SERDP WP-2403

Non-Toxic Multifunctional Silsesquioxane Diamine Monomer for Use in Aerospace Polyimides

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Aerospace Systems Directorate 30 Apr 19

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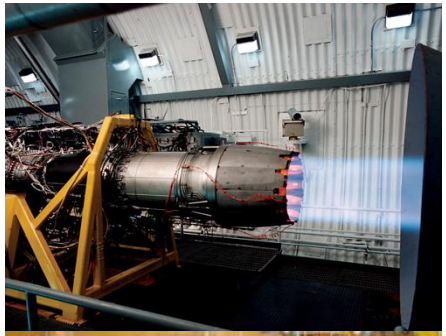
Project Objectives and Background Information

WPSON-14-02 (Development of New Material Systems That Replace Methylene Diamine (MDA) in Composite Resins)

- Project solicitation seeks a replacement for 4,4'-methylene dianiline (MDA) in high temperature capable (800 ° F) fiber reinforced polyimide composite aerospace structural materials because it is a liver toxin and possible carcinogen in humans
- PMR-15 and Monsanto Skybond 701 resins implement MDA
- Usage: ~20,000 lbs/yr of PMR-15 – significant DoD applications
  - ♦ Aircraft engines, rocket casings, engine bypass ducts, nozzle flaps, bushings, bearings, missile fins, structural wing components, radar domes, and other DoD applications requiring high temperature composites
  - ♦ Largest use: Outer Bypass Duct of GE Aviation's F/A-18E/F & EA-18G engines
  - ♦ Most versatile polyimide – excellent balance of processing, mechanical, and thermal properties
- Toxicity poses added cost to government in increased production costs and decreased competition



EPA Composite Manufacturing and Repair National Emission Standard for Hazardous Air Pollutants regulations, Army Environmental Requirements and Technology Assessments, and REACH prohibit new use of MDA-containing resin systems

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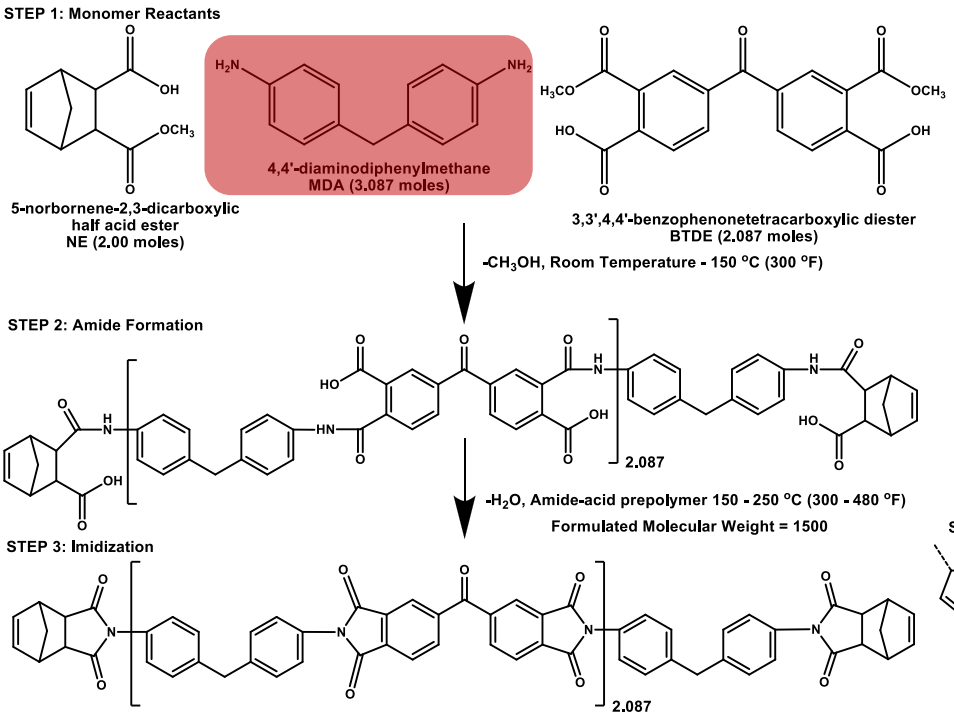
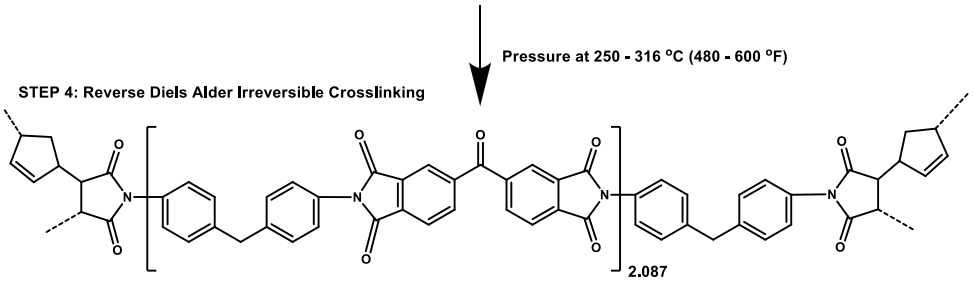
Technical Background – PMR-15

MDA uses and quantities:

- polyurethanes, coating materials, glues, Spandex fiber, dyes, rubber, epoxies, and aerospace polyimides including PMR-15
- US production + imports ~100-500M lbs/year

Chemical Synthesis of PMR-15





Health Effects from MDA Exposure

- Skin irritation
- Liver damage/jaundice
- Eye and thyroid injuries in animals
- Carcinogenic to animals (liver and thyroid) and possibly humans
- *OSHA occupational exposure limit of 0.081 mg/m^3 of air for an 8-hour workday, 40-hour workweek*
- *Breathing limit 0.03 mg/m^3 of MDA during a 10-hour workday, 40-hour workweek*

