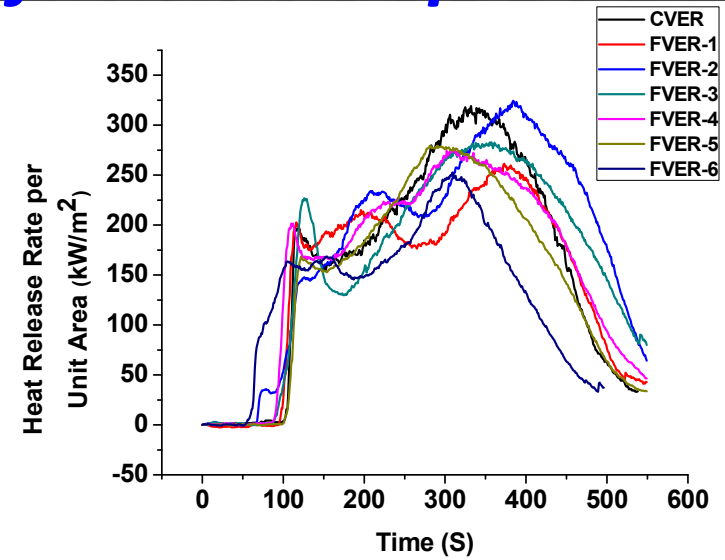
Thermal Energy (Pyrolysis)
Sound Energy (Sonication Based Depolymerization)
Electromagnetic Radiation (Microwave Based Depolymerization)

Flammability and Mechanical Testing

CVER	'C' Fabric Reinforced Vinyl Ester Resin	
FVER-1	20% Green VER and 80% Derakane Momentum 411-350	
FVER-2	50% GVER and 50% Derakane Momentum 411-350	
FVER-3	80% GVER and 20% Derakane Momentum 411-350	
FVER-4	100% GVER with 40 wt. % Styrene	
FVER-5	100% GVER with 30% Styrene	
FVER-6	100% GVER with 20% Styrene	

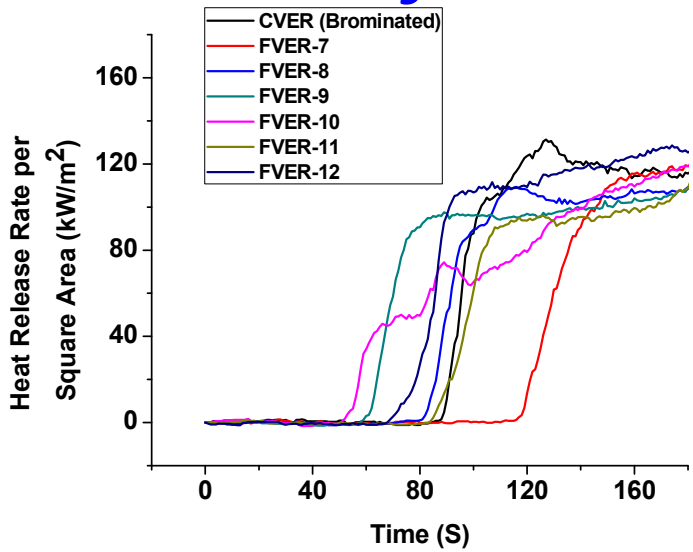
Br-VER	'C' Fabric Reinforced / Brominated Vinyl Ester Resin	
FVER-7	20% Brominated GVER and 80% Derakane 510A-40	
FVER-8	50% Brominated GVER and 50% Derakane 510A-40	
FVER-9	80% Brominated GVER and 20% Derakane 510A-40	
FVER-10	100% Br-GVER with 40 wt. % Styrene	
FVER-11	100% Br-GVER with 30 wt. % Styrene	
FVER-12	100% Br-GVER with 20 wt. % Styrene	

Heat Release Rate of GVER Composites



Sample ID	Time to Ign. (sec)	Flame Duration (sec)	% Mass Loss	Average Effective Heat of Combustion (MJ/kg)	Avg. HRR at 60 sec (kW/m^2)	Avg. HRR at 180 sec (kW/m^2)	Avg. HRR at 300 sec (kW/m^2)	Peak HRR (kW/m^2)	Time of Peak HRR (sec)	Total HRR/A (MJ/m^2)	SEA (m^2/kg)
VER	103	408	25	30	144	183	224	317	341	80	1327
FVER-1	97	502	29	28	162	185	202	265	368	83	1190
FVER-2	87	488	32	27	118	176	213	333	378	101	1454
FVER-3	96	489	31	27	152	165	207	295	274	91	1319
FVER-4	87	469	29	27	146	183	213	284	320	88	1376
FVER-5	101	481	27	27	131	184	212	290	312	80	1302
FVER-6	56	429	27	22	111	141	172	257	309	65	1333

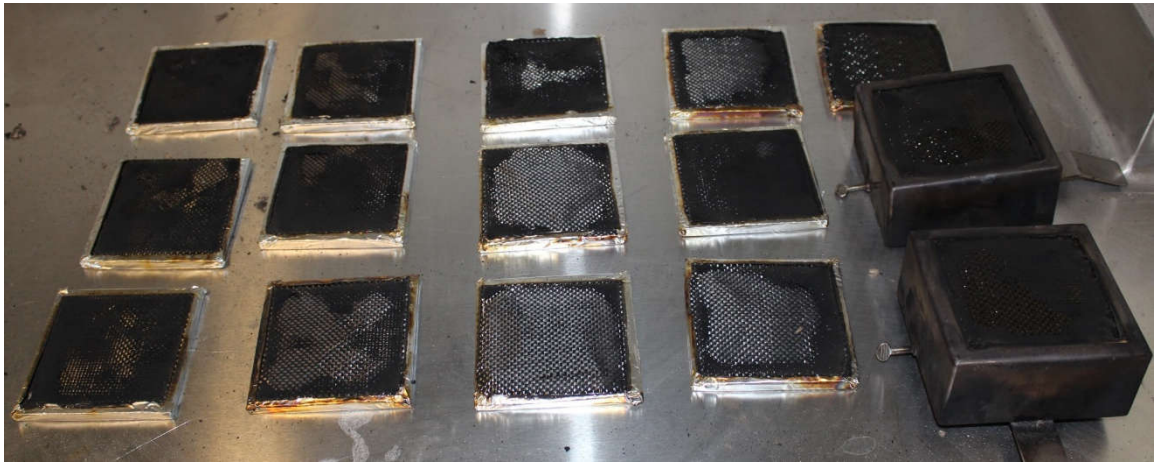
Heat Release Rate of Br-GVER Composites



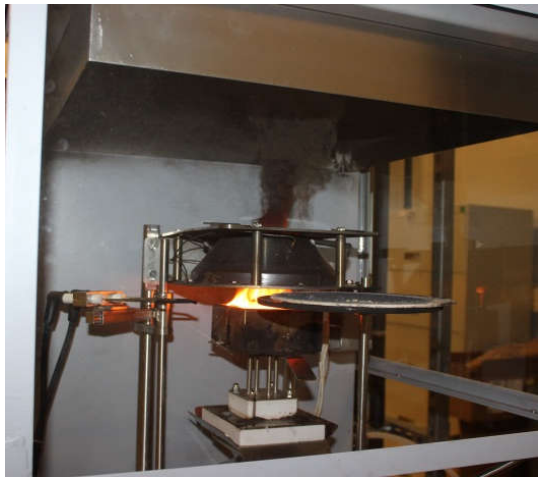
Sample ID	Time to Ign. (sec)	Flame Duration (sec)	% Mass Loss	Average Effective Heat of Combustion (MJ/kg)	Avg. HRR at 60 sec (kW/m^2)	Avg. HRR at 180 sec (kW/m^2)	Avg. HRR at 300 sec (kW/m^2)	Peak HRR (kW/m^2)	Time of Peak HRR (sec)	Total HRR/A (MJ/m^2)	SEA (m^2/kg)
Br-VER	91	339	29	13	108	119	128	159	318	41	1809
FVER-7	123	333	27	12	98	118	120	160	313	37	1737
FVER-8	78	382	28	12	81	102	114	142	316	40	1720
FVER-9	60	364	29	12	83	98	111	147	318	40	1560
FVER-10	59	456	32	12	65	96	109	144	319	46	1566
FVER-11	89	404	29	12	81	104	116	150	296	41	1294
FVER-12	74	251	25	11	93	115	DNR	161	264	30	1094

Samples After Testing

Sample at Maximum Flame

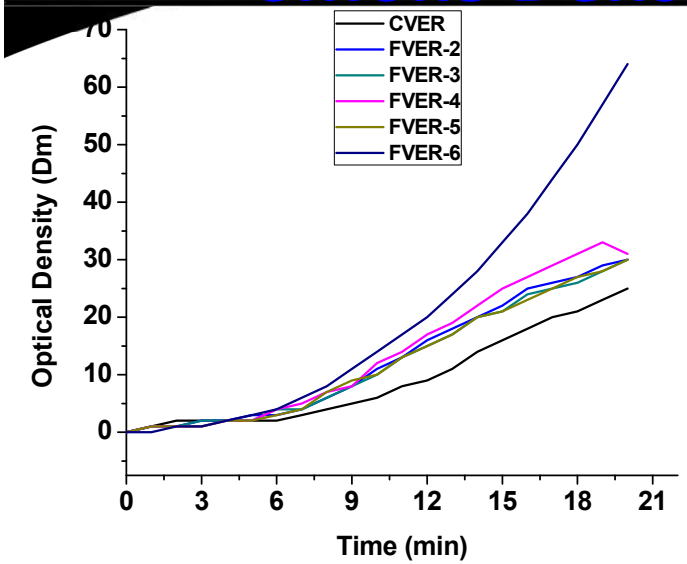


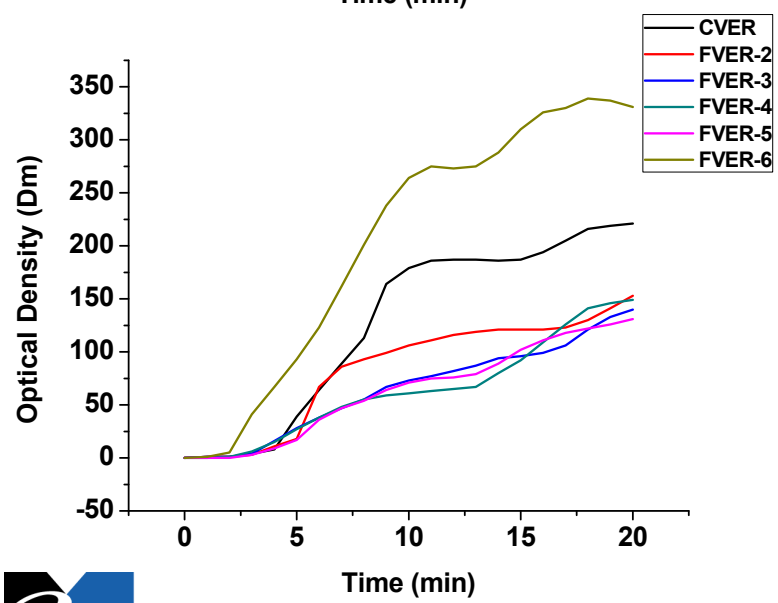
GVER Composites



Br-GVER Composites

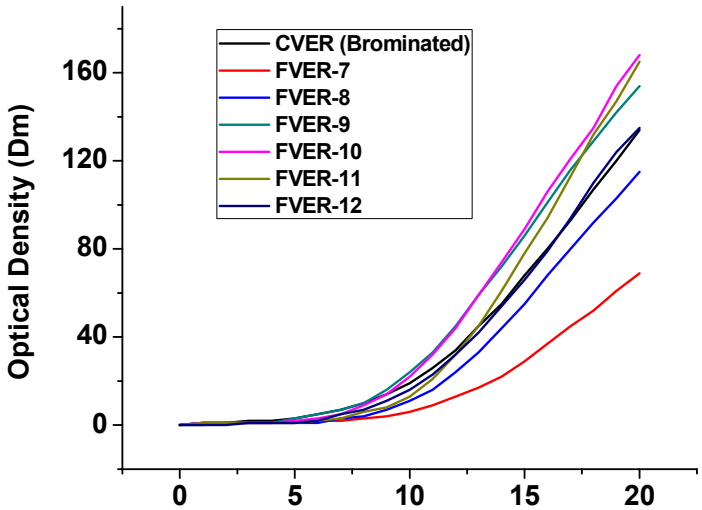
Smoke Density Test of GVER Composites

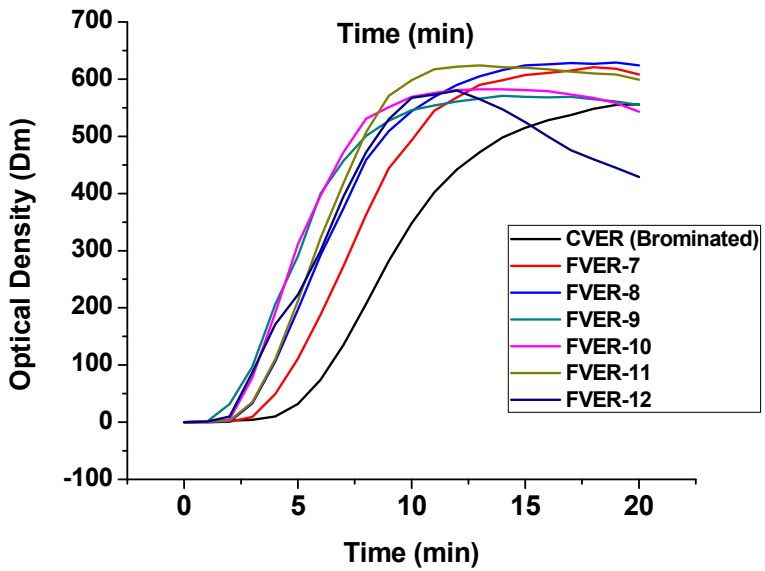




Sample ID	Mode of Combustion	D_m	CO (ppm)	CO_2 (%)	HCN (ppm)	HCl (ppm)
VER	Non-Flaming	25	10	N/D	1	N/D
	Flaming	330	367	1	4	N/D
FVER-1	Non-Flaming					
	Flaming	221	500	2	0.5	N/D
FVER-2	Non-Flaming	30	22	N/D	N/D	N/D
	Flaming	153	153	500	1.8	0.5
FVER-3	Non-Flaming	30	10	N/D	N/D	N/D
	Flaming	142	500	1.5	0.5	N/D
FVER-4	Non-Flaming	35	20	N/D	N/D	N/D
	Flaming	150	500	1.0	0.7	N/D
FVER-5	Non-Flaming	30	20	N/D	N/D	N/D
	Flaming	131	500	0.5	0.7	N/D
FVER-6	Non-Flaming	64	50	N/D	Trace	Trace
	Flaming	339	500	1.0	1.3	Trace

Smoke Density Test of Br-GVER Composites





Sample ID	Mode of Combustion	D_m	CO (ppm)	CO_2 (%)	HCN (ppm)	HCl (ppm)
Br-VER	Non-Flaming	134	10	N/D	1	0.2
	Flaming	559	150	0.5	2	Trace
FVER-7	Non-Flaming	69	10	N/D	N/D	N/D
	Flaming	623	500	0.5	0.7	0.5
FVER-8	Non-Flaming	115	37	N/D	Trace	Trace
	Flaming	630	1167	0.5	Trace	1
FVER-9	Non-Flaming	154	58	N/D	Trace	Trace
	Flaming	572	833	0.5	0.5	1
FVER-10	Non-Flaming	168	50	N/D	Trace	1
	Flaming	582	1167	0.5	#DIV/0!	N/D
FVER-11	Non-Flaming	165	70	N/D	N/D	8
	Flaming	631	367	0.5	Trace	2
FVER-12	Non-Flaming	136	67	N/D	Trace	4
	Flaming	580	583	0.5	0.5	4.0

Samples After Testing

Non-Flaming **Flaming**

FVER-2

FVER-3

FVER-5

FVER-4

FVER-6

Non-Flaming

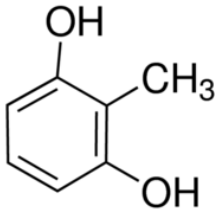
Flaming

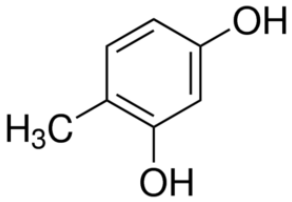
Application of Green Phenolics

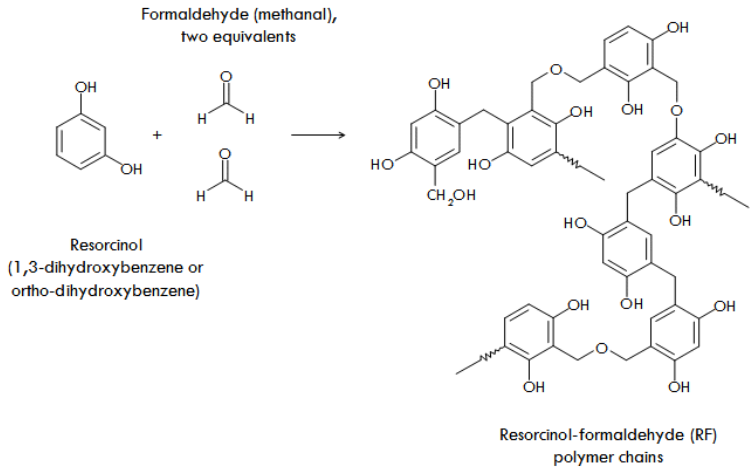
1. Green Resorcinol – Formaldehyde Resins and Aerogels

2-methylresorcinol and 4-methylresorcinol

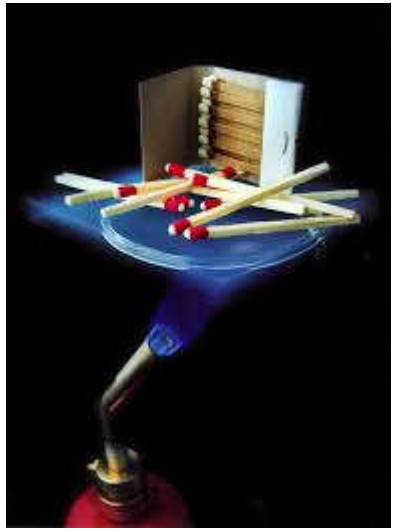
Obtained from microwave pyrolysis of lignin

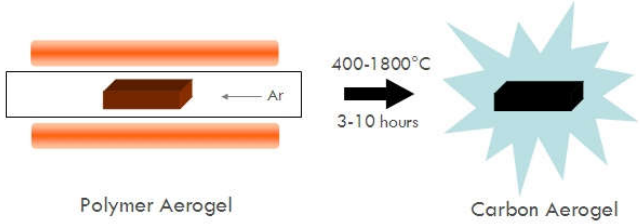






Resorcinol-Formaldehyde (RF) aerogels





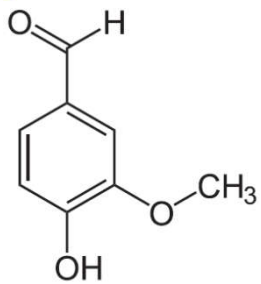
Collaborations with NASA, ARL and NRL

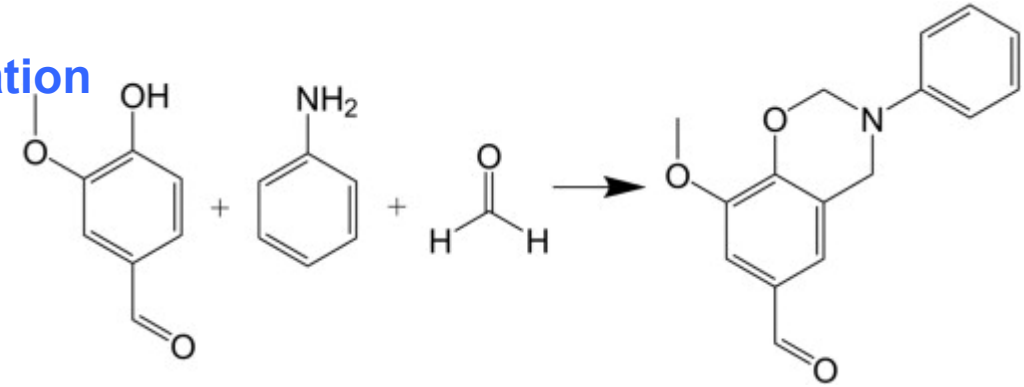
Application of Green Phenolics

2. Green Vanillin based Benzoxazine Resins

Vanillin

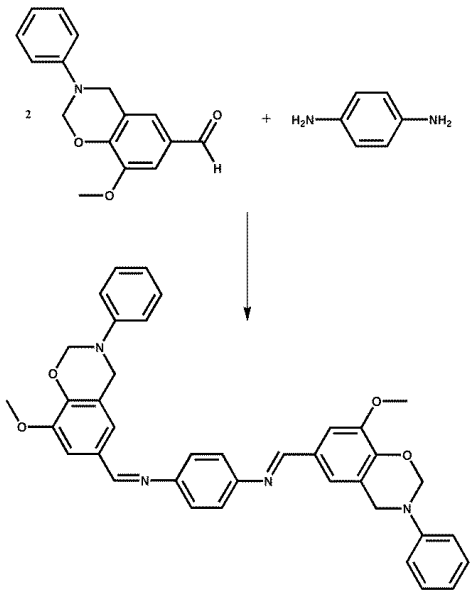
Obtained from base catalyzed sonication assisted degradation of of lignin





