Environmentally Friendly High Performance Bio-Based Composites for DoD Applications

SERDP WP-1758 and SERDP WP-2402

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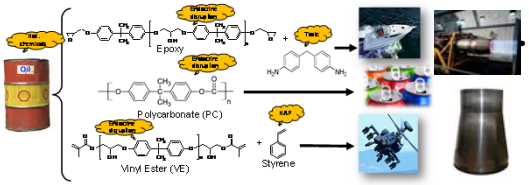
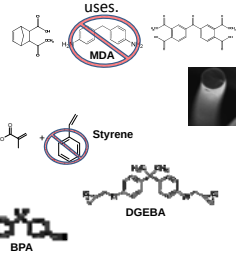
High Performance Polymers are NOT Sustainable:

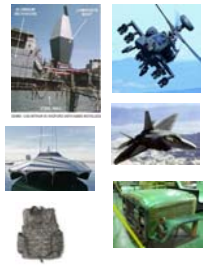


- Toxicity poses added cost to government in increased production costs and decreased competition and prohibition in new uses.
- ~20,000 lbs/yr PMR-15 usage which contains 4,4'-methylenedianiline (MDA), a liver toxin and carcinogen for aircraft parts requiring high temp durability.
- 100M lbs/yr Carbon fiber usage which generates HCN.
- Vinyl esters generate styrene hazardous air pollutant emissions.
- Epoxy resins can cause sensitization (e.g., blisters, hives) and use toxic epichlorohydrin.
- Bisphenol A (BPA) causes endocrine disruption and is a component of epoxies, vinyl esters, and polycarbonates

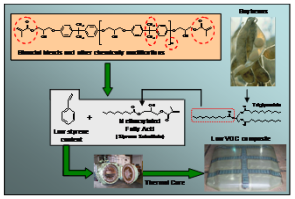


DoD Composites and Polymer Use

- Increasing use of polymers and composites in DoD and commercially for light-weighting and corrosion control
- *Challenge:* Increased demand requires key property improvements while reducing toxicity, cost, and environmental concerns.
- Key properties:
  - Viscosity – processing
  - T_g, T_d – operating temp. window
  - E, σ, G_{ic} – weight and durability



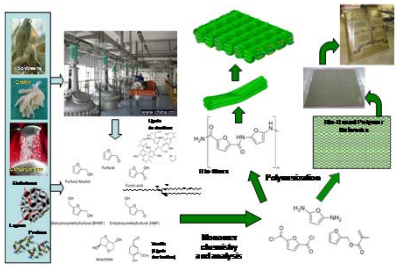
Successes and Limitations of Fatty Acid-Based Composites



J.J. La Scala, M.S. Logan, J.M. Sands, G.R. Palmese *Comp. Sci. and Tech.*, **68**, 1869-1876 (2008).

- We can use renewable oils to make high performing polymers and composite materials.
- *But*...We are limited in the amount we can use and still maintain high performance

Paradigm Change in Polymer Manufacture



- Overall Hypothesis: Use of renewable resources gives access to new molecular structures and monomers that can:
  1) Reduce toxicity 2) Produce novel polymers 3) Improve polymer properties

- *Gap:* Chemistries and Structure-Property-Toxicity characterization

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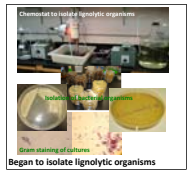
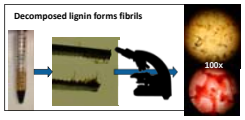
Biological Degradation of Lignin to Prepare Fibers

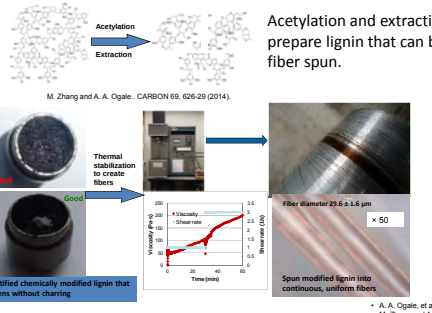


Began to isolate lignolytic organisms

Identified lignolytic organisms that decompose lignin to enables fiber formation



Chemical Modification of Lignin to Prepare Fibers

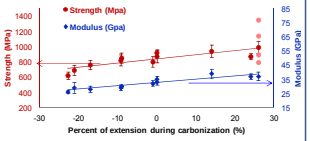


Acetylation and extraction to prepare lignin that can be fiber spun.

M. Zhang and A. A. Ogale.. CARBON 69, 626-29 (2014).

- A. A. Ogale, et al., *Journal of Applied Polymer Science*. 2016, DOI: 10.1002/APP.43794
- M. Zhang and A. A. Ogale, J. Appl.. Polym. Sci. 2016, DOI: 10.1002/APP.43663.

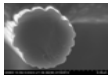
Lignin-Based Carbon Fibers



- Successfully stabilized and carbonized under tension
- Fibers extended 700% during stabilization and 25% during carbonization
- Tensile strength improved by 125%
- 1.3 GPa strength is higher than any value previously reported by any research group!

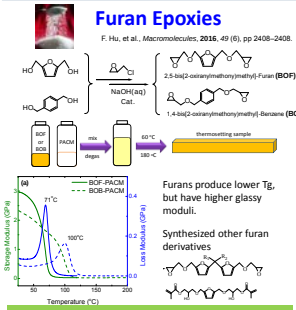
The electrical resistivity = 14 µΩ-m (very low, i.e., high graphitic content)

Crenulation can be controlled and increases fiber-matrix adhesion



Furan Epoxies

F. Hu, et al., *Macromolecules*, **2016**, *49* (6), pp 2408–2408.



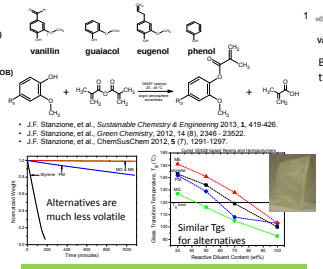
Furans produce lower Tg, but have higher glassy moduli.