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Key PMR-15 Resin Properties

Property	Literature	Measurement Technique	Screen Threshold
Zero Shear Viscosity (@ 150 °C, P)	1.16×10^6	Parallel Plate Rheometer	$\leq1.3\times10^6$
T_g (°C, no postcure)	299	TMA	≥299
T_g (°C, postcured in air at 316 °C for 24 hrs)	333	TMA	≥333
Weight Loss (% @ 288 °C/1400 hrs in air)	1.52	Oven Aging/Gravimetric	1.44
Weight Loss (mg/cm^2 @ 288 °C/3024 hrs in air)	13.6	Oven Aging/Gravimetric	12.92
Weight Loss (% @ 316 °C/400 hrs in air)	1.88	Oven Aging/Gravimetric	≤1.97
Weight Loss (% @ 316 °C/500 hrs in air)	4.97	Oven Aging/Gravimetric	4.72
5% Weight Loss Temperature (°C, 1 °C/min ramp, N_2 purge	440	TGA	≥440
Coefficient of Thermal Expansion (μm/mm·°C)	55	TMA	-
Tensile Strength (MPa)	4.2	ASTM D 638-08	≥4.0
Flexural Strength (MPa)	4.2	ASTM D 790-07	≥4.0
Moisture Uptake (100 hrs, 80 °C/80 RH)	4.0	Humidity Chamber/Gravimetric	≤4.0

- Key properties of cured PMR-15 resin compiled from literature summarized in table
- Properties in red cells used as screening criteria for this project
- A measured property must exceed respective threshold property delineated in table
- Over 20 years of R&D to identify a viable replacement for MDA have failed

46 MDA replacement studies found in literature – no other substitute monomer demonstrates same combination of properties that MDA provides

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Key PMR-15 Composite Properties

Property	Literature	Measurement Technique	Threshold
T_g (°C, G´ onset)	348	DMA	340
T_g (°C)	346	TMA	340
Flexural Strength (MPa, 23 °C)	1082 ± 89	ASTM D 7264	1028
Flexural Modulus (MPa, 23 °C)	58 ± 2	ASTM D 7264	55
Flexural Strength (MPa, 288 °C)	747 ± 66	ASTM D 7264	710
Flexural Modulus (MPa, 288 °C)	57 ± 2	ASTM D 7264	54
Interlaminar Shear Strength (MPa, 23 °C)	61 ± 2	ASTM D 2344	58
Interlaminar Shear Strength (MPa, 288 °C)	43 ± 2	ASTM D 2344	41
Weight Loss (% @ 288 °C, air, 1000 hrs)	0.77	Oven Aging/Gravimetric	0.81
Weight Loss (% @ 288 °C, air, 1500 hrs)	1.05	Oven Aging/Gravimetric	1.10

Test	L	W	T	A	Samples	Total Area
	in	in	in	in^2		in^2
ASTM D 2344	0.6	0.2	0.1	0.12	5	0.6
ASTM D 7264	6	0.5	0.15	3	5	15

- Flexural and interlaminar shear composite properties selected for testing in this project because they are resin dominated properties
- Values obtained from literature shown in table
- For this project, two 8"×8" panels were fabricated (one for testing and one for a deliverable to SERDP)
- ~110 g resin required to complete composite fabrication

Specimen Type:		PANEL (COMPOSITE)		
Reinforcement		CARBON WOVEN FABRIC		
Reinforcement Densi		1.78	g/cc	
Dimension	inches	cm		
L	8	20.32		
W	8	20.32		
T	0.1	0.25		
Panel Area	64	in^2		
Weight Fraction Polymer			0.378	
Weight Fraction Reinforcement			0.622	
Volume Fraction Polymer			0.450	
Volume Fraction Reinforcemen			0.550	
Resin Weight Required			52.28	g
MDA Weight Required			17.67	g

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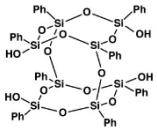
Bis(aniline, methyl)siloxy-Octaphenyl Silsesquioxane Monomer

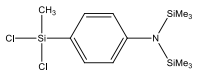
Monomer Synthesis Steps

a)

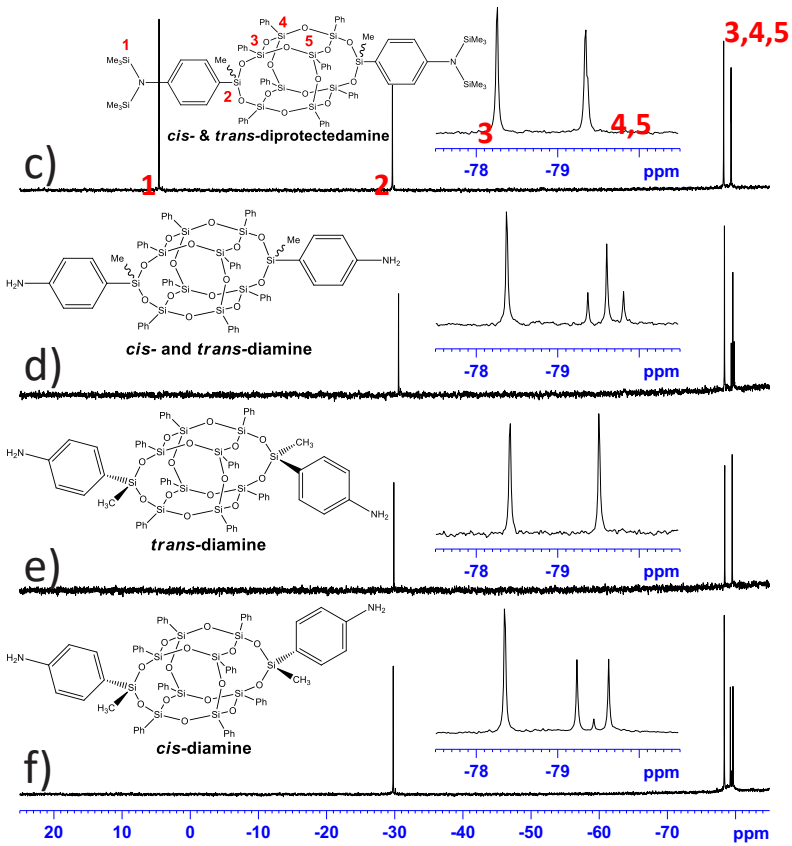


TetraSilanolPhenyl POSS starting material
100 g/286 USD (1300 USD/lb)