Ishida, H. et al. *Polymer* **2014**, *55*, 1443 - 1451

Can be dimerized using p-phenylenediamine



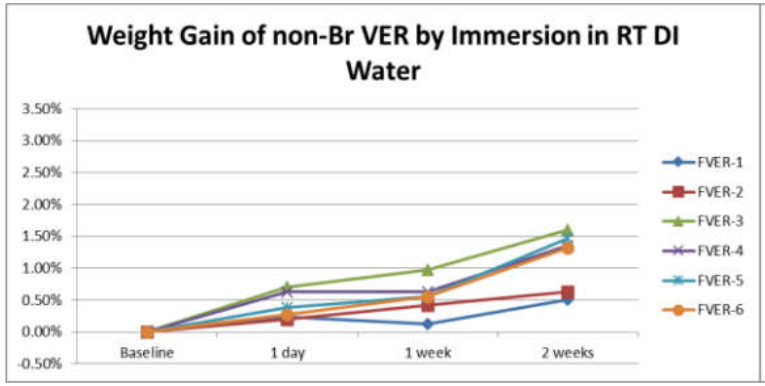
Composites
products for manufacturing fiber reinforced structural components

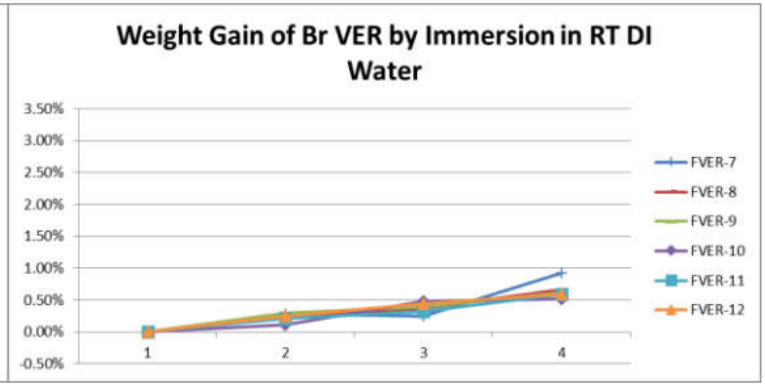
Assembly
materials for bonding, surface preparation and protection

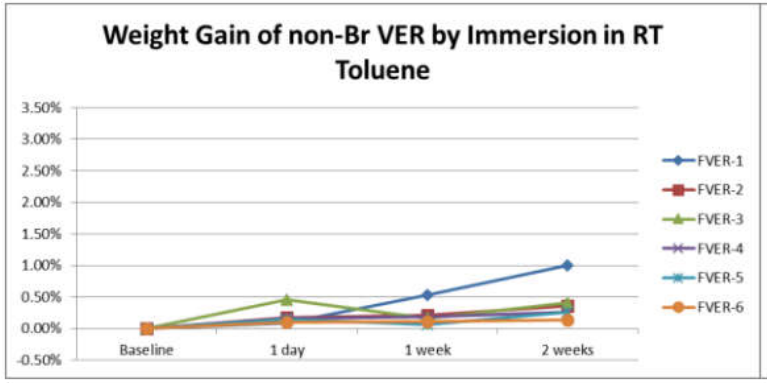
MRO
repair solutions for composite and metal structures to support your commitment to the aircraft lifecycle

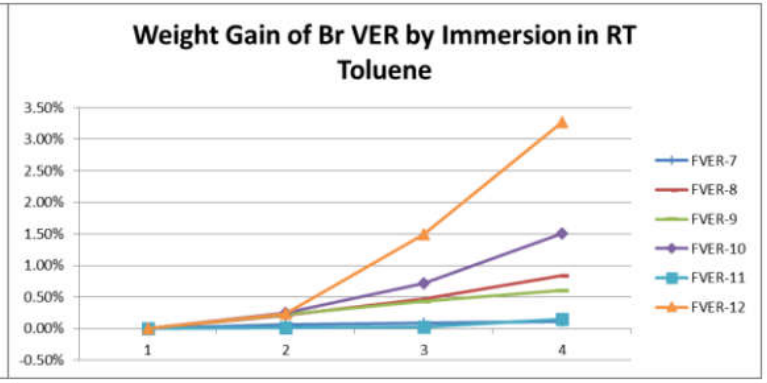
Collaborations with AFRL, NRL and NASA

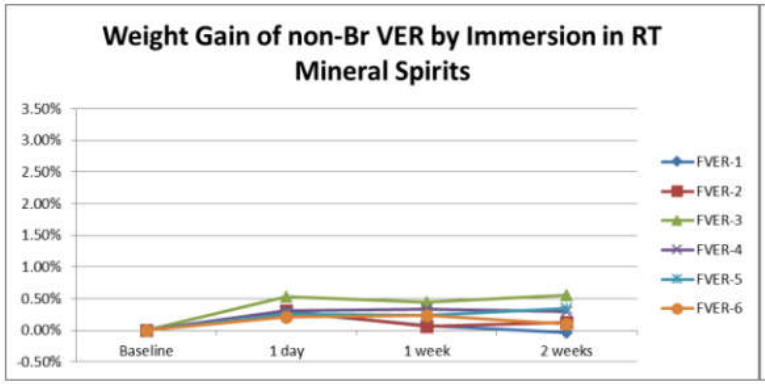
Fluid Uptake Studies (UML)

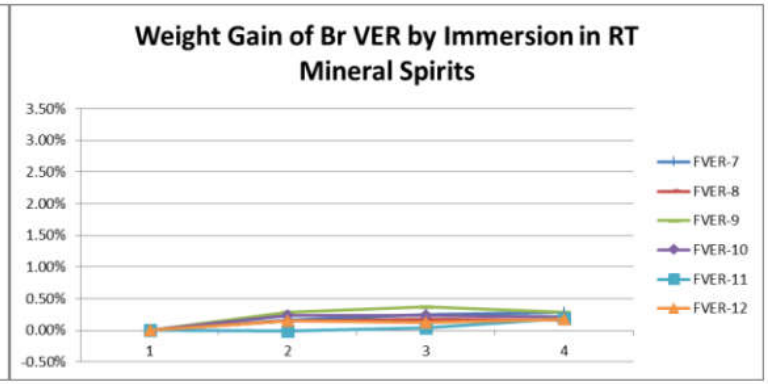




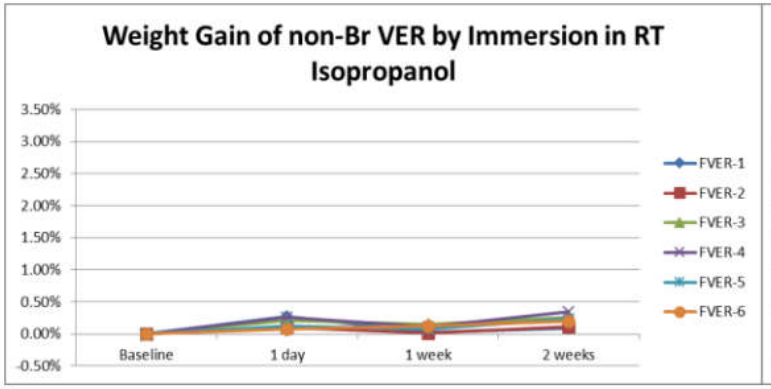


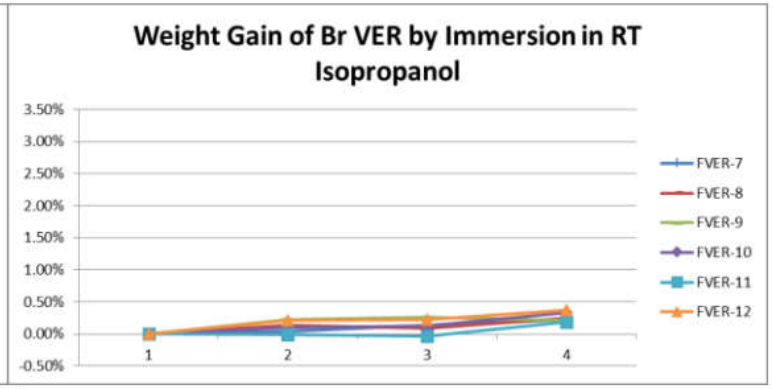


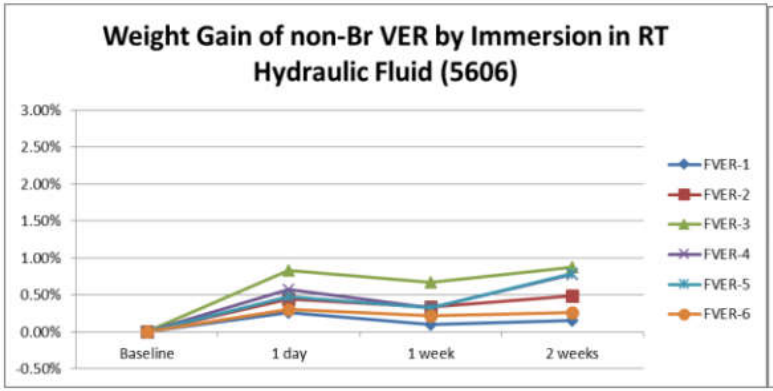


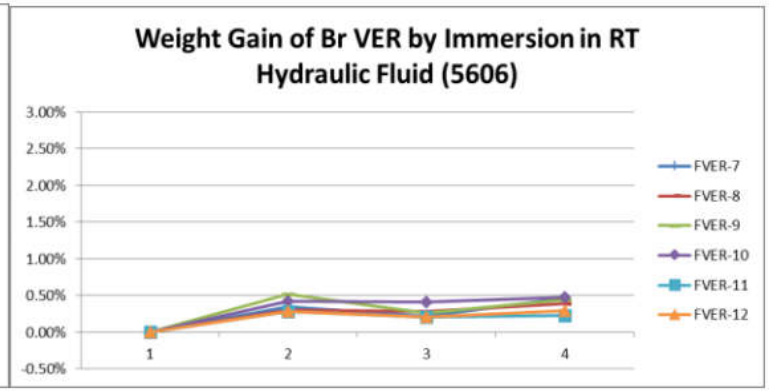


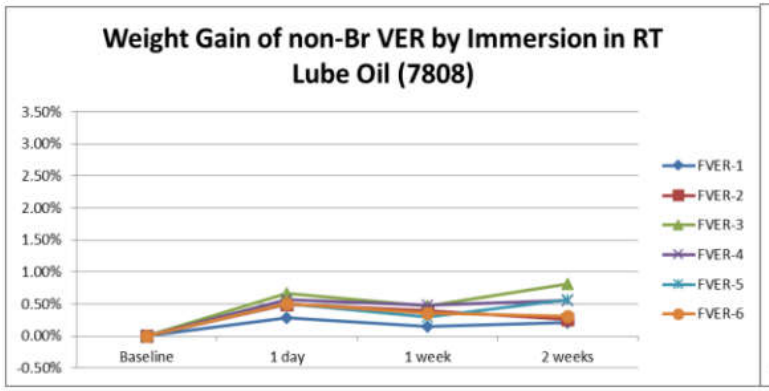
Fluid Uptake Studies (UML)

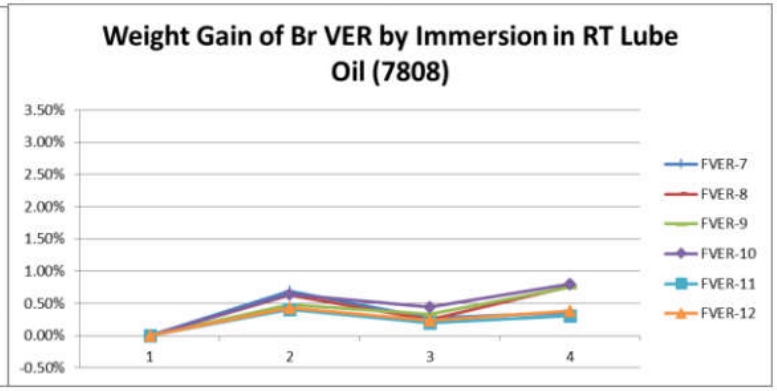




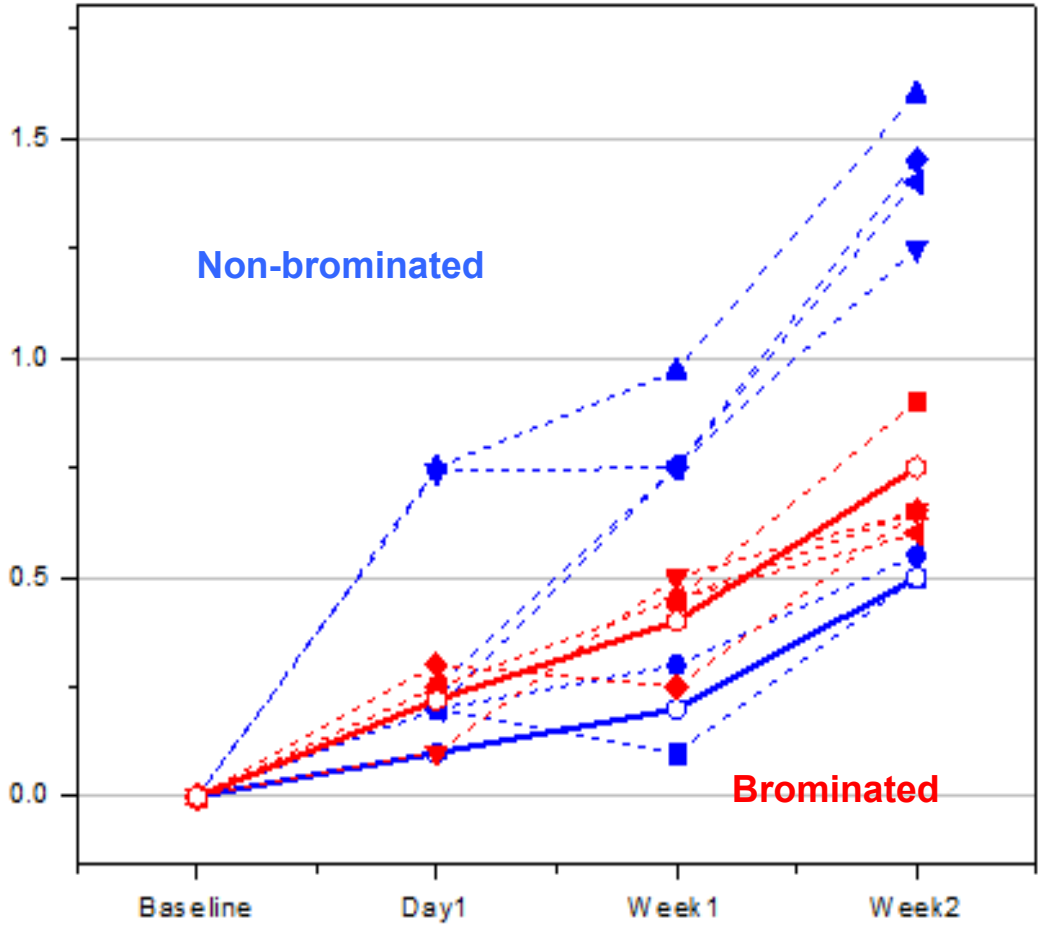








Fluid Uptake Studies



Appendix T

UNIVERSITY OF MASSACHUSETTS
And
MAINE STANDARD BIOFUELS

CONFIDENTIAL DISCLOSURE AGREEMENT

This Agreement, effective as of August 4, 2014 ("Effective Date"), is between the University of Massachusetts, as represented by its Lowell Campus, located at 1 University Avenue, Lowell, Massachusetts, 01854, and Maine Standard Biofuels, located at 51 Ingersoll Drive, Portland, ME, 04103.

Within one (1) year after the Effective Date (the "Term"), the parties intend to exchange and evaluate confidential information relating to "Bio-derived glycerine", and commercial applications of such technology, so that each party may evaluate a potential research collaboration, licensing transaction and/or a new business venture.

In consideration of each party making Confidential Information available to the other party, the parties agree as follows:

1. "Confidential Information" means any technical or business information furnished by one party to the other pursuant to this Agreement that is specifically designated as confidential. The disclosing party shall clearly mark written Confidential Information with a legend indicating its confidential status. All orally and visually disclosed Confidential Information will be identified as Confidential at the time of presentation. The disclosing party shall document Confidential Information that is disclosed orally or visually in a written notice and deliver the notice to the receiving party as soon as possible within fifteen (15) days after the disclosure. In the notice, the disclosing party shall summarize the Confidential Information and reference the date, time and place of disclosure.

2. Obligations and Limitations.

(a) The receiving party shall maintain Confidential Information in confidence, except that the receiving party may disclose or permit the disclosure of Confidential Information to its directors, officers, employees, consultants, and advisors who are obligated to maintain its confidential nature and who need to know the Confidential Information for purposes of this Agreement. (b) The receiving party may only use and reproduce Confidential Information to the extent necessary to carry out the purposes of this Agreement.

3. Exceptions. The obligations of Section 2 do not apply to the extent the receiving party can demonstrate that Confidential Information:

(a) was publicly known prior to the time of its disclosure under this Agreement; (b) became publicly known after its disclosure under this Agreement through means other than an unauthorized disclosure by the receiving party; (c) was previously known to or independently developed or discovered by the receiving party without use of the Confidential Information; (d) is or

was disclosed to the receiving party by a third party having no obligation of confidentiality with respect to the Confidential Information; or (e) must be disclosed to comply with applicable laws or regulations or with a court or administrative order, as long as the disclosing party receives prior written notice of the disclosure.

4. Ownership; No License. The receiving party acknowledges that the disclosing party (or a third party entrusting Confidential Information to the disclosing party) owns the Confidential Information and all patent, copyright, trademark, trade secret, and other intellectual property rights associated with the Confidential Information. Neither party grants an option, license, or conveyance of any intellectual property rights to the receiving party under this Agreement.

5. Return of Confidential Information; Obligations. At the end of the Term, or earlier at the request of the disclosing party, the receiving party shall return all originals, copies, and summaries of documents, materials, and other tangible manifestations of Confidential Information in its possession or control. However, the receiving party may retain one copy of the Confidential Information in the possession of its legal counsel solely to monitor its obligations under this Agreement. The obligations of this Agreement remain in effect for two (2) years after the Term or earlier return of Confidential Information, except that the obligation of the receiving party to return Confidential Information to the disclosing party survives until fulfilled.

6. Governing Law. This Agreement is governed by and construed in accordance with the laws of the Commonwealth of Massachusetts without regard to conflict of laws provisions.

7. Export Regulations. Each party covenants and warrants to the other that it will not disclose to the other any information that contains information, technology or data identified on any U.S. export control list, including the Commerce Control List and the U.S. Munitions List, unless and until it obtains the written consent of the other party's export control compliance officer.

8. Counterparts. This Agreement may be executed in counterparts and delivered by facsimile or email with the same effect as an original.

IN WITNESS WHEREOF, the parties have executed this Agreement by their duly authorized representatives as of the Effective Date set forth above.

THE UNIVERSITY OF MASSACHUSETTS	**COMPANY NAME**
By:_____	By: _____
Name: _____	Name: _____
Title: _____	Title: _____
Date: _____	Date: _____

Appendix U

UNIVERSITY OF MASSACHUSETTS
And
MAINE SEED COMPANY

CONFIDENTIAL DISCLOSURE AGREEMENT

This Agreement, effective as of September 26, 2014 ("Effective Date"), is between the University of Massachusetts, as represented by its Lowell Campus, located at 1 University Avenue, Lowell, Massachusetts, 01854, and Maine Seed Company, 263 Pulcifur Rd, Mapleton, ME 04757.

Within one (1) year after the Effective Date (the "Term"), the parties intend to exchange and evaluate confidential information relating to "Bio-derived Lignin" (SERDP WP-2317) and commercial applications of such technology, so that each party may evaluate a potential research collaboration, licensing transaction and/or a new business venture.