Synthesized other furan derivatives

Furans represent a potential building block for high performance polymers

Styrene Alternatives

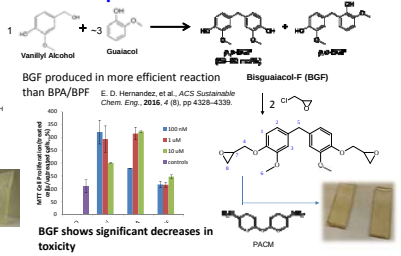
Lignin-derived compounds



- J.F. Stanzione, et al., *Sustainable Chemistry & Engineering* 2013, **1**, 419-426.
- J.F. Stanzione, et al., *Green Chemistry*, 2012, 14, (8), 2346 - 23522.
- J.F. Stanzione, et al., *ChemSusChem* 2012, **5** (7), 1291-1297.

Methacrylated lignin model compounds are potential styrene replacements

Bisphenol A Alternatives



BGF produced in more efficient reaction than BPA/BPF

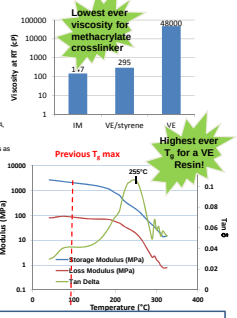
E. D. Hernandez, et al., *ACS Sustainable Chem. Eng.*, **2016**, *4* (8), pp 4328–4339.

BGF shows significant decreases in toxicity

DGEBGF/PACM Tg of 125˚C Is lower than that of DGEBA/PACM because of methoxy groups and smaller phenolic coupler

Lignin compounds can be used to sustainably replace BPA

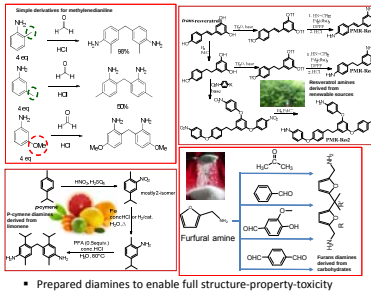
Isosorbide Methacrylate Crosslinkers



- Sadler, J.M. et al. *Journal of Materials Chemistry A*, (2013) 1, 12579-12586.
- J.M. Sadler, P. Lam, G.R. Palmese, J.J. La Scala, Renewable Bio-Based (Meth)Acrylated monomers as Vinyl Ester Crosslinkers" PCT Patent Application PCT/US2012050235.

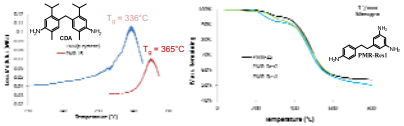
- **Eliminates need for volatile diluents**
- **Enables cheaper processing**
- **High temp epoxy performance at 1/10th the cost**

Prepared Potential MDA Alternatives

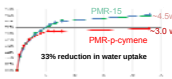


F. Hu, et al., *Macromolecular Chemistry and Physics*, 2015, 216 (13), 1441-1446.

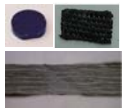
- Prepared diamines to enable full structure-property-toxicity evaluation of diamines in PMR polyimide.
- Prepared numerous novel polyamines from renewable resources.



- Renewably–derived polyimides have thermal properties within a few percent of PMR-15.



p-Cymene based polyimides have reduced water uptake due to increased hydrophobicity.



Alternatives produce high quality polymers and composites

Processing of MDA Alternatives

	Mutagenic?	Aquatic Toxicity	Acute Toxicity
	Yes	High	High
	Yes	Low to Moderate	Yes
	No	Low	Low
	Some derivatives	Low to High	Low to High
	No	Low	Low
	No	Low	Low

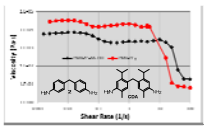
Positives

- Inexpensive reactants
- Low toxicity
- High thermal properties
- Can have improved thermal properties
- Low toxicity
- Improved processing
- Reasonable thermal properties
- Low toxicity

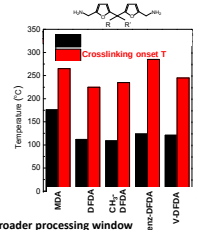
Negatives

- High toxicity
- More difficulty in processing (crosslinking)
- Relatively expensive reactants (currently)
- Reduced TOS
- Low polymer properties (poor reactivity)

Structure-Property-Toxicity of MDA Alternatives



Polyimides of p-cymene diamine have similar viscosity/processing vs. that of methylenedianiline



Broader processing window and lower cure temperature for furan polyimides

Summary And Conclusions

- Developed various structure-property relationships for furan, isosorbide, and lignin-derived polymers.
- Renewable polymers can have outstanding properties, if designed properly.
  - Isosorbide methacrylate has best ever properties
  - Highest achieved properties for lignin-based carbon fibers.
  - High temperature polyimides possible with renewables
- Bio-based polymers can be designed to have reduced toxicity vs. petroleum analogs.
- Highly promising resin technology for transition to industry.
- DoD positioned well to develop and make use of sustainable resin technology

Acknowledgements

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