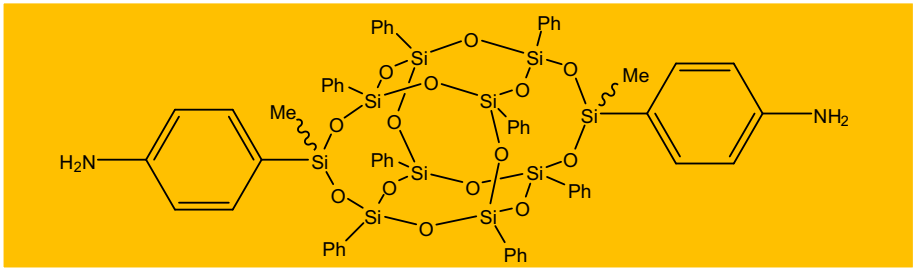
b)



NMR Spectra



Bis(aniline, methyl)siloxy-Octaphenyl Silsesquioxane



- Bis(aniline, methyl)siloxy-Octaphenyl Silsesquioxane monomer chosen for this project as replacement for MDA
- Developed and synthesized at AFRL
- Well defined inorganic cage
- Peripherally aromatic promoting thermal stability required of polyimides
- Bi-reactive functionality is equivalent to MDA
- Isomer suite to facilitate molecular design

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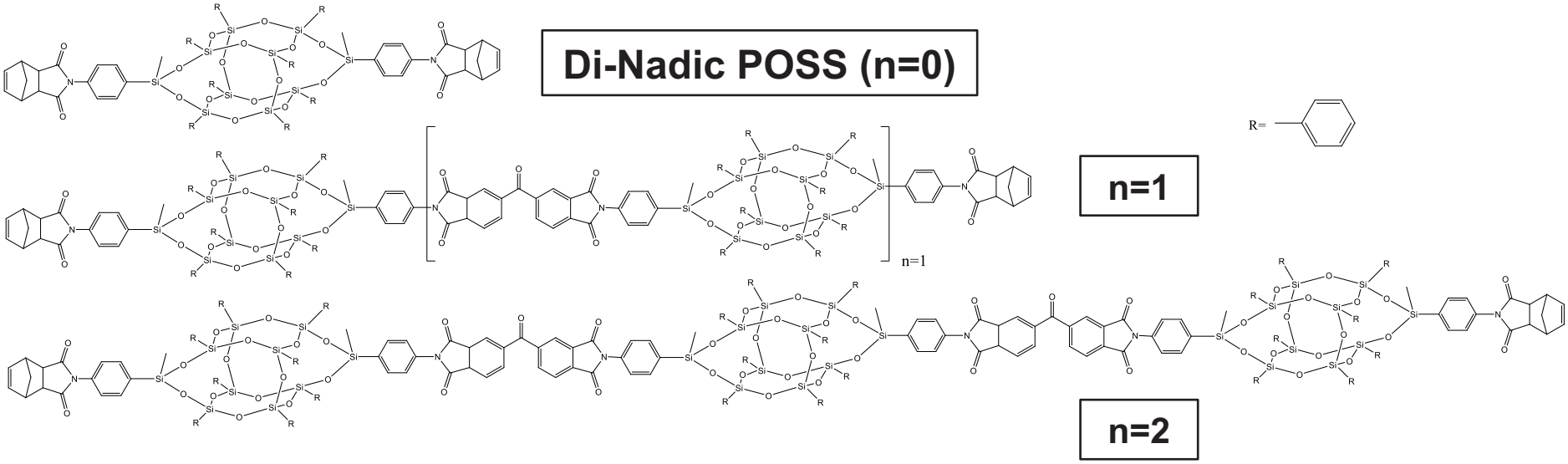
WP-2403 Project Framework

- Heritage PMR-15 chemistry used (BTDA + nadic anhydride end cap)
- MDA replaced with POSS dianiline
- Oligoimide molecular weight, nadic concentration, and therefore crosslink density systematically altered through synthesis of the three oligoimides shown below
- Synthesized oligoimides characterized for key properties and compared with those of PMR-15
- Oligomides used in fabrication of carbon fiber reinforced composites, and those composites tested for key properties and compared to those measured from PMR-15 composites



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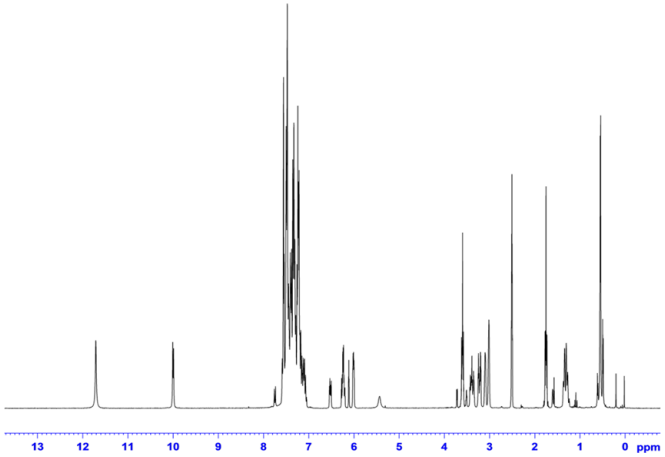
Experimental Results

PMR-15 Oligoimide Synthesis

NMR peak integration values (expected vs. measured)

Region (ppm)	PMR-15 (MeOH)		PMR-15 (THF)	
	Expected	Measured	Expected	Measured
1-2	4	4	4	4
2.5-4.5	14.2	15.3	14.2	14.0
6-6.5	4	3.9	4	3.3
6.8-7.5	24.7	29.2	24.7	30.5
7.9-8.5	12.5	12.7	12.5	9.9



H^1 NMR spectrum of PMR-15

- PMR-15 synthesized in both methanol (conventional method) and in tetrahydrofuran (THF) because POSS oligoimide synthesis must be performed in THF due to POSS insolubility in methanol
- Nuclear Magnetic Resonance (NMR) spectroscopy was conducted on products
- H^1 NMR peaks integrated and theoretical values compared to measured as shown in table
- Both synthesis solvents result in viable product, therefore THF can be used for synthesis of the POSS oligoimides with confidence