In consideration of each party making Confidential Information available to the other party, the parties agree as follows:

1. "Confidential Information" means any technical or business information furnished by one party to the other pursuant to this Agreement that is specifically designated as confidential. The disclosing party shall clearly mark written Confidential Information with a legend indicating its confidential status. All orally and visually disclosed Confidential Information will be identified as Confidential at the time of presentation. The disclosing party shall document Confidential Information that is disclosed orally or visually in a written notice and deliver the notice to the receiving party as soon as possible within fifteen (15) days after the disclosure. In the notice, the disclosing party shall summarize the Confidential Information and reference the date, time and place of disclosure.

2. Obligations and Limitations.

(a) The receiving party shall maintain Confidential Information in confidence, except that the receiving party may disclose or permit the disclosure of Confidential Information to its directors, officers, employees, consultants, and advisors who are obligated to maintain its confidential nature and who need to know the Confidential Information for purposes of this Agreement. (b) The receiving party may only use and reproduce Confidential Information to the extent necessary to carry out the purposes of this Agreement.

3. Exceptions. The obligations of Section 2 do not apply to the extent the receiving party can demonstrate that Confidential Information:

(a) was publicly known prior to the time of its disclosure under this Agreement; (b) became publicly known after its disclosure under this Agreement through means other than an unauthorized disclosure by the receiving party; (c) was previously known to or independently developed or discovered by the receiving party without use of the Confidential Information; (d) is or

RK

was disclosed to the receiving party by a third party having no obligation of confidentiality with respect to the Confidential Information; or (e) must be disclosed to comply with applicable laws or regulations or with a court or administrative order, as long as the disclosing party receives prior written notice of the disclosure.

4. Ownership; No License. The receiving party acknowledges that the disclosing party (or a third party entrusting Confidential Information to the disclosing party) owns the Confidential Information and all patent, copyright, trademark, trade secret, and other intellectual property rights associated with the Confidential Information. Neither party grants an option, license, or conveyance of any intellectual property rights to the receiving party under this Agreement.

5. Return of Confidential Information; Obligations. At the end of the Term, or earlier at the request of the disclosing party, the receiving party shall return all originals, copies, and summaries of documents, materials, and other tangible manifestations of Confidential Information in its possession or control. However, the receiving party may retain one copy of the Confidential Information in the possession of its legal counsel solely to monitor its obligations under this Agreement. The obligations of this Agreement remain in effect for two (2) years after the Term or earlier return of Confidential Information, except that the obligation of the receiving party to return Confidential Information to the disclosing party survives until fulfilled.

6. Governing Law. This Agreement is governed by and construed in accordance with the laws of the Commonwealth of Massachusetts without regard to conflict of laws provisions.

7. Export Regulations. Each party covenants and warrants to the other that it will not disclose to the other any information that contains information, technology or data identified on any U.S. export control list, including the Commerce Control List and the U.S. Munitions List, unless and until it obtains the written consent of the other party's export control compliance officer.

8. Counterparts. This Agreement may be executed in counterparts and delivered by facsimile or email with the same effect as an original.

IN WITNESS WHEREOF, the parties have executed this Agreement by their duly authorized representatives as of the Effective Date set forth above.

THE UNIVERSITY OF MASSACHUSETTS	MAINE SEED COMPANY
By: [signature]	By: [signature]
Name: RAJNISH KAUSHIK	Name: Tate A McPherson
Title: Licensing & Bus. Dev. Manager, CVIP	Title: Owner 100%
Date: Sep 30, 2014	Date: 9-27-14

Appendix V

CONFIDENTIAL DISCLOSURE AGREEMENT

This Agreement, effective as of January 27th, 2016 ("Effective Date"), is between the **University of Massachusetts,** as represented by its Lowell Campus ("UOM"), located at 1 University Avenue, Lowell, Massachusetts, 01854, and **Ashland Inc.** ("Ashland"), located at 5200 Blazer Parkway, Dublin, Ohio 43017.

Within one (1) year after the Effective Date (the "Term"), the parties intend to exchange and evaluate confidential information relating to a **possible collaboration between UOM and Ashland related to the preparation and use of vinyl ester resins made from bio-based raw materials during an update meeting scheduled on Feb. 5th, 2016,** and commercial applications of such technology, so that each party may evaluate a potential research collaboration, licensing transaction and/or a new business venture.

In consideration of each party making Confidential Information available to the other party, the parties agree as follows:

1. "Confidential Information" means any technical or business information furnished by one party to the other pursuant to this Agreement that is specifically designated as confidential. The disclosing party shall clearly mark written Confidential Information with a legend indicating its confidential status. All orally and visually disclosed Confidential Information will be identified as Confidential at the time of presentation. The disclosing party shall document Confidential Information that is disclosed orally or visually in a written notice and deliver the notice to the receiving party as soon as possible within thirty (30) days after the disclosure. In the notice, the disclosing party shall summarize the Confidential Information and reference the date, time and place of disclosure.

The subject matter of Ashland's Confidential Information includes, but is not limited to, technical and marketing information related to Ashland's vinyl ester and unsaturated polyester resins. The subject matter of UOM's Confidential Information includes, but is not limited to, the preparation and performance of vinyl ester resins made with bio-based raw materials.

2. Obligations and Limitations.

(a) The receiving party shall maintain Confidential Information in confidence, except that the receiving party may disclose or permit the disclosure of Confidential Information to its directors, officers, employees, consultants, and advisors who are obligated to maintain its confidential nature and who need to know the Confidential Information for purposes of this Agreement. (b) The receiving party may only use and reproduce Confidential Information to the extent necessary to carry out the purposes of this Agreement.

3. Exceptions. The obligations of Section 2 do not apply to the extent the receiving party can demonstrate that Confidential Information:

(a) was publicly known prior to the time of its disclosure under this Agreement; (b) became publicly known after its disclosure under this Agreement through means other than an unauthorized disclosure by the receiving party; (c) was previously known to or independently developed or discovered by the receiving party without use of the Confidential Information; (d) is or was disclosed to the receiving party by a third party having no obligation of confidentiality with respect to the Confidential Information; or (e) must be disclosed to comply with applicable laws or regulations or with a court or administrative order, as long as the disclosing party receives prior written notice of the disclosure.

(b) Disclosures relating to Confidential Information which are specific, e.g., as to operating procedures, process conditions, raw material or product specifications, equipment and control specifications, and the like, shall not be deemed to be within the foregoing exceptions merely because they are embraced by more general information in the public domain, in the possession of the receiving party or received from a third party. In addition, any combination of features shall not be deemed to be within the exceptions merely because the individual features are in the public domain, in the possession of the receiving party or received from a third party, unless the combination itself and its principle of operation are in the public domain, in the possession of the receiving party or received from a third party. Information shown to fall within the foregoing exceptions shall not be identified by the receiving party to any third party as information which is used by or considered proprietary by the disclosing party.

4. Ownership; No License. The receiving party acknowledges that the disclosing party (or a third party entrusting Confidential Information to the disclosing party) owns the Confidential Information and all patent, copyright, trademark, trade secret, and other intellectual property rights associated with the Confidential Information. Neither party grants an option, license, or conveyance of any intellectual property rights to the receiving party under this Agreement.

5. Return of Confidential Information; Obligations. At the end of the Term, or earlier at the request of the disclosing party, the receiving party shall return all originals, copies, and summaries of documents, materials, and other tangible manifestations of Confidential Information in its possession or control. However, the receiving party may retain one copy of the Confidential Information in the possession of its legal counsel solely to monitor its obligations under this Agreement. The obligations of this Agreement remain in effect for five (5) years after the Term or earlier return of Confidential Information.

6. Governing Law. This Agreement is governed by and construed in accordance with the laws of the Commonwealth of Massachusetts without regard to conflict of laws provisions.

7. Export Regulations. Each party covenants and warrants to the other that it will not disclose to the other any information that contains information, technology or data identified on any U.S. export control list, including the Commerce Control List and the U.S. Munitions List, unless and until it obtains the written consent of the other party's export control compliance officer.

8. The receiving party may, if required by a local, state, or federal governmental agency, court or body, disclose Confidential Information protected hereunder to said agency, court or body, provided, however, that prior to release of Confidential Information, the receiving party must inform the disclosing party of the need to disclose the Confidential Information, and that upon disclosure to the agency, court or body, the receiving party must advise the agency, court or body of the confidential status of Confidential Information.

9. Assignment. This Agreement shall be assignable by either party hereto without the consent of the other party, provided the party to whom this Agreement is assigned agrees in writing to be bound by the obligations of this Agreement. Any such assignment shall not relieve the receiving party of its obligations hereunder.

10. Counterparts. This Agreement may be executed in counterparts and delivered by facsimile or email with the same effect as an original.

IN WITNESS WHEREOF, the parties have executed this Agreement by their duly authorized representatives as of the Effective Date set forth above.

THE UNIVERSITY OF MASSACHUSETTS

By:_____
Name: Rajnish Kaushik
Title: Assistant Director, OTC
Date: _____

Rajnish Kaushik
Rajnish Kaushik (Feb 9, 2016)

ASHLAND INC.

JRF

By: _____
Name: Andrew J. Boor
Title: V.P. Composites, North America
Date: Feb. 5, 2016

Appendix W

CONFIDENTIAL DISCLOSURE AGREEMENT

This Agreement, effective as of April 4, 2016 ("Effective Date"), is between the University of Massachusetts, as represented by its Lowell Campus, located at 1 University Avenue, Lowell, Massachusetts, 01854, and **Dixie Chemical Co.**, located at **10601 Bay Area Blvd. Pasadena TX, 77507**.

Within one (1) year after the Effective Date (the "Term"), the parties intend to exchange and evaluate confidential information relating to **Vinyl Ester Resin Composites,** and commercial applications of such technology, so that each party may evaluate a potential research collaboration, licensing transaction and/or a new business venture.

In consideration of each party making Confidential Information available to the other party, the parties agree as follows:

1. "Confidential Information" means any technical or business information furnished by one party to the other pursuant to this Agreement that is specifically designated as confidential. The disclosing party shall clearly mark written Confidential Information with a legend indicating its confidential status. All orally and visually disclosed Confidential Information will be identified as Confidential at the time of presentation. The disclosing party shall document Confidential Information that is disclosed orally or visually in a written notice and deliver the notice to the receiving party as soon as possible within thirty (30) days after the disclosure. In the notice, the disclosing party shall summarize the Confidential Information and reference the date, time and place of disclosure.

2. Obligations and Limitations.

(a) The receiving party shall maintain Confidential Information in confidence, except that the receiving party may disclose or permit the disclosure of Confidential Information to its directors, officers, employees, consultants, and advisors who are obligated to maintain its confidential nature and who need to know the Confidential Information for purposes of this Agreement. (b) The receiving party may only use and reproduce Confidential Information to the extent necessary to carry out the purposes of this Agreement.

3. Exceptions. The obligations of Section 2 do not apply to the extent the receiving party can demonstrate that Confidential Information:

(a) was publicly known prior to the time of its disclosure under this Agreement; (b) became publicly known after its disclosure under this Agreement through means other than an unauthorized disclosure by the receiving party; (c) was previously known to or independently developed or discovered by the receiving party without use of the Confidential Information; (d) is or was disclosed to the receiving party by a third party having no obligation of confidentiality with respect to the Confidential Information; or (e) must be disclosed to comply with applicable laws or

regulations or with a court or administrative order, as long as the disclosing party receives prior written notice of the disclosure.

4. Ownership; No License. The receiving party acknowledges that the disclosing party (or a third party entrusting Confidential Information to the disclosing party) owns the Confidential Information and all patent, copyright, trademark, trade secret, and other intellectual property rights associated with the Confidential Information. Neither party grants an option, license, or conveyance of any intellectual property rights to the receiving party under this Agreement.

5. Return of Confidential Information; Obligations. At the end of the Term, or earlier at the request of the disclosing party, the receiving party shall return all originals, copies, and summaries of documents, materials, and other tangible manifestations of Confidential Information in its possession or control. However, the receiving party may retain one copy of the Confidential Information for archival purposes. The obligations of this Agreement remain in effect for two (2) years after the Term or earlier return of Confidential Information, except that the obligation of the receiving party to return Confidential Information to the disclosing party survives until fulfilled.

6. Governing Law. This Agreement is governed by and construed in accordance with the laws of the Commonwealth of Massachusetts without regard to conflict of laws provisions.

7. Export Regulations. Each party covenants and warrants to the other that it will not disclose to the other any information that contains information, technology or data identified on any U.S. export control list, including the Commerce Control List and the U.S. Munitions List, unless and until it obtains the written consent of the other party's export control compliance officer.

8. Counterparts. This Agreement may be executed in counterparts and delivered by facsimile or email with the same effect as an original.

IN WITNESS WHEREOF, the parties have executed this Agreement by their duly authorized representatives as of the Effective Date set forth above.

THE UNIVERSITY OF MASSACHUSETTS	**DIXIE CHEMICAL CO.**
By:_____	By: _____
Name: Rajnish Kaushik	Name: _____
Title: Assistant Director, OTC	Title: _____
Date: _____	Date: _____

Signature: Rajnish Kaushik
Rajnish Kaushik (Apr 15, 2016)

Email: rajnish_kaushik@uml.edu

Appendix X

Action Item 1:

In an email to Robin Nissan (robin.a.nissan.civ@mail.mil), Lisa Miller (lisamiller@hgl.com), and Sarah Barlow (sbarlow@hgl.com) by December 12, 2014, provide justification for bromination of bisphenol-A.

Email:

We have synthesized two different kinds of vinyl ester resin, a) bisphenol-A based resin (VER) and b) tetrabromobisphenol-A (TBBPA) based resins (Br-VER). We have prepared neat resin panels and carbon fabric reinforced resin panels of VER and Br-VER. We have characterized all these panels thoroughly using cone calorimeter and smoke density testing in flaming and non-flaming conditions. The results suggested that the Br-VER has much lower heat release rate compared with VER. So, Br-VER is suitable for anti-flammability application compared with VER. Currently, Ashland has commercial epoxy vinyl ester resin DERAKANE 510A-40, which is brominated bisphenol-A based and used in building outer structure of NAVY ship.

We have performed bromination of bisphenol A using potassium bromide and bromine in acetonitrile.[i] A. the reaction time is only 5-10 min at room temperature. The TBBPA was synthesized with 99 % yields and high purity. We have used very mild reaction conditions and simple workup. In the current synthetic route, the KBr and solvent can be recovered and reused without any significant loss. Currently, we are studying other possibility of reduces usage of brominated bisphenol A in epoxy vinyl ester resin, at the same time make bromination reaction fast, economical and environmentally less hazardous.

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[i] "Instantaneous, Facile and Selective Synthesis of Tetrabromobisphenol A using Potassium Tribromide: An Efficient and Renewable Brominating Agent" Kumar, L., Sharma, V., Mahajan, T., and Agarwal, D. D., Organic Process Research & Development 14, 174–179, (2010).

Appendix Y

Dr. Yongwoo Lee
Research Professor of Chemistry
University of Massachusetts Lowell

To,
Dr. Robin Nissan,
Program Manager for Weapons Systems and Platforms
Strategic Environmental Research and Development Program (SERDP)
4800 Market Center Drive, Suite 17D08
Alexandria, VA 22350-3605
Phone: 571-372-6399
E-Mail: robin.a.nissan.civ@mail.mil

Subject: Response to Action Item on "Uptake of water, hydraulic fluids, or hydrocarbon fuels by Green Vinyl Ester Resins (GVER)".

Dear Dr. Nissan,

We have received list of action items after the first in-progress review meeting of SERDP WP-2317 on "Sustainable Green Vinyl Ester Resin". Herein, as a reply to the Action Item-III, we have investigated uptake of water, hydraulic fluids, or hydrocarbon fuels by our cured carbon fabric reinforced Derakane Momentum 411-350 and Derakane 510A-40. In future, these will be used as a reference to compare with liquid uptake values of Green Vinyl Ester Resin (GVER).

Action Item 1:

In an email to Robin Nissan (robin.a.nissan.civ@mail.mil), Lisa Miller (lisamiller@hgl.com), and Sarah Barlow (sbarlow@hgl.com) by January 9, 2015, address whether you will be considering the uptake of water, hydraulic fluids, or hydrocarbon fuels by your vinyl ester resins.

Response:

Generally vinyl ester resin possesses strong resistance to jet fuel, mineral oils and water. Initially, we were very much focused on the mechanical and flammability properties of the green vinyl ester resin. After receiving the list of action item regarding water, hydraulic fluid and hydrocarbon fuels uptake of vinyl ester resin; we realized that the water, hydraulic fluid and hydrocarbon fuels uptake are very critical parameter for evaluating performance of green vinyl ester resin as we have targeted application for them in building ships for US Navy. So, we will peruse water, hydraulic fluid and hydrocarbon fuel uptake studies at UML and NAVAIR.

Our collaborator, NAVAIR has performed series of experiments for fluid uptake on commercial carbon fabric reinforced Derakane Momentum 411-350 and Derakane 510A-40 as can be seen in Enclosure 1. The fluids used included deionized (DI) water, toluene, mineral spirits, isopropanol, hydraulic fluid (MIL-PRF-5606), and lubricating oil (MIL-PRF-7808). The baseline specimens were weighed after immersion for 24 hours, 7 days, and 14 days. The initial trend suggested that compared with brominated VER and non-brominated VER had high resistance to water, oil, aliphatic and aromatic solvents.

Fluid uptake by GVER will be investigated at UML and NAVAIR. For testing, cured specimen of Derakane Momentum 411-350 and GVER will be prepared following ASTM D570-98. We will investigate water, hydraulic fluid and hydrocarbon fuels uptake by Derakane Momentum 411-350 and Derakane 510A-40 and GVER. UML has just started study of fluid uptake by VER, so we are in middle of procuring several solvents and preparing proper setup for accurate liquid uptake studies. We

will report a detailed dataset in next IPR. The next interim report will also contain initial analysis of water uptake of VER. The detailed work-plan of UML with timeline is attached as Enclosure 2.

Please let us know your suggestions and comments.

Sincerely,

Yongwoo Lee
(January 09, 2015)

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Encl. 1: NAVAIR report on liquid uptake of commercial VERs.
Encl. 2: UML work-plan on uptake of water, hydraulic fluids, or hydrocarbon fuels by Green Vinyl Ester Resins (GVER).

Dr. Yongwoo Lee
Research Professor of Chemistry
University of Massachusetts Lowell

NAVAIR report on liquid uptake of commercial VERs

Objective

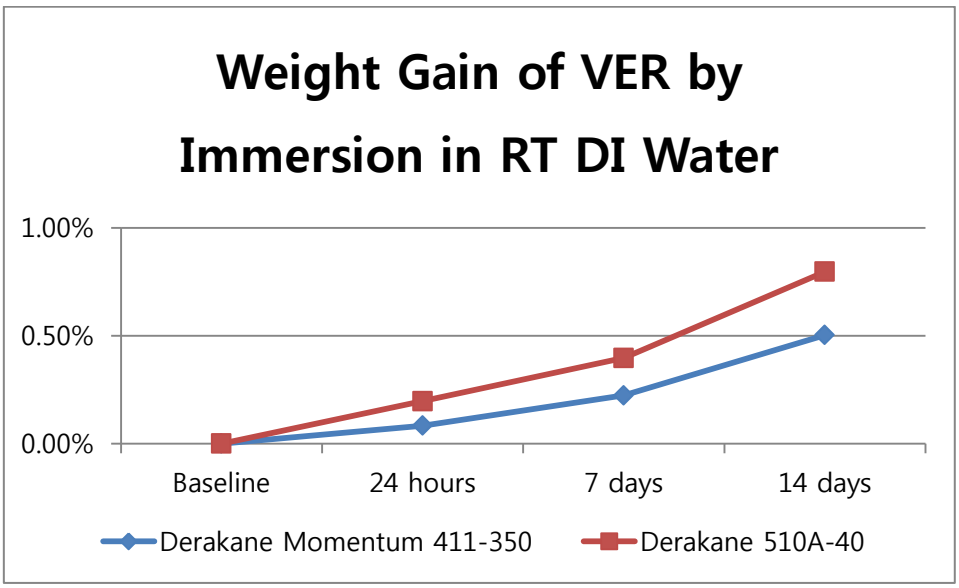
This study seeks to compare the fluid uptake properties of two commercially available composite resins, Derakane Momentum 411-350 and Derakane 510A-40. Fluids studied include common solvents and chemicals frequently used in aerospace applications.