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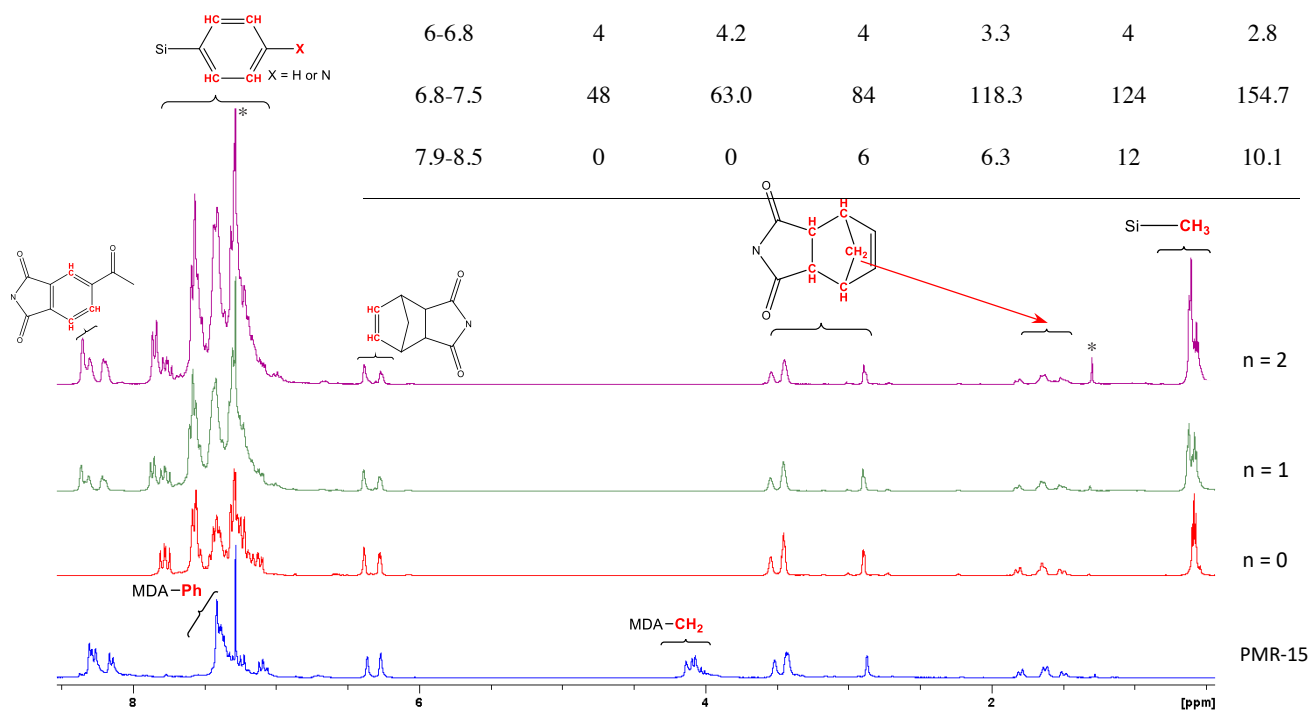
POSS Oligoimide Synthesis

	0N		1N		2N	
Region (ppm)	Expected	Measured	Expected	Measured	Expected	Measure
0.5-0.6	6	7.17	12	11.9	18	15.7
1-2	4	4	4	4	4	4
2.5-4.5	8	8.7	8	7.3	8	6.3
6-6.8	4	4.2	4	3.3	4	2.8
6.8-7.5	48	63.0	84	118.3	124	154.7
7.9-8.5	0	0	6	6.3	12	10.1



H^1 NMR analysis comparing theoretical to actual values for POSS oligoimides demonstrates that viable materials were also synthesized

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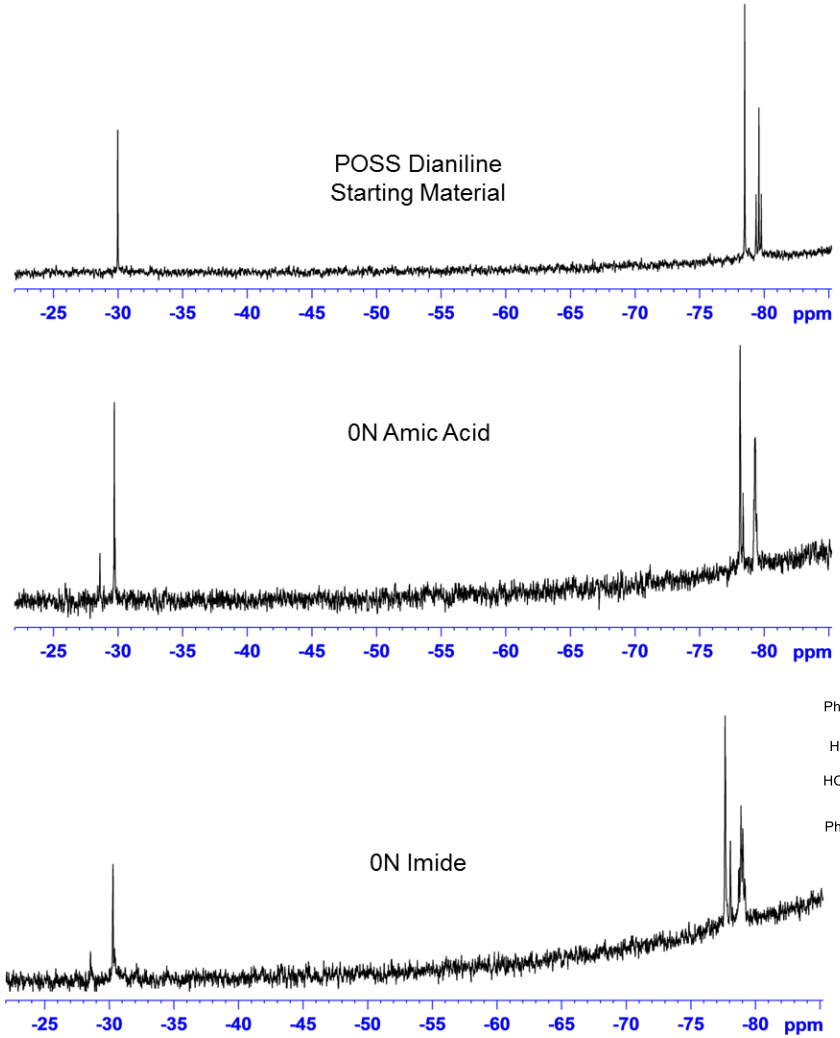
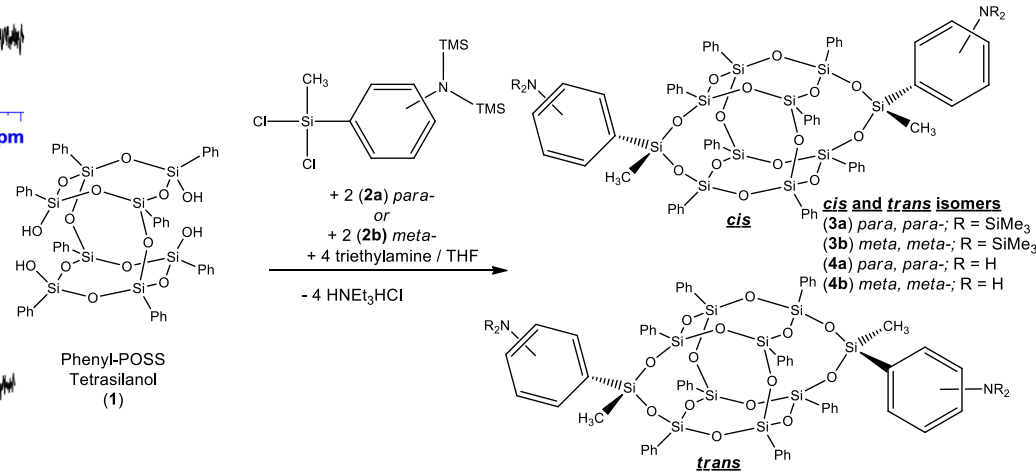
NMR Spectra of POSS Materials



- ^{29}Si NMR spectra of starting monomer and oligoimides was performed to determine if POSS cages remained intact during synthesis steps
- No evidence of cage scrambling or disassembly



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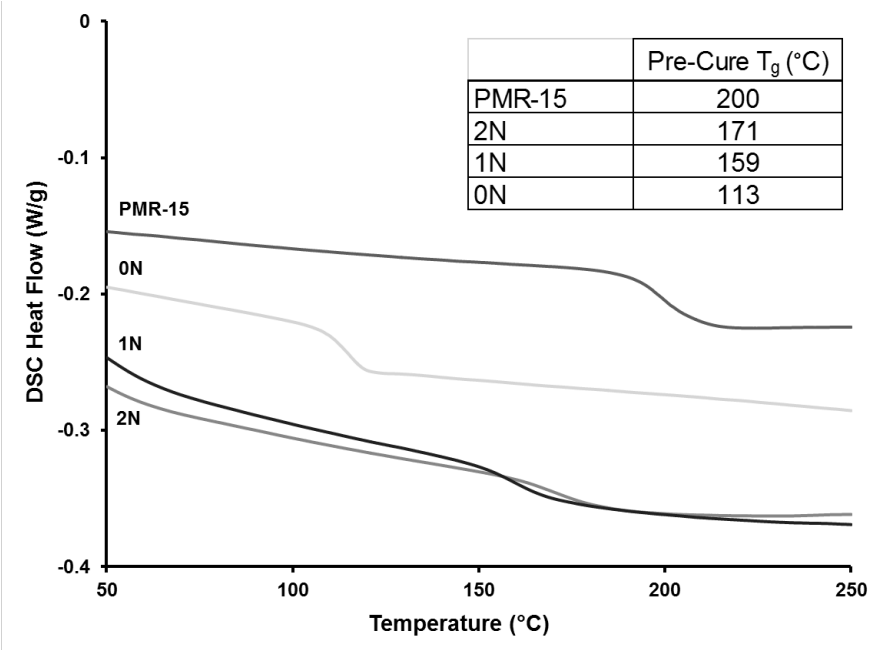
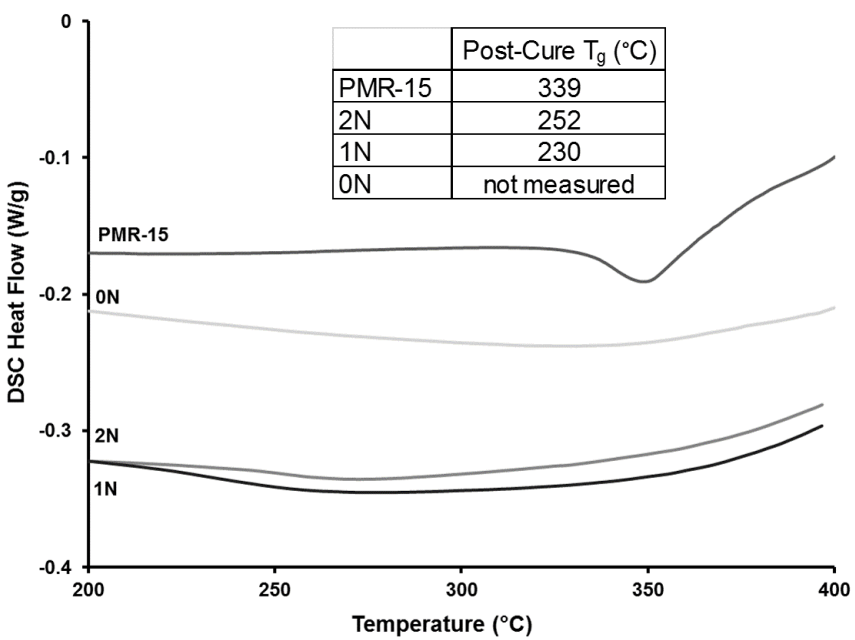
Differential Scanning Calorimetry (DSC)