Methods

Beginning with panels of composite already fabricated according to the VARTM process, small specimens were cut, dried, and weighed to establish a baseline moisture content. Then, three specimens of each resin type (for a total of 36 specimens) were immersed in a jar of each fluid. The fluids used included deionized (DI) water, toluene, mineral spirits, isopropanol, hydraulic fluid (MIL-PRF-5606), and lubricating oil (MIL-PRF-7808). The baseline specimens were weighed after immersion for 24 hours, 7 days, and 14 days. The resulting weights were recorded and percent weight gain calculated based on the baseline measurements. These results are shown as averages of the three specimens for each condition.

Data

After two weeks, the weight gain of each resin type ranged from 0.02% to almost 7%, depending on the fluid used. The results can be seen in the following six charts, one for each fluid type, contrasting the weight gain of Derakane Momentum 411-350 with that of Derakane 510A-40. In general it appears that Derakane 510A-40 tends to absorb more fluid than Derakane Momentum 411-350, but the effects of this tendency on the resin's mechanical properties are unknown.



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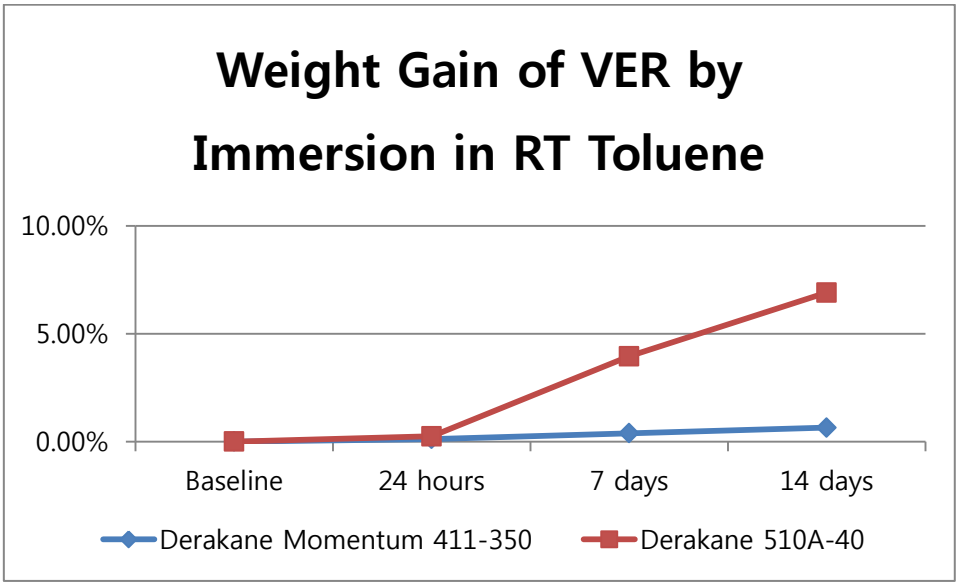

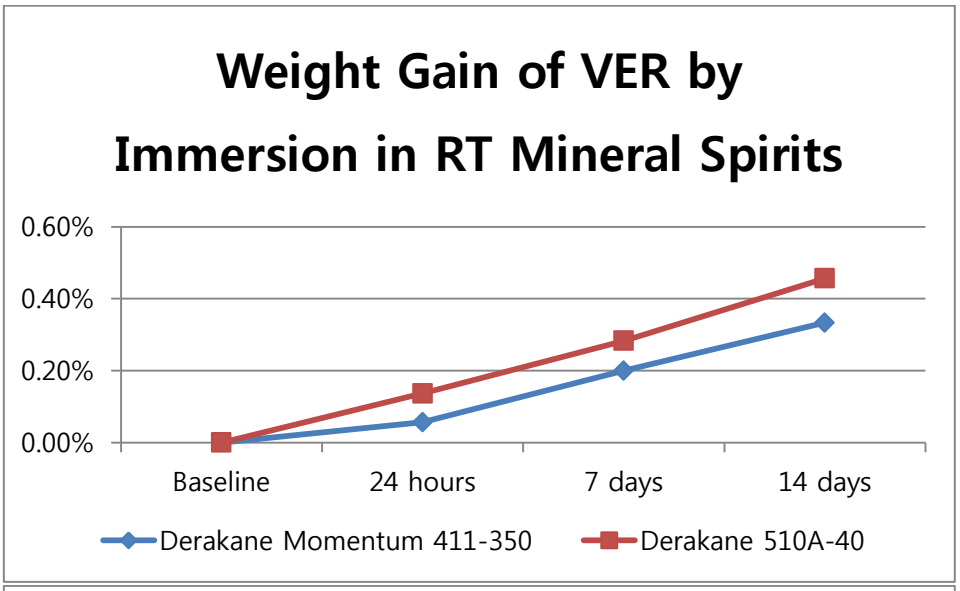

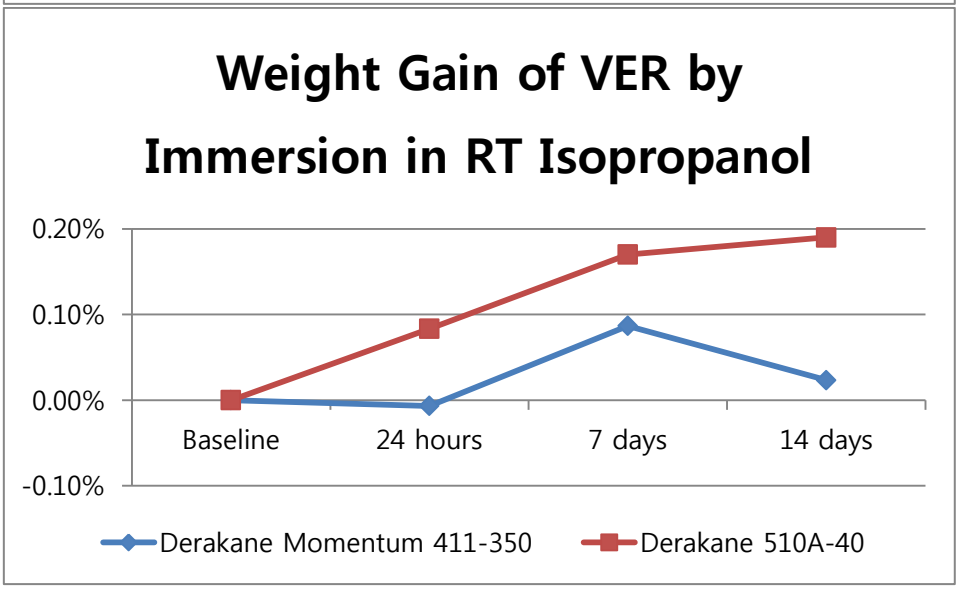

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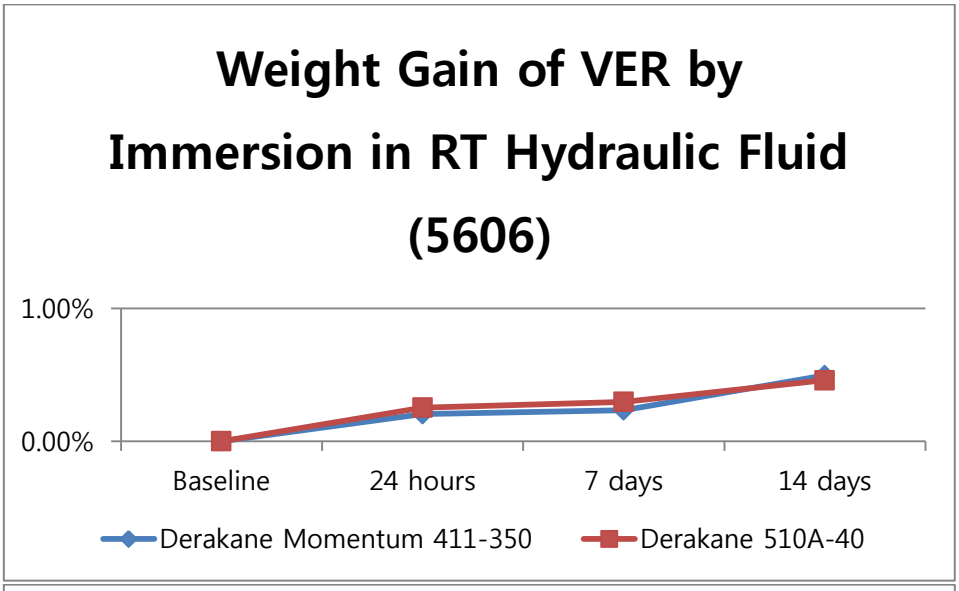

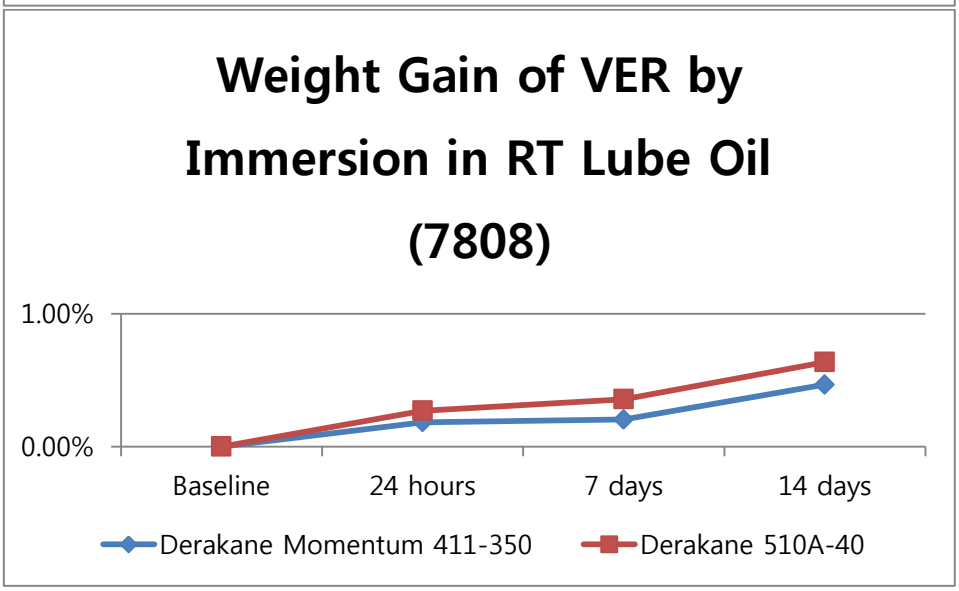

Future Directions

In order to further determine the fluid uptake properties of these vinyl ester resins, the immersion studies will be continued until 30 days have elapsed in total. Additional studies recommended include measuring moisture saturation in a humid environment and conducting further immersion studies in which the fluids are heated to speed diffusion. To establish the impact of fluid uptake on resin properties, mechanical testing could also be performed. This mechanical testing should include a batch of short beam shear testing of the dried specimens prior to fluid conditioning, as well as a batch of testing after a defined fluid exposure.

Dr. Yongwoo Lee
Research Professor of Chemistry
University of Massachusetts Lowell

UML work-plan on uptake of water, hydraulic fluids, or hydrocarbon fuels by Green Vinyl Ester Resins (GVER).

In Year-II of Phase-II:

- Samples will be prepared meeting criteria described in ASTM-D570 using commercial Derakane Momentum 411-350 (Bisphneol-A based vinyl ester resin) and GVER. The study on fluid uptake of brominated resin will be very limited or can be eliminated as instructed by SERDP.
- A proper study on uptake of water, hydraulic fluid and hydrocarbon fuel will be initiated.
- The obtained results will be presented in quarterly progress reports (QPRs), interim progress reports, and inprogress review meetings.

In Year-III of Phase-II:

- Carbon fabric reinforced samples will be prepared using closed mold vacuum assisted resin transfer molding (VARTM), which meets criteria described in ASTM-D570 using commercial Derakane Momentum 411-350 and Green Vinyl Ester Resin. Closed mold VARTM will provide smooth surface on both sides of the samples.
- A study on uptake of water, hydraulic fluid and hydrocarbon fuel will be completed.

Appendix Z

Selective Depolymerization of Lignin Using Environmentally Benign Approaches for Isolation of High-Value Natural Food Flavoring Agents

1. Objective

In response to SERDP on their action item related to submission of a white paper for additional approaches for optimization of the yield of phenol and other valuable phenolic; we would like to expand depolymerization of lignin using several environmentally benign approaches and selective metal organic frameworks (MOFs)-catalysis for isolation of high value natural flavoring agents and other high value phenolic for various other applications. In pyrolysis, very high temperature is required to achieve the activation energy for depolymerization of lignin. We will use different catalyst to reduce the activation energy for depolymerization and achieve selectivity. Lignin will be procured from various commercial sources as well as our collaborators Flambeau River paper LLC (FRPLLC), (Park Falls, WI) and Maine Seed Company (MSC), (Mapleton, ME). The main source of lignin will be soft wood, hard wood and corn. Moreover, lignin will be identified on the basis of different processes of its isolation. It will be depolymerized by selective-metal catalysis using platinum or lanthanum based catalyst, and several environmentally benign approaches by newly proposed MOF-based catalysis. The product composition obtained by gas chromatography (GC) in each reaction will be analyzed for process and product optimization from technical aspects. The process cost calculation and the market price of the products will be used to examine feasibility of the process from economic aspects.

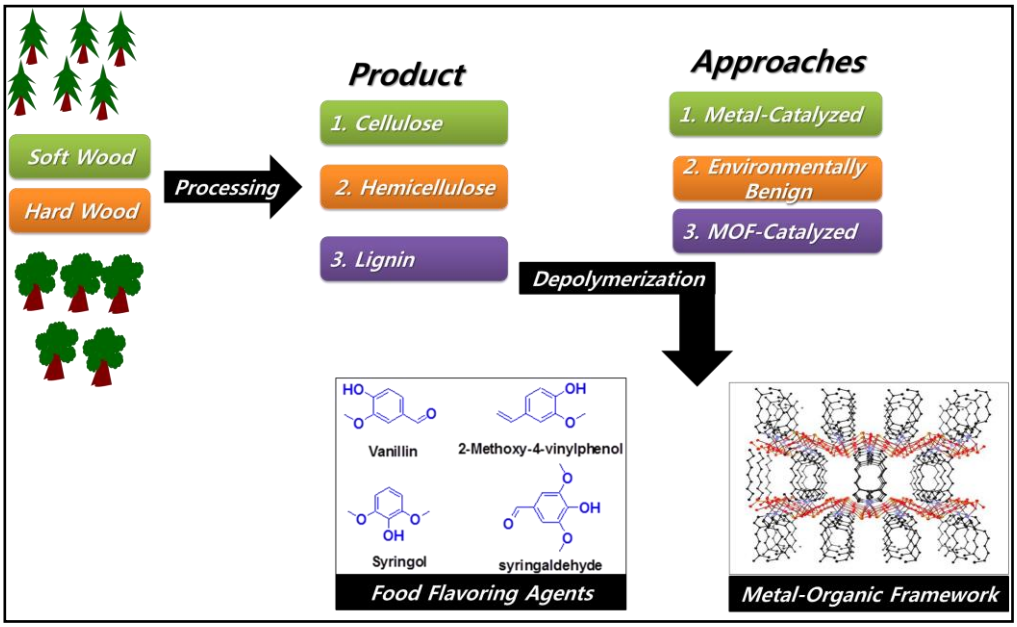

Figure 1. Various Approaches for Depolymerization of Lignin

At University of Massachusetts Lowell, a team lead by Dr. Yongwoo Lee (Principle Investigator) will perform depolymerization of lignin using various approaches. Dr. Lee has expertise in the MOF catalysis, which will be used for the depolymerization of lignin. It is expected that due to unique properties of MOFs such as light weight, high surface area and porous character; they can reduce the activation energy for the depolymerization reaction significantly. FRPLLC and MSC will provide lignin from different sources to UML under the NDA. Different kinds of linkage and bonding in different sources of the lignin will be identified. Depolymerized lignin will be analyzed by GC-MS. The economic aspects of the depolymerization reactions will be analyzed on the basis of the market value of each food flavoring agents by Professor Ryan Bouldin at Bentley University (Waltham, MA). Prof. Seongkyu Yoon at

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Chemical Engineering Department of the UML will support experimental design during the project and conduct process/product optimization with the data obtained.
Specific Technical Objectives of this proposed work will be as follow:

- Finish a preliminary toxicological assessment of different approaches for the depolymerization of lignin that demonstrates environmental compliance and report to SERDP for their approval.
- Selective metal-catalyzed and green MOF-catalyzed depolymerization of lignin to obtain higher amount of food flavoring agents.
- Perform ionic-liquid, microwave, sonication or metal-catalyzed depolymerization and compare the product composition.
- Investigate the market value of the major food flavoring materials isolated during pyrolysis of lignin.
- Perform design of experiment and data analysis for optimizing condition to make depolymerization more economical on the basis of the source of lignin and kinds of product composition obtained.
- Demonstrate conditions and sources, which give highest amount of food flavoring ingredients out of lignin depolymerization.
- Complete and submit a final report to SERDP that documents the successful development on selective metal catalyzed depolymerization of lignin.

During the program, the UML team will work closely with SERDP, Prof. Yoon, Prof. Ryan, MSC and FRPLLC. We will collaborate with different food flavoring companies and various other paper companies to identify different sources of lignin and understand basic industrial demand. Upon successful completion of the limited scope, one year program, UML is expected to have a green and economical pathway of isolation of higher amount of the food flavoring agents by depolymerization of lignin.

The pyrolyzed materials have applications not only as a flavoring agents in food industries, but they are also used as a preliminary building blocks in wide range of resins, which are used in building critical components of US Army vehicles, aircrafts or US Navy ships. As an example, one of the products for the depolymerization of lignin is vanillin, which is used to prepare a vanillin based bisphenol and subsequently used as a precursor for the synthesis of cyanate ester.[i] Because of high glass transition temperature and low dielectric constant, these materials are being widely used in building outer structures of aircrafts. So, while exploring the applications of pyrolyzed materials in food industries, we will continue our efforts in exploring their applications in preparing different material for US Army, US Navy or US Air Force.

2. Background

Current Pyrolysis Setup and its Economic Aspects

The current pyrolysis process has several advantages as well as few disadvantages. The process of pyrolysis consumes high energy and mainly produces phenol, guaiacol, and catechol, which are relatively cheap materials. The feed-stock of the lignin always varies in the composition of the softwood and hardwood, which makes it extremely difficult to maintain similar product composition every-time. The lignin is basically composed of different kinds of monomeric units such as p-hydroxyphenyl, guaiacyl, and syringyl. Hardwood generally have higher amount of methoxy content compared with softwood.[ii] Currently, we are working on the optimization of the pyrolysis process and using the gases and char generated at the end of the pyrolysis as fuel for heating of the pyrolysis apparatus.

Selective Metal-Catalyzed Depolymerization

The higher selectivity of depolymerization of lignin can be achieved using various kinds of metal-based catalysis systems. During metal-catalysis, the activation energy for depolymerization can be decreased to great extent; as a result, mild reaction condition can be achieved. Various approaches have been employed for depolymerization of lignin as mentioned in Table 1. Generally, metal-catalysis targeted the C–O and C–C cleavages of the lignin in presence of hydrogen sources like ethanol or water. Moreover,

solid catalysts such as nickel provided accessible metal sites in the external surface for occurrence of chemical reactions. Metal-catalysis not only increased the selectivity but also decreased the reaction temperature, which makes process more economical.[iii]

Table 1. Catalytic depolymerization of lignin and their conditions and product formation.

No	Lignin	Catalyst	Temperature (°C)	Products
1[iv]	Kraft lignin	Si-Al catalyst ZrO_2-Al_2O_3-FeO_x	200–350	Phenols, methoxyphenol
2[v]	Lignosulfonate	Ni/C, NiLa/C, NiPt/C, NiCu/C, NiPd/C, and NiCe/C	200	methoxyphenols
3[vi]	Corn stalk lignin	Pt/C, Pd/C, Ru/C	200–250	4-Ethylphenol 4-Ethylguaicol

MOF and Zeolytic Imidazolate Framework (ZIF) have large surface area (i.e., 2,000 - 5,000 m^2/g) and offer very attractive compositional flexibility, which results in catalytic materials with tailored surface area, pore size volume and distribution. Different adsorptive and reactive strengths can be achieved by varying the chemical composition (backbone of the linker) from aromatic to amine based hydrocarbon.[vii] Benzenetricarboxylic acid complex of Cu (II) and Fe (III) was used as a catalyst for depolymerization of lignin.[viii] BASF has demonstrated that aluminum based MOF Basolite A520 is non-toxic, environmentally benign, synthesized in water and can be easily scaled up for industrial application.[ix] We will use Basolite A520 kinds of MOF as catalysts for depolymerization of lignin.

Environmentally Benign Depolymerization Methods

Several environmentally benign approaches such as sonication, microwave or ionic-liquid based depolymerization of lignin have expanded scope of the work by maintaining safer environment and generation of high value food flavoring agents. (a) Microwave catalyzed depolymerization as described in Table 2. (b) The degradation of lignin using ultrasound irradiation also yielded interesting results and reported degradation mainly by rupturing of the aromatic skeletal. [x] (c) Ionic liquid has been used for selective depolymerization of lignin as described in Table 2.

Table 2. Environmentally benign approaches for depolymerization of lignin.

No	Lignin	Approach	Catalyst	Products
1[xi]	Organosolv olive tree lignin	Microwave catalyzed (140 °C)	Ni, Pd, Pt, or Ru supported by Mesoporous Al-SBA-15	Syringaldehyde, vanillin
2[xii]	*Pinus radiata* lignin	Ionic liquid catalyzed (250 °C)	1-butyl-3-methylimidazolium acesulfamate	Methoxyphenols
3[xiii]	Organosolv beech lignin	Ionic liquid catalyzed (100 °C)	1-ethyl-3-methylimidazolium-trifluoromethansulfonate with $Mn(NO_3)_2$	2,6-Dimethoxy-1,4-benzoquinone

Process Optimization

The structure of lignin is extremely complex and it varies from source to source of wood. The product composition obtained at the end of the depolymerization reaction has a wide range of phenolic products; as a result, the depolymerization of lignin is extremely complex procedure. To optimize the process by carefully selecting all resources will help to make process more economical. Design of Experiment (DOE) will be used to screen important resources from process economics perspective and find optimum operating conditions. After performing the depolymerization of the lignin using different methods and determining the composition of each reagent by GC analysis; the data will be analyzed with regression analysis and multivariate statistics. The extensive data analysis will help us in optimizing the reaction conditions. Secondly, the cost analysis will be performed for several processes.

In conducting experimentation, we will use the methodologies of the design of experiment for identification of important resources, product/process optimization and robustness test by (a) *Screening Design*. As the final product quantity and quality are affected by various sources material and process

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conditions, it is important to identify important sources of variability. We will first try to collect information on what is experimentally possible, and how one should proceed to exert some kind of influence on the investigated system or process. We will determine dominating factors and their optimal ranges. In general, 80% of the effects on the responses are caused by 20% of the investigated factors. These strong factors are the ones we want to identify with the screening design. (b) *Optimization Design*. This step is to extract in-depth information about the few dominating factors. This will be achieved with designs of the composite family, which support quadratic polynomial models by encoding between three and five levels of each factor. A quadratic model is flexible and may closely approximate the true relation between the factors and the responses. We have to conclude that the experimental region explored is unlikely to contain the optimum. In such a situation, it is warranted to move the experimental region into a domain more likely to include the desired optimal point. (c) *Robustness testing*. Robustness testing is carried out before the release of an almost finished product, or analytical system, as a last test to ensure quality. We will identify factors, which might have an effect on the result and regulate them in such a manner that the outcome is within given specifications. Usually a fractional factorial design or Plackett-Burman design is used.

Several Reactions for Converting Depolymerized Lignin to High Value Product.
Many one step simple organic reactions can generate more high value products from the intermediates isolated during depolymerization of lignin such as (a) syringaldehyde; gives spicy, smoky, hot and smoldering wood aromas; can be isolated by one step Duff reaction from syringol.[xiv] (b) bisphenol A from phenol, (c) cyanate esters from vanillin, (d) Guaifenesin (Robitussin®) from guaiacol and many more. So, by several simple organic reactions one pyrolyzed material can be easily converted to more economical products.

3. Technical Approach

The University of Massachusetts, Lowell (UML) proposes to develop a method for selective depolymerization of lignin in order to get high value food flavoring agents such as vanilla; syringol, syringolaldehyde (smoky aroma); and 2-methoxy-4-vinylphenol (buckwheat aroma) and drug apocynin. The depolymerization will be performed by selective catalysis, which will increase yield of high value food flavoring agents. The process will be optimized from the technical and economic aspects as well. The main technical approaches will be as follow

- Preliminary Toxicological Assessment
- Metal-catalyzed depolymerization of lignin
- MOF-catalyzed depolymerization
- Environmentally benign depolymerization using microwave, sonochemistry, or ionic liquids.
- Process/product optimization and robustness analysis
- Examining economic aspect of the process
- Reporting

We have mentioned that we will perform depolymerization of lignin through different environmentally benign ways. We will eliminate/reduce the usage of any hazardous reagent during depolymerization process. Before starting depolymerization of the lignin; a detailed toxicology assessment will be performed for all synthetic protocol. A report will be written and submitted to SERDP for their approval for depolymerization of lignin.

3.1 Task 1. Metal-Catalyzed Depolymerization of Lignin.
UML will perform selective metal catalyzed depolymerization of different lignin obtained from various commercial and collaborative resources for comparison purpose. Lignin will be depolymerized using (a) metal based catalysis systems made up of platinum or lanthanum supported on different substrate materials. The metal-based selective catalysis of different lignin will reduce the activation energy for

depolymerization and (b) Metal-organic framework catalysis, as green MOF Basolite A520 has excellent heterogenous catalysis properties due to very high surface area and a pore size.

3.2 Task 2. Environmentally Benign Approaches for Depolymerization of Lignin.

In order to reduce the activation energy for the depolymerization we will attempt several environmentally benign approaches such as (a) microwave assisted and (b) sonication induced depolymerization in presence of green MOF and (c) ionic liquid catalyzed depolymerization.

3.3 Task 3. Analysis, Purification and Process Optimization

(a) *Analysis and Process Optimization*: UML has already optimized a gas chromatography method for the analysis of the pyrolyzed lignin. The results obtained by GC-MS will confirm the amount of food flavoring agents in total pyrolyzed materials. Prof. Seongkyu Yoon will optimize the process by methodology of design of experiment by i) screening design, ii) optimization design and iii) robustness testing. The economic aspects will be examined using different sources by Prof. Ryan Bouldin. (b) *Purification*: The food flavoring agents will be isolated by solvent extraction using standard followed by distillation of the pyrolyzed material.

3.4. Task 4. Reporting and Management

UML will compile and submit Quarterly Reports and a Final Report detailing the results of Phase I feasibility work. An assessment of feasibility determination will be presented.

4. Program Schedule and Milestones

Task Description	Months after Contract Award									
	1	2	3	4	5	6	7	8	9	10
Task 1 – Metal-Catalyzed Depolymerization of Lignin										
Sub-Task 1.1 – Metal-Catalyzed										
Sub-Task 1.2 – MOF-Catalyzed										
Task 2 – Environmentally Benign Approaches for Depolymerization of Lignin.										
Sub-Task 2.1 – Microwave-based										
Sub-Task 2.2 – Ultrasound-based										
Sub-Task 2.3 – Ionic-liquid-based										
Task 3 – Analysis and Purification of Depolymerized Products										
Sub-Task 3.1 – GC-MS Analysis of Solvent Extracted Product										
Sub-Task 3.2 – DOE for Screening, Optimization and Robustness										
Sub-Task 3.3 – Process Cost Calculation										
Task 4 – Reporting and Management										
Final Milestone										
1 – Preliminary Toxicological Assessment of Depolymerization Processes.										
2 – Metal and MOF-Catalyzed System Optimization										
3 – Environmental Benign Approaches Optimization										
4 – Isolation of Pure Food Flavoring Agents and Characterize by ^{1}H NMR										

5. Cost

The total cost of this limited scope, 10-month duration project is $150,000.

6. Research Team

Dr. Yongwoo Lee, Research Professor at the University of Massachusetts, Lowell, MA (UML), will be the Principal Investigator. He will be assisted by Dr. Priyank Shah, a research chemist at UML, currently reporting to Dr. Lee. Polymer Consultant, Dr. Robert F. Kovar, will provide guidance regarding various depolymerization processes and expand new scope of the work by exploring possible usage of other phenolic isolated in food flavoring industries as well as some military composite materials. Professor Seongkyu Yoon at department of chemical engineering will perform the Design of Experiment and Data Analysis for process optimization. Professor Ryan Bouldin at Bentley University will examine economic aspects of the process.

Appendices

i. Abbreviated Curriculum Vitae

(a) Curriculum Vitae of Dr. Yongwoo Lee, Principal Investigator.

Yongwoo Lee is a research professor at UMass-Lowell (Dept. of Chemistry, Olney Hall 520, 265 Riverside St., Lowell MA 01854); Yongwoo_Lee@uml.edu.

Lee has recently worked on development of a protective suit utilizing highly selective enzyme-based self-decontaminating materials for comprehensive protection against chemical attacks, an area he researched for many years as principal senior scientist at QinetiQ North America. Dr. Lee also has extensive research experience in optically active NLO materials and flexible polymer transistors. Lee received his PhD in chemistry from Case Western Reserve University. Prior to his doctoral training, he worked for KAIST as a synthetic-organic chemist on multistep synthesis of antibiotic ß-lactam. He also worked for over 15 years at major national research institutions: BF-Goodrich (Brecksville OH), Los Alamos National Laboratory (NM), MIT (Cambridge, MA), and US Naval Research Laboratory (Washington DC). While at the Naval Research Laboratory, he and his research team were recognized with the 37th Alan Berman Research Award (2006) and NRL Edison Award (2005) for work leading to three breakthroughs US patents on development of specialty enzyme-based catalytic self-decontaminating materials ("Self-cleaning fabrics for decontamination," March 2005 *Materials Today*). Lee has 12 US patents and more than 30 peer-reviewed papers, including the following:

SELECTED PATENTS.

1. Y. Lee et al. US 2010 / 0081186 A1, "Self-decontaminating Metal Organic Framework (SD-MOF)" (published April 2010)
2. Y. Lee et al. Serial numbers 12/802,995,-956,-960, "Sorption-Reinforced Catalytic Coatings System and Method for the Degradation of Threat Agents" (issued on Aug. 23rd 2013)
3. Y. Lee et al. Serial numbers 12/802,956, "Sorption-Reinforced Catalytic Coatings System and Method for the Degradation of Threat Agents" (issued on Aug. 23rd 2013)
4. Y. Lee et al. Serial numbers 12/802960, "Sorption-Reinforced Catalytic Coatings System and Method for the Degradation of Threat Agents" (submitted July 2010)
5. Y. Lee et al. Serial number 61/455,504, "Metal Organic Framework-Supported Enzymes and Their Incorporation into Active Decontaminating Fabrics" (submitted Oct 2010)
6. Y. Lee et al. 7,501,259, "Method for making catalytic enzyme-modified textiles for active protection from toxins" (2009)
7. Y. Lee et al. 7,348,169, B2, "Method of making bioactive catalytic material" June 2008
8. Y. Lee et al. 7,270,973, B2, "Catalytic enzyme-modified textiles for active protection from toxins," Sept. 2007
9. Y. Lee et al. 7,067,294, "Catalytic surfaces for active protection from toxins" B2, June 2006

SELECTED PUBLICATIONS:

1. Y. Lee, "Dynamic Nanocomposite Self-Deactivating Fabrics for the Individual and Collective Protection," 25th Army Science Conference Proceeding, Orlando FL, Dec. 2006
2. Y. Lee, "Self-Decontaminating & Self-Repairing Enzyme-Bearing Polymeric Substrates-CPS," 2006 Scientific Conference on Chemical & Biological Defense Research Proceeding
3. W.J. Dressick, Y. Lee and A. Singh, "Self-Cleaning Fabrics for Decontamination of Organophorous Pesticides and Related Chemical Agents," *Advanced Materials* 2004.
4. W.J. Dressick, Y. Lee and A. Singh, "Self-Cleaning Catalytic Filters against Pesticides and Chemical Agents," *NRL Review* 2004

(b) Curriculum Vitae of Dr. Robert F. Kovar, Senior Polymer Consultant

Dr. Kovar is a Principal Scientist with more than 40 years of experience in the synthesis, processing and application of advanced polymeric materials. He is a specialist in applying high temperature thermoset and thermoplastic polymers to the development of new and improved fuel cell membranes and polymeric coatings. Dr. Kovar's research team developed thermally stable, VARTM-processed AFR-700 composites for advanced aircraft.

Dr. Kovar has been the Principal Investigator the following successful SBIR programs:

1. "Non-Thermal Deicing/Anti-icing Coating for Rotary Wing Aircraft Leading Edge" – Contract No. N68335-08-C-0293.
2. "Low VOC, Chromium-Free, Flexible Coating" – Contract No. FA9550-07-C-0124.
3. "High Temperature VARTM Resin and Process" – Contract No. FA9550-07-C-0101.
4. "Bonding Agent for Rocket Propellants" – Contract No. N00178-08-C-3019.
5. "Light-Cured Anti-tamper Coating"– Contract No. W31P4Q-08-C-0274.
6. "Casualty Patient Warming Device" – Contract No. N00014-05-C-0388.
7. "Photolytically Stable PBO Fiber for Titan Aerobot – NASA Order No. NNX08CB98P.
8. "Shelf-Stable Adhesive For Composite Repair" – Contract No. F33615-98-C-5652.
9. "Microencapsulated Phase Change Materials" – Contract No. DACA42-03-R-00 .
10. "Advanced Composite Body Armor" - Contract No. DAAK60-90-C-0108.
11. "Interface-Modified Thermoplastic Composites" - Contract No. N00014-89-C-0283.
12. "Biaxially-Oriented LaRC-CPI Polyimide Film" - Contract No. NASI-18846.
13. "Low Cost PBZT Synthesis" - Contract No. F33615-87-C-5341.
14. "PBZT/Sol-Gel Microcomposites"- Contract No. F49620-87-C-0022.
15. "High Compressive Strength PBO/Sol-Gel Fibers" - Contract No. F33615-89-C-5636.
16. "High Compressive Strength Composites" - Contract No. DAAH01-91-C-R012.
17. "Applications of Ordered Polymers" - Contract No. F33615-84-C-5101.
18. "ElastiGlass Barrier Film" – NASA Order No. NNJ06JD60C.

Selected Patents:

1. "Composite solid polymer electrolyte"; US Pat. 6248469; March 3, 1999.
2. "Composite solid polymer electrolyte membranes"; US Pat. 7052793;(Dec. 2000).
3. "No VOC radiation curable resin compositions"; US Pat. 6894084; February 12, 2001.
4. "Protective coating underwater applicator"; US Pat. 6422777; August 24, 2000.
5. "Polyester/vinyl dioxolane based coating compositions"; US Pat. 6150429; and US Patent 6150429;November 2.
6. "Polyester/polyurethane vinyl dioxolane coating"; US Pat. 6300457; November 2, 1999.
7. "Polyester/vinyl dioxolane coating"; US Pat. 5977269; October 30, 1997.
8. "Method for preparing interpenetrated polymer films"; US Pat. 5501831; (1994).
9. "Ordered polymer/sol-gel microcomposite laminates"; US Pat. 5296296; June 1991 and US Pat. 5344703; (1993).
10. "Poly(quinoxalinobisimidazonaphthyldiimide) polymers"; US Pat. 3740374.
11. "Oriented semicrystalline polymer films"; US Pat. 5264534; October 31, 1991.
12. "Interpenetrated polymer fibers"; US Pat. 5168011; June 14, 1989.

Dr. Kovar received his Ph.D. in Chemistry from the University of Massachusetts (Amherst, MA) and B.S. in Chemistry from the Polytechnic Institute of Brooklyn (Brooklyn, NY). He is a member of the American Chemical Society, Materials Research Society and the American Association for the Advancement of Science. He holds more than 30 patents and is an author on at least 51 publications. Dr. Kovar completed the short course entitled, *"Fundamentals of Explosives",* presented by Professor Jimmie Oxley at the University of Rhode Island (2009).

(c) Curriculum Vitae of Dr. Priyank Shah, Co-Principle Investigator (Co-PI)

Dr. Priyank Shah is a Research Fellow at Department of Chemistry at U-Mass Lowell. He has expertise in synthesis of polymer with controlled architectures such as block, graft and star polymers with well-defined molecular weights and molecular weight distributions. He also has worked on living anionic, living cationic, atom transfer radical polymerization and various other polymerizations techniques. He has extensively worked on various chiral polymers and unveiled various interesting phenomenon. He received his Ph.D. in Materials Science and Engineering, Gwangju Institute of Science and Technology, Korea in 2007, and M.Sc. in Applied Chemistry from India in 2006. He has been working as a Research Fellow at UML since May' 2012. He has seventeen articles as a first and coauthors, one Korean patent and four invention disclosures to his credit.

Korean Patent.

- I.-K. Sung, W.-S. Hwang, H.-S. Kim, J.-S. Lee, B. Kang, J. Min, P. N. Shah, S. Kumar, Product Mixed Copolymer, Triblock Polymers and Star polymer from Aromatic Vinyl Monomer and Conjugated Diene Monomers and Synthesis of the Same. *Kr patent*, Publication No. 10-0995681-00-00.

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- P. N. Shah, J. Min, and J.-S. Lee, Chiroptical Properties of Graft Copolymers Containing Chiral Poly(n-hexyl isocyanate) as a Side Chain, *Macromolecules*, **2011**, *44*, 7917-7925.
- P. N. Shah, J. Min and J.-S. Lee, ''Governing Initiation-Supporting Termination'' in Chiral Poly(n-hexyl isocyanate), *Chem. Commun*., **2011**, *48*, 826-828. (Selected for Journal Back Cover)
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- S. Kumar,* P. N. Shah,* S. Ahn, W. S. Hwang, I. K. Sung, S. R. Shah, C. N. Murthy, T. Chang, and J.-S. Lee, Mechanistic Pathway for the Formation of Radial Polystyrenes Using Diacyl Chloride, *Macromolecules*, **2012**, *45*, 2675−2681. (*equal contribution)
- Y. Rho, J. Min, J. Yoon, B. Ahn, S. Jung, K. Kim, P. N. Shah, J.-S. Lee and M. Ree, Reversible Conformation-Driven Order-Order Transition of Peptide-Mimic Poly(*n*-alkyl isocyanate) in Thin Films via Selective Solvent-Annealing, *NPG Asia Materials*, **2012**, 4, e29.
- X. Wei, K. Bagdi, L. Ren, P. N. Shah, K. Seethamraju, and R. Faust, Polyisobutylene-based Thermoplastic Polyurethanes Exhibit Significant Phase Mixing, *Polymer*, **2013**, 54, 1647-1655.
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- X. Wei, P. N. Shah, K. Bagdi, K. Seethamraju, R. Faust, Enhancing Mechanical Properties of Polyisobutylene-based Thermoplastic Polyurethanes by Adjusting Catalyst Concentration, *J. Macromol. Sci., Part A Pure and Applied Chemistry*, **2014**, *51*, 6-15.
- C.-G. Chae, P. N. Shah, J. Min, H.-B. Seo, J.-S. Lee, Synthesis of Novel Amphiphilic Polyisocyanate Block Copolymer with Hydroxyl Side Group, *Macromolecules*, **2014**, *47*, 1563–1569.
- P. N. Shah,* C.-G. Chae,* J. Min, R. Shimada, T. Kakuchi, T. Satoh, J.-S. Lee, A Model Chiral Graft Copolymer Demonstrates Evidence of the Transmission of Stereochemical Information from the Side Chain to the Main Chain on a Nanometer Scale, *Macromolecules*, **2014**, DOI: 10.1021/ma500544b. (*equal contribution).
- S. Banerjee, P. N. Shah, Y. Jeong, T. Chang, K. Seethamraju, R. Faust, Structural Characterization of Telechelic Polyisobutylene Diol, *J. of Chromatography A*, doi:10.1016/j.chroma.2014.12.022

(d) Curriculum Vitae of Professor Seongkyu Yoon

Dr. Yoon is assistant professor at Department of Chemical Engineering, and Biomedical Engineering and Biotechnology at University of Massachusetts Lowell (UML). He is also a Co-Director of Mass BioManufacturing Center and Founder of Biopharmaceutical Process and Quality Consortium at UML. He joined the University of Massachusetts in 2010 with the New Faculty Award from the Massachusetts Life Sciences Center. He was also awarded the Science and Technology seed fund from the University of Massachusetts President's Office in 2011. With the seed grant, he started the new consortium (Biopharmaceutical Process and Quality Consortium). He is now conducting research projects with NSF (National Science Foundation, Award # DBI-1429212), US FDA (Food and Drug Administration, Grant Number: 1U01FD005294-01), and collaborative researches with several pharmaceutical companies including Pfizer, BiogenIdec, Lonza, and Vertex Pharmaceuticals,. He will contribute to this project in the area of experimental design and data analysis for process/product optimization. Dr. Yoon received his PhD from University of Hamilton, Canada in 2001. Before joining UML as a professor; he had worked with Biogen Idec Biopharmaceutical Inc., Cambridge MA (2005-2010), Umetrics, Kinnelon NJ, (2001-2005), and Hyundai Petrochemical Co., Daesan, South Korea (1990-1996).