	Pre-Cure T_g (°C)
PMR-15	200
2N	171
1N	159
0N	113



	Post-Cure T_g (°C)
PMR-15	339
2N	252
1N	230
0N	not measured

- Differential scanning calorimetry (DSC) performed at a rate of 10 °C/minute prior to oligoimide cure and after cure at 315 °C for 2 hours
- Increasing POSS mass fraction decreases observed glass transition temperature in pre-cured state
- Glass transition temperature of 0N not evident after cure, likely due to very high crosslink density
- Cured glass transition temperature of PMR-15 identical to that reported in literature

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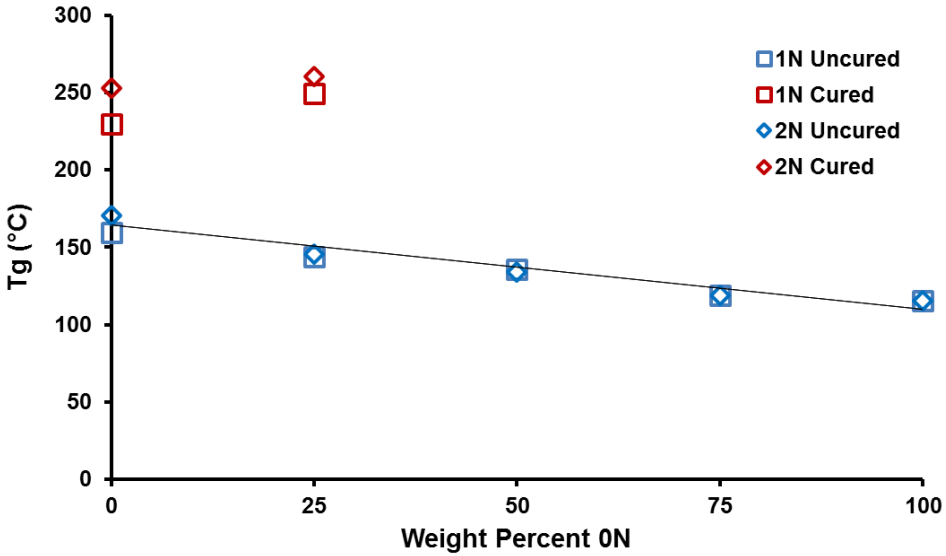
Oligoimide Blending Study



Weight Percent 0N	0	25	50	75	100
1N Uncured	159.3	143.9	135.8	118.8	115.6
1N Cured	229.8	249			
2N Uncured	170.7	145.7	133.7	119.1	115.6
2N Cured	252.5	260.5			

- Because 1N and 2N exhibit lower cured glass transition temperatures than PMR-15, 0N was solution blended with 1N and 2N oligomers in THF to determine if cured glass transition temperatures could be raised
- Singular glass transition temperatures measured suggesting good miscibility
- 25 weight percent 0N blends were the only compositions where a cured glass transition temperature could be measured
- T_g raised 8 and 20 °C for 1N and 2N, respectively, but well short of 315 °C for PMR-15

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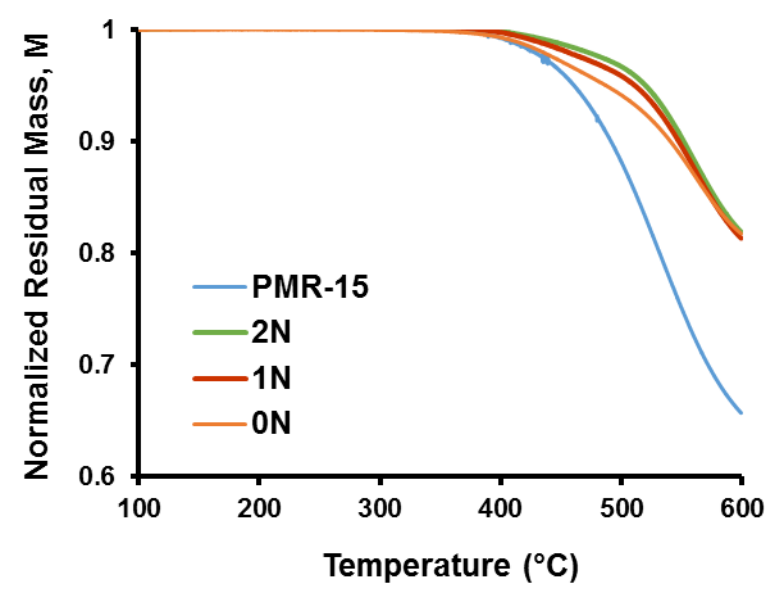
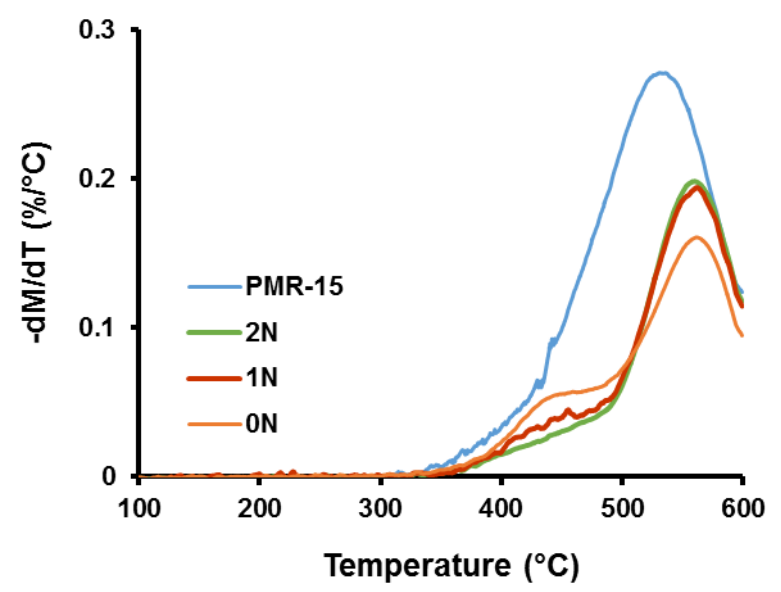
Thermogravimetric Analysis (TGA)