Patents

1. Provisional Patent on Estimation of Viable Cell Density During Late Growth Phase of CHO Cell Culture Using Dielectric Spectroscopy (Inventor: Seongkyu Yoon and Haewoo Lee) – Turn down
2. Provisional Patent (M&E Ref. 118082-00801) on Distributed perfusion bioreactor system for continuous culture of biological cells (Inventors: Olivier Berteau, Apicells; David Sergeant: Ipratech; Seongkyu Yoon: UMass Lowell)
3. WP-2317 Sustainable Green Vinyl Ester Resin (GVER) for Renewable Resources (Inventor: Akshay Kokil, Priyank Shah, Seongkyu Yoon, Robert Kovar, Yongwoo Lee)

Selected Publications.

1. Lee, H., A. Christie, J. Starkey, E. Read, S Yoon (**2014**), Intracellular metabolic flux analysis of CHO cells supplemented with wheat hydrolysates for improved mAb production and cell-growth, Journal of Chemical Technology and Biotechnology (2014), 29 SEP 2014, DOI: 10.1002/jctb.4523
2. Lee, H., J Carvell, K. Brorson, and S. Yoon **(2014**), Dielectric spectroscopy-based estimation of VCD in CHO cell culture, Journal of Chemical Technology and Biotechnology, 23 SEP 2014 DOI: 10.1002/jctb.4522.
3. Ali Yousefian Jazi, Jun-Hyung Ryu, Seongkyu Yoon, J. Jay Liu (**2014**), Decision Support in Machine vision system for monitoring of TFT-LCD glass substrates manufacturing, Journal of Process Control **(**2014**)**, pp. 1015-1023 DOI information: 10.1016/j.jprocont.2013.12.009
4. Bhoskar, P., B. Belongia, R. Smith, S. Yoon, T. Carter, and J. Xu **(2013),** Free Light Chain Content in Culture Media Reflects Recombinant Monoclonal Antibody Productivity and Quality, Biotechnology Progress, DOI:10.1021/btpr.1767
5. Kamga, M, H. Lee, J. Liu, S. Yoon **(2013)** Quantification of Protein Mixture in chromatographic separation using Multi-wavelength UV spectra, Biotechnology Progress 29(3), 664-71
6. Yoon, S., H. Lee, J. Liu, **(2013),** Quality Characterization and Classification of Engineered Stone Countertops Using Soft-sensor Based on Image Analysis I&EC **DOI:** 10.1021/ie303442r
7. Lee H., C. Lawton, Y. Na and S. Yoon **(2013),** Robustness of Chemometrics-based Feature Selection Methods in Early Cancer Detection and Biomarker Discovery, Statistical Application in Genetics and Molecular Biology, 12(2), 207–223
8. Lee, H., A. Bawn, S. Yoon **(2012)** Reproducibility, Complementary Measure of Predictability for Robustness Improvement of Multivariate Calibration Models via Variable Selections, Analytica Chimica Acta, 757 11-18

ii. List of Acronyms

- UML – University of Massachusetts, Lowell, MA
- MOF - Metal-Organic Framework
- BU - Bentley University
- FRPLLC - Flambeau River Paper LLC
- MSC - Maine Seed Company

iii. Supporting Technical Data

Pyrolysis of lignin using helium.

Currently, we are working on the pyrolysis of lignin in our lab under SERDP-WP-2317. We have successfully developed a setup for lignin pyrolysis. We will continue working on the pyrolysis of lignin and trying to develop an efficient purification method as well. The current lignin pyrolysis setup is shown in Figure 2.

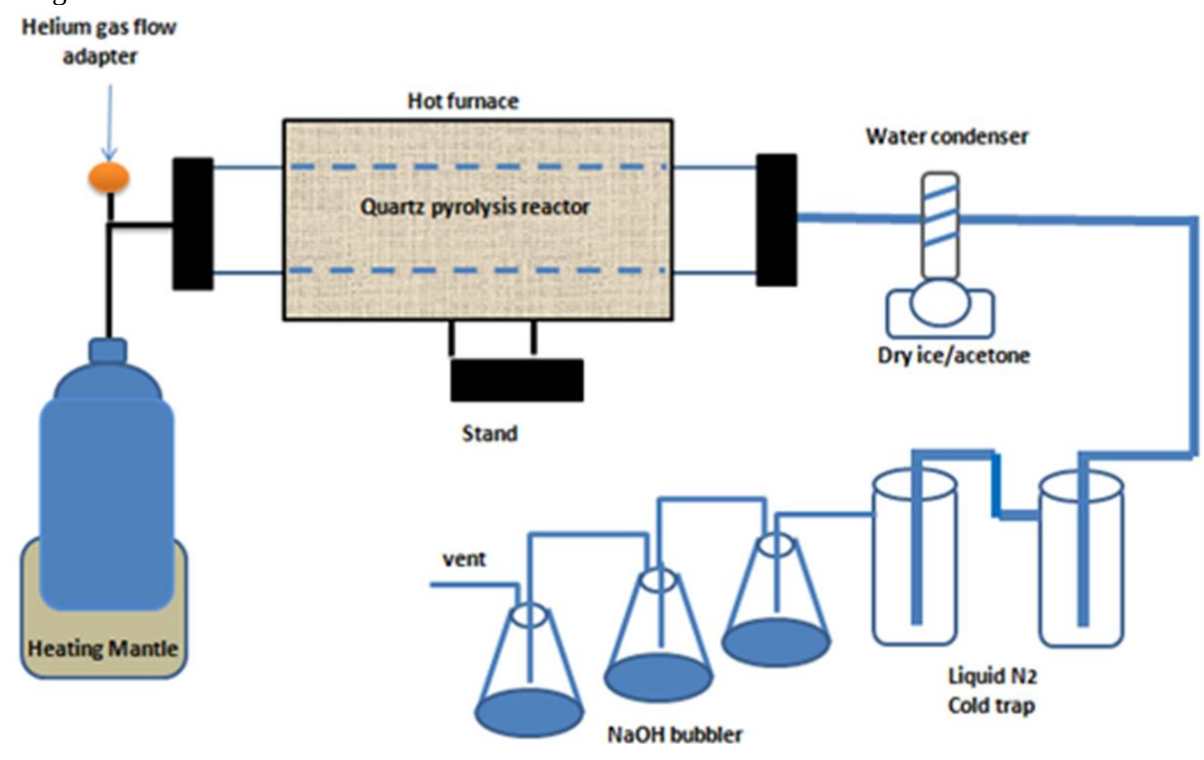


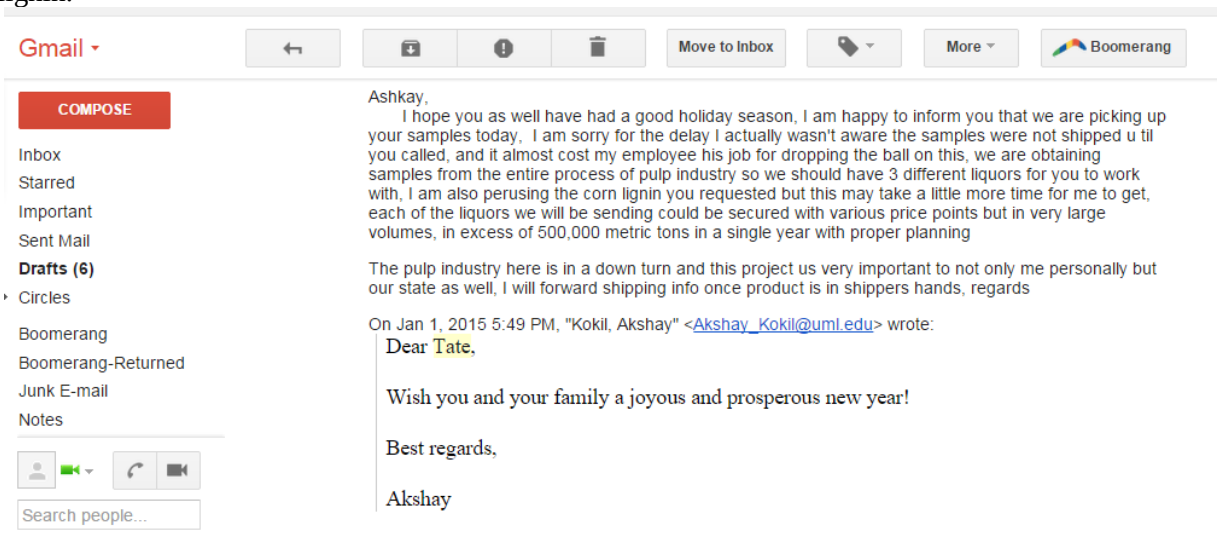
Figure 2: Helium Gas-Flow Based Pyrolysis System at UML.

The pyrolysis of lignin is a simple process, which involve huge energy consumptions. We have proposed several environmentally benign approaches using green catalysts, which will reduce the activation energy for depolymerization and will make the process more green and economical.

iv. Existing Support

(a) We have signed NDA with Flambeau River Paper LLC, and they are going to supply us dried lignosulfonate as much as we need.

(b) We have signed NDA with Maine Seed Company, who are going to provide us different kinds of lignin.



Gmail

Move to Inbox | More | Boomerang

COMPOSE

Inbox
Starred
Important
Sent Mail
Drafts (6)
Circles
Boomerang
Boomerang-Returned
Junk E-mail
Notes

Search people...

Ashkay,

I hope you as well have had a good holiday season, I am happy to inform you that we are picking up your samples today, I am sorry for the delay I actually wasn't aware the samples were not shipped u til you called, and it almost cost my employee his job for dropping the ball on this, we are obtaining samples from the entire process of pulp industry so we should have 3 different liquors for you to work with, I am also perusing the corn lignin you requested but this may take a little more time for me to get, each of the liquors we will be sending could be secured with various price points but in very large volumes, in excess of 500,000 metric tons in a single year with proper planning

The pulp industry here is in a down turn and this project us very important to not only me personally but our state as well, I will forward shipping info once product is in shippers hands, regards

On Jan 1, 2015 5:49 PM, "Kokil, Akshay" <Akshay_Kokil@uml.edu> wrote:

Dear Tate,

Wish you and your family a joyous and prosperous new year!

Best regards,

Akshay

(c) We have collaborated with:

- ✓ Dr. Seongkyu Yoon, who will provide us help with experimental design and data analysis for imporatant resoiurce identification, process optimization and product robustness testing.
- ✓ Dr. Ryan Bouldin at Bentely University will help us in making the depolymerization process more economical by performing process cost calculation.
- ✓ Dr. David Ryan, who will help us with all analytical techniques.

(d) Letter of Support from Prof. Yoon.

Confirmation of support for the SERDP invited white paper

Inbox x Yongwoo Lee x

Yoon, Seongkyu 8:06 AM (5 hours ago)

to Yongwoo, me

Dear Professor Lee,

I acknowledge that I am listed as a co-PI (or Sr person) and/or major contributor of the proposal entitled "Selectively Depolymerization of Lignin Using Environmentally Benign Approaches for Isolation of High-Value Natural Food Flavoring Agents" of Massachusetts Lowell. I agree to undertake the tasks assigned to me, as described in the proposal, and I commit to provide or make available the resources therein designated to me.

Regards, -
Seongkyu Yoon, PhD
Assistant Professor, Dept of Chemical Engineering / BMEBT Program
Coordinator, Biopharmaceutical Consortium
Co-Director, Mass BioManufacturing center
Univ. of Massachusetts Lowell
1 University Ave. Lowell MA 01854
T: 978-934-4741

v. Literature Citations

[i] B. G. Harvey, A, J. Guenthner, H. A. Meylemans, S. R. L. Haines, K. R. Lamison, T. J. Groshens, L. R. Cambrea, M. C. Davisa and W. W. Laia, "Renewable thermosetting resins and thermoplastics from vanillin" *Green Chem.*, DOI: 10.1039/c4gc01825g **(2015)**

[ii] J. H. Grabbe, J. Ralph, R. D. Hatfield , and S. Quideau, "p-Hydroxyphenyl, Guaiacyl, and Syringyl Lignins Have Similar Inhibitory Effects on Wall Degradability" *J. Agric. Food Chem.*, 45 (7), 2530–2532 **(1997)**

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[iv] T.Yoshikawa,T.Yagi, S. Shinohara et al., "Production of phenols from lignin via depolymerization and catalytic cracking," *Fuel Processing Technology*, 108, 69–75, **(2012)**

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[xii] A. Pinkert, D. F. Goeke, K. N. Marsh, and S. Pang, "Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids," *Green Chemistry*, 13, 3124–3136, **(2011)**

[xiii] K. St¨ark, N. Taccardi, A. B¨osmann, and P. Wasserscheid, "Oxidative depolymerization of lignin in ionic liquids," *Chem-SusChem*, 3, 719–723, **(2010)**

[xiv] C. F. H. Allen and G. W. Leubner, "Syringic aldehyde", *Org. Synth.; Coll.* 4: 866 **(1963)**

Appendix AA

Appendix E. Biosphenol A Alternatives

There has been increasing concern over bisphenol A (BPA) as an endocrine-disrupting chemicals and its possible effects on human health[15]. BPAs are easily found in plastics, food packages and other products. Scientists, regulators, and the general public have raised concerns about the use of BPA when exposed continuously. As manufacturers have begun to remove BPA from their products, there has been a gradual shift of these analogs-bisphenol S (BPS) and biophenol F (BPF). BPS is used for a variety of industrial applications such as fastening agent in cleaning products, an electroplating solvent, and a constituent of phenolic resin. BPF is also used in many field such as epoxy resins and coatings application. This lead marketing trend so called "BPA-free" to comply the demand of new safe alternative with a BPA. Recent review evaluated the physiological effects and endocrine activities of the BPA substitutes, BPS and BPF. *Johanna et al.* identified the literature (25 in vitro, 7 in vivo studies) reporting BPS and BPF as hormonally active as BPA. They concluded that BPS and BPF have a endocrine-disrupting effects[16] like BPA based on the literature survey.

Most recently, a patent application was submitted on the development of another bisphenol alternative derived from renewable substituted phenolics. In particular, vanilyl alcohol and guaiacol could be derived from lignin and combined to produce a bisphenol alternative, bisguaiacol F (BGF). This new compound is anticipated to have significantly reduced toxicity relative to bisphenol A (BPA), a known endocrine disruptor. Eposyamine, vinyl ester, methacrylates, and polycarbonates can be prepared from BGF. The resulting polymers have slightly lower thermal properties relative to bisphenol A polymers, likely due to the loss of the rigidizing methyl groups on the methyl bridge connecting the phenyl units[17].

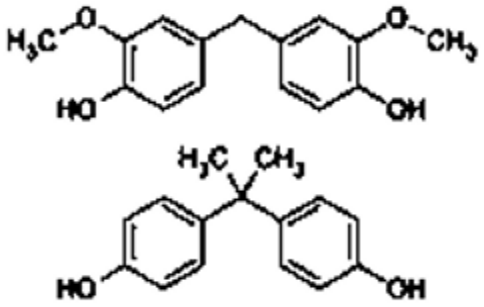

Figure 18. Chemical Structure of bisguaiacol F (BGF, top) and bisphenol A (BPA, bottom)

Appendix AB

EEM-EHS
Environmental Health and Safety

Handling Cobalt Naphthenate

Standard Operating Procedure

SOP Number:	Revision Number: 1	Date of Last Revision: 07/18/2014

Name: Yongwoo Lee and Priyank Shah

Attach description of process that involves the use of cobalt naphthenate.
Please add information about closing the fume hood sash completely after vacuum oven is on in the fume hood.

1.0 Hazards Associated with Cobalt Naphthenate:

Inhalation:

Cobalt Naphthenate is a combustible liquid, suspect carcinogen, as well as a skin and respiratory sensitizer. Target organs are the thyroid, heart, maile reproductive system, and blood. Cobalt metal powder is a known allergen that produces characteristic symptoms of asthma, such as wheezing, dry cough, and labored breathing. Usually the asthma symptoms appear 4-6 hours after exposure and often worsen again later in the same day. Even later asthma reactions to inhaled cobalt may occur up to 48 hours after exposure. Improvement typically occurs when cobalt exposure ceases, e.g. weekends, vacations. Other cobalt-containing compounds such as hard metal dust, but not cobalt powder itself, are associated with sub-acute fibrosis alveoli is and chronic diffuse interstitial pulmonary fibrosis. Causes mild respiratory irritation. Symptoms are more typically seen at air concentrations exceeding the recommended exposure limits. Symptoms of exposure may include irritation (nose, throat, respiratory tract) and central nervous system depression (dizziness, drowsiness, weakness, fatigue, nausea, headache, unconsciousness, possible death. Reports have associated repeated and prolonged overexposure to solvents with permanent brain and nervous system damage (sometimes referred to as Solvent or Painter's syndrome).

Inhalation:

May cause headache, dizziness, nausea, vomiting, gastrointestinal irritation and central nervous system depression.

**Aspiratorion hazard: Small amounts of this product aspirated into the respiratory system during ingestion or vomiting may cause mild to severe pulmonary injury, possibly progressing to death.

Skin Contact:

Based on data for Cobalt metal powder, may cause allergic contact dermatitis if there is prior sensitization. Most rashes associated with cobalt occur on the hands and appear within the first year of occupational exposure to cobalt. Exposure may cause skin irritation. Prolonged or repeated exposure may dry the skin. Symptoms may include redness, burning, drying and cracking, and skin damage. Pre-existing skin disorders may be aggravated by exposure to this material. May cause skin defat with prolonged exposure.

Eye Contact:

May cause irritation.

2.0 Controls:

2.1 Engineering Control:

- Utilize a fume hood.

2.2 Administrative Controls:

- Do not work alone in the lab.
- Implement the buddy system.
- Receive laboratory-specific training on the hazardous procedure.
- Read the applicable safety data sheets and standard operating procedures before performing the hazardous procedure
- Purchase only enough material needed to complete an experiment.
- Wash hands thoroughly with soap and water after removing gloves.
- If gloves become contaminated with one of the chemicals, remove gloves immediately and wash hands with soap and water. Check hands for any signs of contamination.
- Launder lab coats on a periodic basis. (Lab coats that are dropped off for cleaning in the lab coat room are picked up on Monday mornings by the lab coat company and the clean lab coat is delivered to the lab coat room the following Monday. Go to http://www.uml.edu/EEM/Programs/Lab-Safety.aspx and click on lab coat program for more information.)

2.3 Personal Protective Equipment:

2.3.1 Hand Protection

- Wear two layers of disposable nitrile rubber gloves, which must be inspected prior to use especially when handling the pure compounds. Change out top glove layer with new gloves whenever there is visible contamination to avoid chemical permeation and contact. The salts of many heavy metals are toxic or highly toxic and rated as poisons.
- Medium to heavy weight Viton®, polyethylene vinyl alcohol, SilverShield or neoprene gloves. (Refer to a glove compatibility chart and/or contact Kathi Lyon at extension 42746.)
    - NOTE: Gloves must be selected on the basis of their chemical resistance to the material(s) being handled, their suitability for the procedures being conducted as well as temperature extremes. Improper selection may result in permeation of the chemical through the glove and possible personal exposure to the chemical.

2.3.2 Eye Protection

- Safety glasses or safety goggles. If a risk of splashing is present, a face shield must be worn to protect the face and safety glasses or safety goggles must be worn underneath the face shield to protect the eyes.

2.3.3 Skin and Body protection

- A lab coat must be worn.
- Closed toe shoes and pants

3.0 Precautions:

- Avoid contact with eyes and skin.
- Avoid inhalation of vapor or mist.

4.0 Storage and usage:

- Keep container(s) tightly closed. Use and store this material in a cool, dry, well-ventilated area away from heat, direct sunlight, hot metal surfaces, and all sources of ignition. Store only in approved containers. Keep away from any incompatible material (oxidizers).
- The material will be used only inside of the hood and once the coupons made out the material will be placed in ovens, the hood sash will be closed completely. Samples will be in the oven for 2 hours, we will post a sign on the fume hood sash stating that it is on and the hazards of this material.

5.0 Disposal:

Place the UMass Lowell Hazardous Waste Label on the container and fill out the label. Full and/or dated containers of hazardous waste are picked up by EEM-EHS during the weekly inspection checks for satellite accumulation areas or upon request by calling 42543. Remember, the container must be picked up within 3 days after the container is full or dated. Since weekly inspection checks occur every Wednesday, please call extension 42543 for a pick-up if your full and/or dated container of hazardous waste is generated on a Thursday, Friday, or Saturday.

NOTE: Gloves that are not contaminated with Cobalt Naphthenate may be disposed of in the trash. Gloves, KimWipes, and other solid waste contaminated with Cobalt Naphthenate must be disposed of as hazardous waste. Please place contaminated solid waste in an impervious, properly labeled container. Contact the chemical receiving stockroom at extension 42543 if in need of a waste container.