- Thermogravimetric analysis was performed on cured powders to quantify thermal stability; scanning rate is 1 °C/minute in nitrogen atmosphere
- 2N>1N>0N>PMR-15 in terms of measured thermal stability
- In PMR-15, MDA methylene bridge and nadic crosslinking group decomposition occurs simultaneously
- POSS-containing polyimide decomposition is bi-modal suggesting occurrence of two decomposition processes

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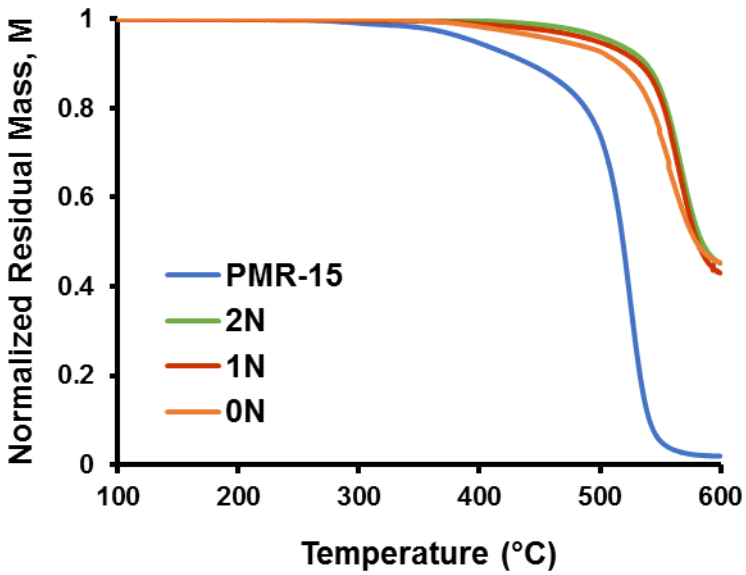
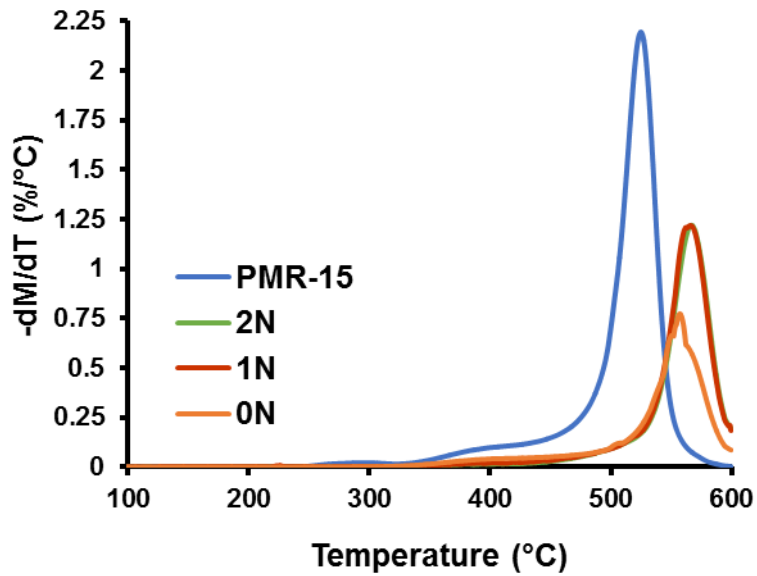
Thermogravimetric Analysis (continued)





- Thermogravimetric analysis was performed on cured powders to quantify thermal stability; in this case scanning rate is 1 °C/minute in air atmosphere
- Residual mass is higher at 600 °C for POSS polyimides than PMR-15 due to conversion of $SiO_{1.5}$ to SiO_2
- 2N>1N>0N>PMR-15 in terms of measured thermal stability as witnessed in nitrogen

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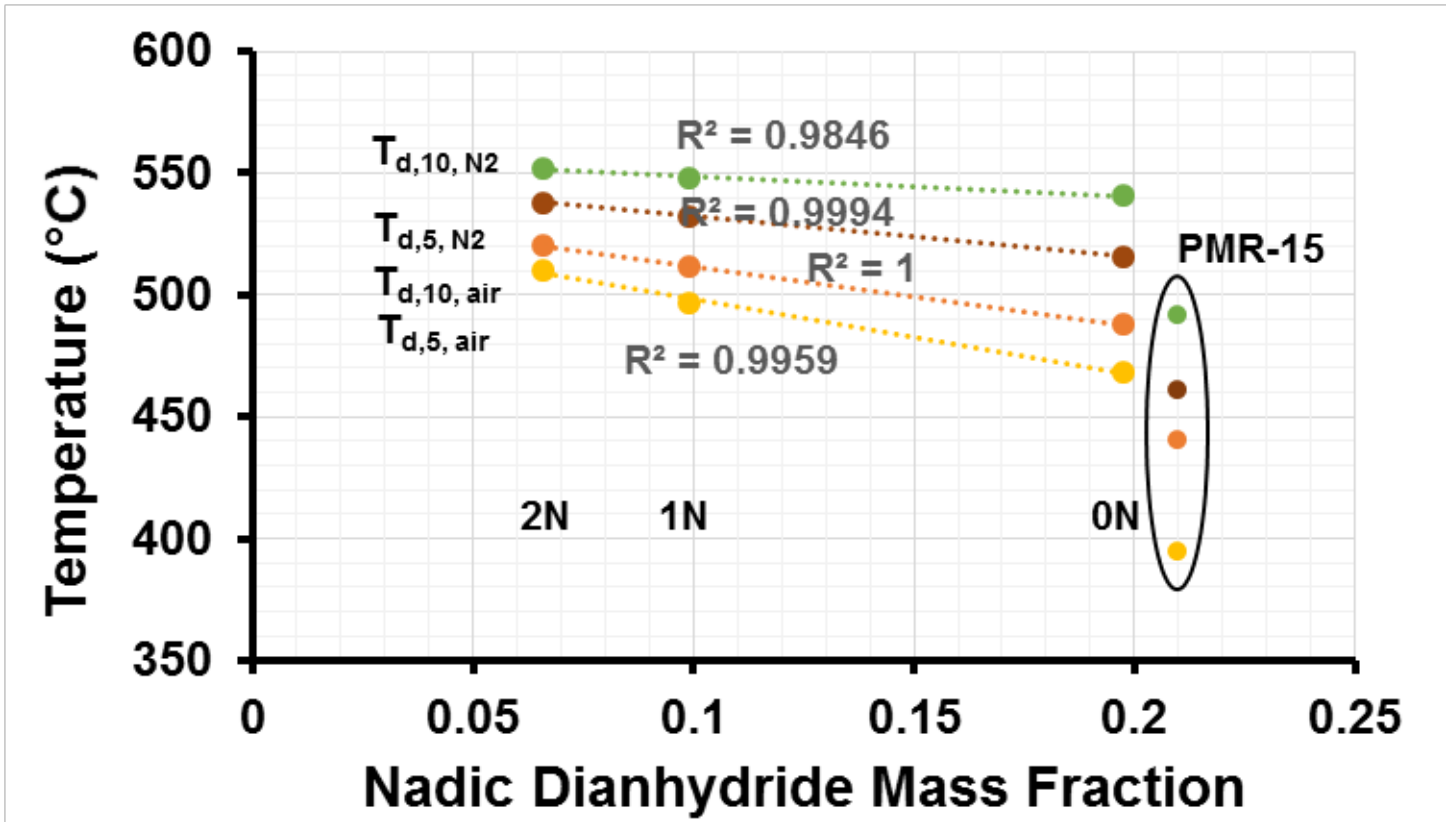
Insights into Thermal Decomposition Mechanisms