6.0 Emergency Procedures:

6.1 Spills

For spills that occur inside of a fume hood (< 100 milliliters)

- If lab group has received proper training and a proper spill kit is available, the spill may be cleaned up by the lab group.
- If the lab group has not received proper training and a spill kit is not available, please contact EEM-EHS at extension 2618.

For spills that occur outside of a fume hood

- Evacuate the lab, post a restriction on the lab door and call UMass Lowell Police at extension 44911.
- Stay close by to answer questions when EEM-EHS and emergency response personnel arrive.

6.2 First Aid

For eyes

- Irrigate the eyes for 15 minutes, holding eyelids apart.
- Call extension 44911 or 978-934-4911 from a cell phone to seek medical assistance and then can keep track of the length of time eyes are being irrigated.

For skin

- For full body exposure, remove contaminated clothing and go under the emergency shower for 15 minutes. If bare hands and/or arms are contaminated, rinse area with soap and water for 15 minutes.
- Call extension 44911 or 978-934-4911 from your cell phone immediately to seek medical assistance.

For inhalation

- Remove to fresh air. Seek medical attention immediately. Call extension 44911 or 978-934-4911 from a cell phone.

6.3 Fire:

- Evacuate the lab, pull the nearest fire alarm pull station and then go to a safe area and call extension 44911 or 978-934-4911 from a cell phone. Follow the fire safety evacuation plan.

NOTE: All work-related injuries must be reported immediately to Human Resources (HR) by calling extension 43560. (HR has some forms that will need to be filled out within 48 hours after the incident.) An Incident/Injury Report Form must be filled out and faxed to EEM-EHS at 978-934-4018. [The Incident/Injury Report Form is available on-line at http://www.uml.edu/ehs. Please double click on the link, under quick links, for permits and forms.]

**The buddy, supervisor, or Principal Investigator may fill out the Incident/Injury Report Form while the injured employee follows first aid procedures and seeks medical attention.*

Appendix AC

University of Massachusetts Lowell

EEM-EHS
Environmental Health and Safety

Handling Styrene

Standard Operating Procedure

SOP Number:	Revision Number: 0	Date of Last Revision: 07/29/2014

Name: Yongwoo Lee and Priyank Shah

Styrene is a flammable liquid that is also an irritant, and should be treated with care by researchers. Styrene is a hazard due to peroxide initiation of polymerization. It is generally used as a monomer for radical polymerizations. This compound should be inspected prior to use for peroxide crystals that may have collected around the cap, on the inside, or on the outside of the bottle by a starch iodide test paper. Styrene should be in a secondary container labeled with "peroxide forming chemical," and should be stored in a cabinet with the same label.

1.0 Potential Hazard and toxicity

Acute toxicity

Oral LD50

LD50 Oral - rat - 2,650 mg/kg

Remarks: Behavioral:Somnolence (general depressed activity). Liver:Other changes.

Inhalation LC50

LC50 Inhalation - rat - 4 h - 12,000 mg/m3

Skin corrosion/irritation

Skin - rabbit - Skin irritation

Serious eye damage/eye irritation

Eyes - rabbit - Eye irritation - 24 h

Germ cell mutagenicity

Laboratory experiments have shown mutagenic effects.

Cal-OSHA Permissible Exposure Limit (PEL): 50 ppm (210 mg/m3)

2.0 Controls:

2.1 Engineering Control:

- Utilize a fume hood.

2.2 Administrative Controls:

- Do not work alone in the lab.
- Implement the buddy system.
- Receive laboratory-specific training on the hazardous procedure.
- Read the applicable safety data sheets and standard operating procedures before performing the hazardous procedure
- Purchase only enough material needed to complete an experiment.
- Wash hands thoroughly with soap and water after removing gloves.
- If gloves become contaminated with one of the chemicals, remove gloves immediately and wash hands with soap and water. Check hands for any signs of contamination.
- Launder lab coats on a periodic basis. (Lab coats that are dropped off for cleaning in the lab coat room are picked up on Monday mornings by the lab coat company and the clean lab coat is delivered to the lab coat room the following Monday. Go to http://www.uml.edu/EEM/Programs/Lab-Safety.aspx and click on lab coat program for more information.)

2.3 Personal Protective Equipment:

2.3.1 Hand Protection

- Wear Poly Vinyl Alcohol rubber based gloves, which must be inspected prior to use especially when handling the pure compounds. Change out top glove layer with new gloves whenever there is visible contamination to avoid chemical permeation and contact. The salts of many heavy metals are toxic or highly toxic and rated as poisons.
- Medium to heavy weight Viton® , polyethylene vinyl alcohol, SilverShield or neoprene gloves. (Refer to a glove compatibility chart and/or contact Kathi Lyon at extension 42746.)
    - NOTE: Gloves must be selected on the basis of their chemical resistance to the material(s) being handled, their suitability for the procedures being conducted as well as temperature extremes. Improper selection may result in permeation of the chemical through the glove and possible personal exposure to the chemical.

2.3.2 Eye Protection

- Safety glasses or safety goggles. If a risk of splashing is present, a face shield must be worn to protect the face and safety glasses or safety goggles must be worn underneath the face shield to protect the eyes.

2.3.3 Skin and Body protection

- A lab coat must be worn.
- Closed toe shoes and pants

3.0 Precautions:

- Avoid contact with eyes and skin.
- Avoid inhalation of vapor or mist.

4.0 Storage and usage:

- Keep container(s) tightly closed. Use and store this material in a cool, dry, well-ventilated area away from heat, direct sunlight, hot metal surfaces, and all sources of ignition. Store only in approved containers. Keep away from any incompatible material (oxidizers).
- The material will be used only inside of the hood and once the coupons made out the material will be placed in ovens, the hood sash will be closed completely. Samples will be in the oven for 2 hours, we will post a sign on the fume hood sash stating that it is on and the hazards of this material.

5.0 Disposal:

Place the UMass Lowell Hazardous Waste Label on the container and fill out the label. Full and/or dated containers of hazardous waste are picked up by EEM-EHS during the weekly inspection checks for satellite accumulation areas or upon request by calling 42543. Remember, the container must be picked up within 3 days after the container is full or dated. Since weekly inspection checks occur every Wednesday, please call extension 42543 for a pick-up if your full and/or dated container of hazardous waste is generated on a Thursday, Friday, or Saturday.

NOTE: Gloves that are not contaminated with Styrene may be disposed of in the trash. Gloves, KimWipes, and other solid waste contaminated with Styrene must be disposed of as hazardous waste. Please place contaminated solid waste in an impervious, properly labeled container. Contact the chemical receiving stockroom at extension 42543 if in need of a waste container.

6.0 Emergency Procedures:

6.1 Spills

For spills that occur inside of a fume hood (< 100 milliliters)

- If lab group has received proper training and a proper spill kit is available, the spill may be cleaned up by the lab group.
- If the lab group has not received proper training and a spill kit is not available, please contact EEM-EHS at extension 2618.

For spills that occur outside of a fume hood

- Evacuate the lab, post a restriction on the lab door and call UMass Lowell Police at extension 44911.
- Stay close by to answer questions when EEM-EHS and emergency response personnel arrive.

6.2 First Aid

For eyes

- Irrigate the eyes for 15 minutes, holding eyelids apart.
- Call extension 44911 or 978-934-4911 from a cell phone to seek medical assistance and then can keep track of the length of time eyes are being irrigated.

For skin

- For full body exposure, remove contaminated clothing and go under the emergency shower for 15 minutes. If bare hands and/or arms are contaminated, rinse area with soap and water for 15 minutes.
- Call extension 44911 or 978-934-4911 from your cell phone immediately to seek medical assistance.

For inhalation

- Remove to fresh air. Seek medical attention immediately. Call extension 44911 or 978-934-4911 from a cell phone.

6.3 Fire:

- Evacuate the lab, pull the nearest fire alarm pull station and then go to a safe area and call extension 44911 or 978-934-4911 from a cell phone. Follow the fire safety evacuation plan.

NOTE: All work-related injuries must be reported immediately to Human Resources (HR) by calling extension 43560. (HR has some forms that will need to be filled out within 48 hours after the incident.) An Incident/Injury Report Form must be filled out and faxed to EEM-EHS at 978-934-4018. [The Incident/Injury Report Form is available on-line at http://www.uml.edu/ehs. Please double click on the link, under quick links, for permits and forms.]

**The buddy, supervisor, or Principal Investigator may fill out the Incident/Injury Report Form while the injured employee follows first aid procedures and seeks medical attention.*

Appendix AD

EEM-EHS
Environmental Health and Safety

Synthesis of Glycidyl Methacrylate from Glycidol

Standard Operating Procedure

Yongwoo Lee and Priyank Shah

Date: 11/20/13

Revision Number: 1

Date of Revision: 11/20/13

Write a brief description of what this process is used for here.

To synthesize glycidyl methacrylate (GMA) from glycidol

1.0 Material Requirements:

1.1 Equipment needed for process:

Magnetic stirrer hotplate with a power cord, lab jack, ring stand, mineral oil bath, two thermometers, two magnetic stir bars, 50-mL 3-neck round bottom flask, two ring stand clamps, water cooled condenser, two pieces of plastic tubing (for water-in and water-out), ground glass joint grease, glass stopper, ground glass thermometer adapter, analytical balance, weigh boats, spatulas, Eppendorf pipet, TLC developing chamber, aluminum-backed TLC plates, tweezers, pencil, permanent marker, handheld UV lamp, culture tubes and rack, disposable glass Pasteur pipettes and rubber bulbs, 20-mL glass scintillation vials, disposable glass capillary tubes (10ul), scissors or paper cutter, ruler

1.2 Chemicals needed for process:

Glycidol, methyl methacrylate (MMA), inhibitor compound (i.e. 6-tert-Butyl-2,4-xylenol), catalyst (i.e. potassium cyanide),

1.2.1 Hazards associated with component chemicals:

1.2.2.1 Glycidol: Combustible liquid. Harmful if swallowed or in contact with skin. Causes skin irritation. Causes serious eye damage. Toxic if inhaled. May cause respiratory irritation. Suspected of causing genetic defects. May cause cancer. May damage fertility or the unborn child.

1.2.1.2 Methyl methacrylate: Highly flammable liquid and vapor. Causes skin irritation. May cause an allergic skin reaction. May cause respiratory irritation.
1.2.1.3 6-tert-Butyl-2,4-xylenol: Causes serious eye irritation, causes skin irritation, harmful if swallowed
1.2.1.4 Potassium cyanide: May be corrosive to metals. Fatal if swallowed, in contact with skin or if inhaled. Causes damage to organs. Causes damage to organs through prolonged or repeated exposure.

1.2.2 Hazards associated with chemicals produced:

1.2.2.1 Glycidyl methacrylate: Combustible liquid. Harmful if swallowed or if inhaled. Toxic in contact with skin. Causes skin irritation. May cause an allergic skin reaction. Causes serious eye irritation.

1.2.3 Hazards associated with other chemicals used

1.3 Engineering controls:

The synthesis, Thin Layer Chromatography (TLC), and purification of Bisphenol A product will be conducted in fume hood #4 located in lab room 303 of Olney Hall.

1.4 Administrative controls:

- Do not work alone in the lab.
- Implement the buddy system.
- Receive laboratory-specific training on the hazardous procedure.
- Read the applicable safety data sheets and standard operating procedures before performing the hazardous procedure. Purchase only enough material needed to complete an experiment.
- Wash hands thoroughly with soap and water after removing gloves.
- If gloves become contaminated with one of the chemicals, remove gloves immediately and wash hands with soap and water. Check hands for any signs of contamination.
- Launder lab coats on a periodic basis. (Lab coats that are dropped off for cleaning in the lab coat room are picked up on Monday mornings by the lab coat company and the clean lab coat is delivered to the lab coat room the following Monday. Go to http://www.uml.edu/EEM/Programs/Lab-Safety.aspx and click on lab coat program for more information.)

1.5 Protective equipment needed:

1.5.1 Hand protection: For incidental contact with both, double glove with heavier weight disposable nitrile gloves (11 mil), inspect gloves prior to use, and change the top layer of gloves whenever there is visible contamination to avoid chemical permeation and contact. Use proper glove removal technique (without touching glove's outer

surface) to avoid skin contact. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

1.5.1.1 Handling A

1.5.1.2 Handling B

1.5.2 Eye protection:
Safety glasses or safety goggles. If a risk of splashing is present, a face shield must be worn to protect the face and safety glasses or safety goggles must be worn underneath the face shield to protect the eyes.
1.5.3 Skin and body protection: A lab coat must be worn.

2.0 Procedure:

Glycidol reacted with methyl methacrylate (MMA) in the presence of 6-tert-Butyl-2,4-xylenol as promoter and potassium cyanide as catalyst. The mixture was heated up to 80C for two hours, with the product being distilled off.

Purification: The product is purified by fractional distillation at reduced pressure by controlling temperature and pressure.

Analysis:
Progression of the reaction will be monitored by using Thin Layer Chromatography (TLC). The success of the reaction (i.e. purity of GMA product) will be determined by H^1-NMR (300 MHz).

Clean-up:
Wash any glassware and hardware that is chemically contaminated, collect the rinsate as liquid hazardous waste. Dispose of used and rinsed glass capillaries in sharps waste container. Dispose of used and rinsed glass culture tubes and vials in broken glass container. Be sure to have a funnel for filling the hazardous waste containers. The funnel must be removed and the hazardous waste must be capped right after filling the hazardous waste container.

3.0 Storage:

Store all flammable liquids in a flammable liquid storage cabinet. The non-flammable liquid will be stored in refrigerator or in cabinet.

4.0 Waste Products:

All solid hazardous waste contaminated with acetone must be disposed of in a solid hazardous waste container. See page 30 of the Chemical Hygiene Plan for more information regarding this. Please review pages 30- 45 in the Chemical Hygiene Plan to see if any hexanes used are f, p or u listed wastes.

Place the UMass Lowell Hazardous Waste Label on the container and fill out the label. Full and/or dated containers of hazardous waste are picked up by EEM-EHS during the weekly inspection checks for satellite accumulation areas or upon request by calling 42543. Remember, the container must be picked up within 3 days after the container is full or dated. Since weekly inspection checks occur every Wednesday, please call extension 42543 for a pick-up if your full and/or dated container of hazardous waste is generated on a Thursday, Friday, or Saturday.

Empty containers that once contained phenol and toluene must be disposed of as hazardous waste. Please properly label the empty container with a hazardous waste label.

Contact the chemical receiving stockroom at extension 42543 if in need of a waste containers, hazardous waste labels, secondary containment or have other questions regarding hazardous waste.

5.0 Emergency Procedures:

5.1 Spills

For spills that occur inside of a fume hood (< 100 milliliters)

- If lab group has received proper training and a proper spill kit is available, the spill may be cleaned up by the lab group.
- If the lab group has not received proper training and a spill kit is not available, please contact EEM-EHS at extension 42618.

For spills that occur outside of a fume hood

- Evacuate the lab, post a restriction on the lab door and call UMass Lowell Police at extension 44911.
- Stay close by to answer questions when EEM-EHS and emergency response personnel arrive.

5.2 First Aid

For eyes

- Irrigate the eyes for 15 minutes, holding eyelids apart.
- Buddy must call extension 44911 or 978-934-4911 from a cell phone to seek medical assistance and then can keep track of the length of time eyes are being irrigated.

For skin

- For full body exposure, remove contaminated clothing and go under the emergency shower for 15 minutes. If bare hands and/or arms are contaminated, rinse area with soap and water for 15 minutes.
- Buddy must call extension 44911 or 978-934-4911 from your cell phone immediately to seek medical assistance.

For inhalation

- Remove to fresh air. Seek medical attention immediately. Call extension 44911 or 978-934-4911 from a cell phone.

5.3 Fire:

- Evacuate the lab, pull the nearest fire alarm pull station and then go to a safe area and call extension 44911 or 978-934-4911 from a cell phone. Follow the fire safety evacuation plan.

NOTE: All work-related injuries must be reported immediately to Human Resources (HR) by calling extension 43560. (HR has some forms that will need to be filled out within 48 hours after the incident.) An Incident/Injury Report Form must be filled out and faxed to EEM-EHS at 978-934-4018. [The Incident/Injury Report Form is available on-line at http://www.uml.edu/ehs. Please double click on the link, under quick links, for permits and forms.]

**The buddy, supervisor, or Principal Investigator may fill out the Incident/Injury Report Form while the injured employee follows first aid procedures and seeks medical attention.*

Appendix AE

EEM-EHS

Fast Pyrolysis of Lignin using helium gas flow

Standard Operating Procedure

Yongwoo Lee and Namjoon Kim

Date: 07/17/2014

Revision Number:

Date of Revision: 7/17/2014

Write a brief description of what this process is used for here.

To synthesize phenol from lignin from flash pyrolysis using helium gas flow

1. Material Requirements:

1.1 Equipment needed for process:

Thermolyne 21100 high-temperature tube furnace reactor with thermocouple embedded, ground-glass joint grease, high temperature resistant joint grease, heating mantle (500ml and 250ml ca.) with on/off temperature controller, water-cooled condenser, 1000mL quartz vessel flasks, vertical lift, clear fused quartz tube (25mm ID x 28.8mm OD, 24" length) with a 24/40 female taper joint on each end, two-ring stand and clamps, two dewars for cold trap with glassware, red tubing for line connection, vacuum pump, lignin powders, glass wool, glass adapters, weigh boats, spatulas, 20-mL glass scintillation vials, Whatman filtering paper, THF solvent, methanol, funnel glassware, polyethylene bottles, foil tape and digital weighing scales were prepared for setting up the reaction in/out of the hood and extraction of products afterward.

1.2 Chemicals needed for process:

Available lignin raw materials:

- Alkali form from Sigma Aldrich (#370959)
- De-sugared lignosulfonate from Flambeau River Paper (Power, Liquid)

- Dealkaline form from TCI America (#L0082)
- Alkaline form from TCI America (#L0045)

Tetrahydrofuran, Diethyl ether, Methanol, Acetone, Dry Ice, liquid nitrogen

1.2.1 Hazards associated with component chemicals:

1.2.1.1 Acetone: Highly flammable liquid and vapor. Causes mild skin irritation. Causes serious eye irritation. May cause drowsiness or dizziness.

1.2.1.2 Tetrahydrofuran: Hazardous in case of skin contact (irritant), of eye contact (irritant). Slightly hazardous in case of skin contact (permeator), of ingestion, of inhalation.

1.2.1.3 Dithyl ether: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator)

1.2.1.4 Methanol: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator). Severe over-exposure can result in death.

1.2.2 Hazards associated with chemicals produced:

1.2.2.1 Phenol: Very hazardous in case of skin contact (corrosive, irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (sensitizer, permeator). The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

1.2.2.2 Guaiacol: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator).

1.2.2.3 Catechol: Extremely hazardous in case of skin contact (corrosive, irritant), of eye contact (irritant), of ingestion, of inhalation. Very hazardous in case of skin contact (sensitizer, permeator). The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust

will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness,
watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering

1.2.3 Hazards associated with other chemicals used

N/A

1.3 Engineering controls:

The pyrolysis of lignin will be conducted in fume hood located in lab room 303 of Olney Hall.

1.4 Administrative controls:

- Do not work alone in the lab.
- Implement the buddy system.
- Receive laboratory-specific training on the hazardous procedure.
- Read the applicable safety data sheets and standard operating procedures before performing the hazardous procedure. Purchase only enough material needed to complete an experiment.
- Wash hands thoroughly with soap and water after removing gloves.
- If gloves become contaminated with one of the chemicals, remove gloves immediately and wash hands with soap and water. Check hands for any signs of contamination.
- Launder lab coats on a periodic basis. (Lab coats that are dropped off for cleaning in the lab coat room are picked up on Monday mornings by the lab coat company and the clean lab coat is delivered to the lab coat room the following Monday. Go to http://www.uml.edu/EEM/Programs/Lab-Safety.aspx and click on lab coat program for more information.)

1.5 Protective equipment needed:

1.5.1 Hand protection:

For incidental contact with phenolic compound, double glove with heavier weight disposable nitrile gloves (8 mil), inspect gloves prior to use, and change the top layer of gloves whenever there is visible contamination to avoid chemical permeation and contact. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

1.5.1.1 Handling phenol:

Neoprene or butyl rubber gloves are recommended for extensive use of phenol such as working with the pure material or making solutions.

1.5.1.2. Handling Tetrahydrofuran (THF):

Double glove with heavier weight (8 mil) nitrile gloves (incidental contact) or use 15 mil or heavier nitrile gloves; remove outer glove at once if THF contacts glove

1.5.1.3. Handling Acetone:

Heavier weight (8 mil) natural rubber (incidental contact); for extended contact with acetone the *only* recommended glove type is butyl rubber.

1.5.1.4 Handling Methanol: nitrile gloves; Methanol should never be allowed to make contact with the skin, as it is fairly easily absorbed by the skin. Methanol is a poison.

1.5.1.5 Diethyl Ether:

double glove with heavier weight (8 mil) nitrile gloves (incidental contact) or use 15 mil or heavier nitrile gloves; remove outer glove at once if exposed to diazomethane in ether.

1.5.2 Eye protection:

Safety glasses or safety goggles. If a risk of splashing is present, a face shield must be worn to protect the face and safety glasses or safety goggles must be worn underneath the face shield to protect the eyes.

1.5.3 Skin and body protection:

A lab coat must be worn.

---

2. Procedure:

2.1 Reactor Setup

1. All pyrolysis tube will be connected. One end of quartz pyrolysis tube will be connected to 2-3 trap glassware which is connected to the NaOH bubbler. The other end of quartz tube will be connected to the 3-way adapter for N_2 flow and sample vessel.
2. Place the sample lignin (20~100g) in the quartz vessel flasks(1000ml ca.) with 24/40 female joint in the heating mantle on top of a lab jack in the fume hood. Use high temperature resistant joint grease to make tight sealing for vacuum application.
3. Before turn on the furnace, O_2 gas in the furnace reactor will be removed by Helium flow over 10min.

2.2 Pyrolysis of lignin

4. Turn on the furnace and set reactor temperature at 500C. The quartz pyrolysis reactor will be placed within a cylindrical insulated furnace equipped with heaters, thermocouple and controller. The both side of furnace/reactor tube will be fully covered with glass wool to maintain the temperature during the reaction. The temperature will be measured by a thermocouple embedded and displayed on a pyrometer in a control base.
5. Place the dry ice and acetone on the bottom of water condenser to cool down gaseous vapor pyrolysate.
6. Place the 2-3 liquid nitrogen trap to cool down the trap.
7. Turn on the mantle and heat up to 400C under continuous helium gas flow. Thermocouple will be inserted underneath of vessel in the mantle to maintain the set up temperature by on and off temperature controller.
8. Run pyrolysis ~60min until significant vapor generation stops. The reaction time will be adjusted based on the lignin amount applied in the preheating unit.

2.3 Replacement of vessel after pyrolysis

9. Turn off the mantle and wait to cool down while running helium gas. Vessel is extremely hot.
10. New vessel will be replaced for next run.
11. Turn on the mantle and heat up at 400C to start.
12. Repeat the above pyrolysis procedure until the vapor generation stops.

2.4 Sample collection from the vessel and trap

13. Clean the vacuum grease in 24/40 joint with Kimwipes. Products will be collected through the cold traps immersed in dry ice/acetone (or liquid nitrogen). Product of pyrolysis in the trap will be dissolved with THF (or Methanol) carefully at the end of day work (3~4 sets).
14. Remained materials (Char) in the vessel will be ground with mortar and pestle in the fume hood and will be dissolved with methanol (or THF). Place the ground char mixed with THF in the wide mouth jars with caps (2000ml ca.I-CHEM™). Place the magnetic stirrer inside of jar and spins at least 1 hour in the fume hood to obtain maximum extraction of phenol.
15. Label the samples with different number as planned according to the lab notebook. Name will be given based on the lignin kinds. Quantitative pyrolysis yield will be calculated based on weight measurement after GC-MS analysis.

2.5 Phenol extraction

16. Filtration will be followed by next day with Whatman filter paper in the glass funnel.

17. Filtrate will be concentrated using rotary evaporator at 50C until reach the significant volume decrease and getting the oily crude mixture on both trap and char extracted sample.

2.6. Phenol refinement

18. Concentrated crude mixture obtained from char and trap samples will be placed in the round bottom flask separately. Mix with 100ml of diethyl ether to each flask.
19. Precipitant which is not solubilized with diethyl ether will be filtered out using Whatman filter paper using reparatory funnel (250ml ca.). Insoluble materials has been known to be anhydrosugars, anhydro-oligomers and hydroxyacids (C<10).
20. Bottom layer in the funnel (possible water layer) will be separated from the ether layer on the top which contains our phenol to purify.
21. Concentrate the diethyl ether layer using rotary evaporator. Further purification will be proceed if it is necessary
22. Measure the weight of concentrate for yield calculation. Set apart (100mg) for GC-Analysis to evaluate the extraction yield from original lignin.

2.7 Reactor washing procedure

23. Pyrolysis quartz tube will be cleaned at 600C with air blow for 1 hour.
24. Turn off the furnace (mantle must be turned off before the vessel get disconnected).
25. After day-work (3~4sets), disconnect all the tubing glassware including the trap glassware. Clean with THF (or methanol) for next use. Make sure the tubing path may not blocked by char or crude mixture generated during pyrolysis.
26. Dry overnight in the hood.

Clean-up

Wash any glassware and hardware that is chemically contaminated, collect the rinsate as liquid hazardous waste. Dispose of used and rinsed glass capillaries in sharps waste container. Dispose of used and rinsed glass culture tubes and vials in broken glass container. Be sure to have a funnel for filling the hazardous waste containers. The funnel must be removed and the hazardous waste must be capped right after filling the hazardous waste container.

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3. Storage:

Store all flammable liquids in a flammable liquid storage cabinet.

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4. Waste Products:

Phenol and toluene are u listed hazardous waste so all solid hazardous waste contaminated with phenol and/or toluene must be disposed of in a solid hazardous waste container. Also, acetone is an f listed hazardous waste. All solid hazardous waste contaminated with acetone must be disposed of in a solid hazardous waste container. See page 30 of the Chemical Hygiene Plan for more information regarding this. Please review pages 30- 45 in the Chemical Hygiene Plan to see if any hexanes used are f, p or u listed wastes.

Place the UMass Lowell Hazardous Waste Label on the container and fill out the label. Full and/or dated containers of hazardous waste are picked up by EEM-EHS during the weekly

inspection checks for satellite accumulation areas or upon request by calling 42543. Remember, the container must be picked up within 3 days after the container is full or dated. Since weekly inspection checks occur every Wednesday, please call extension 42543 for a pick-up if your full and/or dated container of hazardous waste is generated on a Thursday, Friday, or Saturday.

Empty containers that once contained phenol and toluene must be disposed of as hazardous waste. Please properly label the empty container with a hazardous waste label.

Contact the chemical receiving stockroom at extension 42543 if in need of a waste containers, hazardous waste labels, secondary containment or have other questions regarding hazardous waste.

5. Emergency Procedures:

5.1 Spills

For spills that occur inside of a fume hood (< 100 milliliters)

- If lab group has received proper training and a proper spill kit is available, the spill may be cleaned up by the lab group.
- If the lab group has not received proper training and a spill kit is not available, please contact EEM-EHS at extension 42618.

For spills that occur outside of a fume hood

- Evacuate the lab, post a restriction on the lab door and call UMass Lowell Police at extension 44911.
- Stay close by to answer questions when EEM-EHS and emergency response personnel arrive.

5.2 First Aid

For eyes

- Irrigate the eyes for 15 minutes, holding eyelids apart.
- Call extension 44911 or 978-934-4911 from a cell phone to seek medical assistance and then can keep track of the length of time eyes are being irrigated.

For skin

- For full body exposure, remove contaminated clothing and go under the emergency shower for 15 minutes. If bare hands and/or arms are contaminated, rinse area with soap and water for 15 minutes.
- Call extension 44911 or 978-934-4911 from your cell phone immediately to seek medical assistance.

For inhalation

- Remove to fresh air. Seek medical attention immediately. Call extension 44911 or 978-934-4911 from a cell phone.

5.3 Fire:

- Evacuate the lab, pull the nearest fire alarm pull station and then go to a safe area and call extension 44911 or 978-934-4911 from a cell phone. Follow the fire safety evacuation plan.

NOTE: All work-related injuries must be reported immediately to Human Resources (HR) by calling extension 43560. (HR has some forms that will need to be filled out within 48 hours after the incident.) An Incident/Injury Report Form must be filled out and faxed to EEM-EHS at 978-934-4018. [The Incident/Injury Report Form is available on-line at http://www.uml.edu/ehs. Please double click on the link, under quick links, for permits and forms.]

**The buddy, supervisor, or Principal Investigator may fill out the Incident/Injury Report Form while the injured employee follows first aid procedures and seeks medical attention.*

Appendix AF

Phenol refinement using purification technique from crude product of lignin pyrolysis and aqueous basic samples from fast pyrolysis using helium gas flow

Standard Operation Procedure

Yongwoo Lee and Namjoon Kim
Date: 07/17/2014
Revision Number:
Date of Revision: 7/17/2014

Objective:

Phenols are very important organic compounds used as starting materials or intermediates for the preparation of many aromatic derivatives. Phenol also found as an important feature in biologically and pharmacologically active substances. Large amount of phenol can be obtained from the pyrolysis of lignin. However, it has small portion from the mixture of pyrolysed lignin product. We would like to increase the yield of recovery of phenol from the various phenolic reaction mixtures using a refinement procedure.

Goal:

Extracted and purified phenol product will be analyzed using GC/MS spectrometry technique. Preliminary experiment showed that lots of background compounds were in the crude reaction mixture of lignin other than phenol itself. We would like to check whether we can reduce the number of peaks generated after the purification step. Or, we would like to see the increment of phenol intensity, semi-quantitatively, with the same retention time in GC/MS.

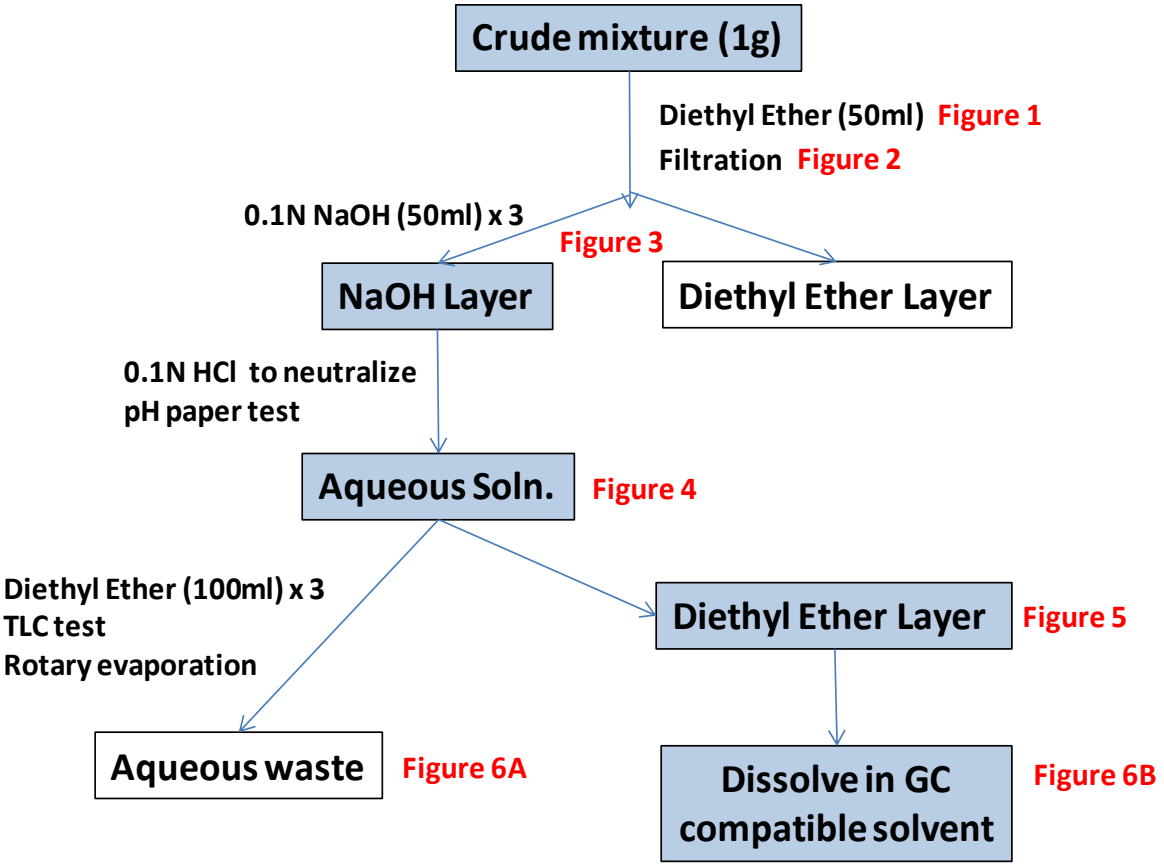
Materials and instruments:

Pyrolysis reaction mixture, diethyl ether, 0.1N NaOH, Separatory funnel (250ml, 500ml) /stopper, 0.1N HCl, pH paper, vials, rotary evaporator /round bottom flask, filter paper and flasks

Experimental procedure:

1. Concentrated pyrolysate of lignin is placed in the round bottom flask bottle (500ml ca.).
2. Diethyl ether (100ml) will be added and mixed
3. Precipitant which is not solubilized with diethyl ether will be filtered out using filter paper in separatory funnel (500ml ca.).
4. 0.1N NaOH will be added and mixed together vigorously. (note: vapor pressure has to be removed carefully). Washing will be done 3 times with same 0.1 NaOH.
5. Aqueous phase will be separated using separatory funnel. Phenolic components will move to the aqueous phase, leaving most of others in the ether layer.
6. 0.1N HCl will be added to neutralize the mixture. Neutralized mixture will be placed in a separatory funnel (500ml ca.).
7. Ether will be added to extract acidified solution. Phenolic compound should be transferred into the ether layer. Wash 3 times with ether. Ether layer will be concentrated with rotary evaporator.
8. The presence of phenol will be tested on TLC plate with fluorescence indicator.
9. Comparison of crude product versus refined product will be made using GC/MS.

* Aqueous basic samples from 0.1N NaOH bubblers will be treated as above (follow from step 6)



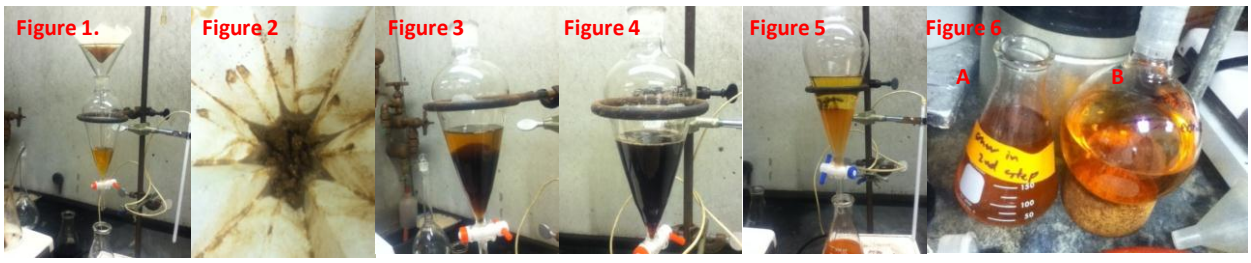


Figure 1: Reaction scheme for refinement of crude mixture dissolved in THF

Appendix AG

Appendix D. Meeting Summary at Main Forum on June 3rd, 2016

Attending Bio Based Maine's 2016 Plants to Products Forum;

Bio based 2016 Maine's 2016 Plants to Products Forum was held in Maine Standard Biofuel (MSB) (Portland, ME) on June 3rd 2016. Dr. Fred Moesler, CTO of Renmatix (Philadelphia, PA) and Dr. Bret Chisholm, Co-founder and CTO of Renuvix LLC (Fargo, North Dakoda), respectively, were invited to give their speeches to small business leaders and manufacturers and seriously discuss the potential for Maine to respond to the global demand for products made from plants, not petroleum.

Renmatix LLC is well-known for a cost-effective process for converting wood chips into cellulosic sugars that can be used as an alternative to fossil fuels. Renuvix LLC is known to develop a method to turn soybeans into nontoxic polymers that can replace unhealthful chemicals in diverse products including paint, plastics, and shampoo.

Attendees: Yongwoo Lee (UML), Alex Pine (Maine Standard Biofuels), Charlotte Mace (Director of Biobased Maine)

Program Highlights

9:45 am:	Video Remarks by Senator Angus King
10:00 am:	Keynote: Fred Moesler, CTO of Renmatix
10:30 am:	Roundtable Discussion #1 (Moderated by Carla Dickstein, CEI) or Tour of Maine Standard Biofuels
11:00am:	Roundtable Discussion #2 (Moderated by Jamie Chittum, Grow-Tech LLC) or Tour of Maine Standard Biofuels
11:30 am:	Lunch
11:45 am:	Biobased Maine Annual Meeting
12:00 pm:	Lunch Keynote: Bret Chisholm, Renuvix LLC
12:30 pm:	Closing Remarks, Mike Bilodeau, Treasurer of Biobased Maine and Director of the Process Development Center and Nanocellulose Pilot Plant at the University of Maine

Appendix AH

Weekly Newsletter Published at Ashland, Philadelphia, PA

The following article was published at Philadelphia based Ashland's production plant, which was sent to Dr. Priyank Shah by Jill Kunsner by email on 5th June 2014.

University of Massachusetts Visits Philadelphia Plant

On Wednesday, 3 chemists from the University of Massachusetts and 4 Ashland employees from Dublin visited the Philadelphia Plant. The chemists are working on a project to produce "green" vinyl ester resins. Basically they are trying to make TBBPA and GMAA from renewable/recycled resources and then to produce vinyl ester resins from these "green" raw materials.

The project is being funded by the Department of Defense and Ashland is one of the industry sponsors for the project. The chemists asked to visit the Philadelphia Plant so they could see a vinyl ester reactor and how vinyl ester resins are made.

The project is in phase 1 of 4 phases so it is a long way from commercially available technology but the chemists are definitely showing positive results. The chemists are schedule to visit our Dublin laboratories later this month.

Sponsoring these types of projects is one way Ashland tries to stay on the forefront of technology in one of our most important product lines.

Appendix AI

University of Massachusetts UMASS Lowell

Summary of the Ashland, Dublin, OH

When : Monday June 23 10am-3.00 pm, 2014 (EDT)
Where : Umass Lowell
Who : Dr. Yongwoo Lee, Dr. Robert F. Kovar, Dr. Priyank Shah, Dr. Namjoon Kim, Dr. Joe Fox, Dr. Charles Lewis, Dr. Bruce Colley, and Dr. Michael Stevens.
Meeting Agenda:

On 23rd June 2014, Dr. Yongwoo Lee, Dr. Namjoon Kim and Dr. Priyank Shah visited Ashland Inc's Dublin based research center. There Priyank presented the work done in the year I of the SERDP WP#2317 in presence of Dr. Joe Fox, Michael Stevens, Bruce Colley, and Dr. Chrlie Lewis. Michael Stevens took all members of UML on the tour of their facility and had a lunch together with Charlie Lewis. During meeting following points were discussed.

- Joe Fox expressed more interested in biodiesel based glycerin compared with soap based glycerin. He also asked price of glycerin from soap industry. Whether it is synthetic commercial or crude? He used to have a joint program with Biodiesel Company in Iowa (renewable energy group using animal fat as a raw material). They produced a lot of glycerin as a byproduct. They could not continue the joint program for a certain reason. He compared the source of glycerin from soap industry.

- Dr. Fox asked about phenol yield from lignin? Dr. Kovar said it is authentic phenol with the yield of 35-40%. It must be all the sum of phenolic compound. We have only 5% (max.) yield of phenol out of total phenolic compounds. Joe has some link to pulp industry. These companies wanted to find the possible alternative use of lignin. Currently, they use the sugar units from lignin. But lignin is not further processed. He may contact with Flamebeau River Paper LLC for their willingness to work in the area of the pyrolysis of lignin and start a phenol manufacturing unit.

- He suggested the Ashland as one of composite building site. He clearly mentioned that they can do the VARTEM for us during the site tour. They have VARTEM system available in their lab facility.

- Dr. Fox also asked the difference between commercial TBBPA vs. our product? How similar or how different in color or purity? He asked about scale expectation of the GVER for the program. For example, Ashland need 3-400 g for resin mechanical testing. Several kg of resin for VARTEM. They also mentioned the viscosity range which has to be set up. For example 100-200 range is the current condition. We have to find the range for validation and optimization.

- They showed their willingness to fabricate some composites coupons as Ashland and investigate its properties.

- They will have internal meeting to evaluate the feasibility of the project, and what role can Ashland play in advancing this technology with the joint filling of IP and signing Cooperative Research and Development agreement (CRADA).

- They showed concerns regarding the unreacted -OH in the final GVER and informed that we should try to achieve 100 % conversion without any side reactions; such as, involvement of the secondary -OH in the ring opening of epoxy.