- For POSS polyimides, the 5% and 10% decomposition temperatures follow a linear trend with nadic dianhydride monomer end group mass fraction
- PMR-15 does not follow this trend due to simultaneous decomposition pathways of MDA methylene bridge and nadic anhydride crosslinking group

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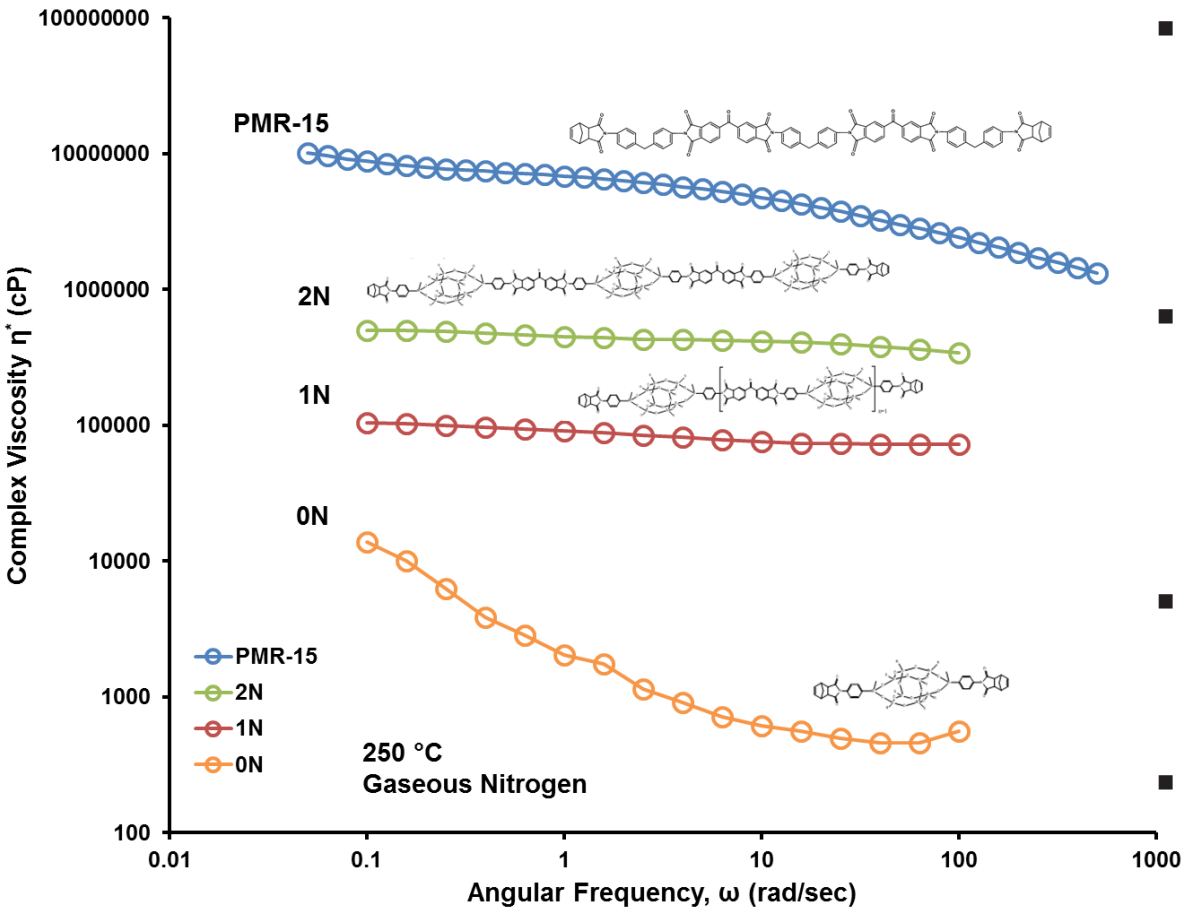
Parallel Plate Rheology



- Oscillatory parallel plate rheology tests conducted to gain further understanding of synthesized molecular architectures
- Complex viscosity measured as a function of angular frequency at 250 °C, at a gap spacing of 0.7-0.8 mm and oscillatory strain of 1%
- For BTDA-POSS-NA oligomers, complex viscosity increases with MW
- di-Nadic POSS exhibits very low viscosity

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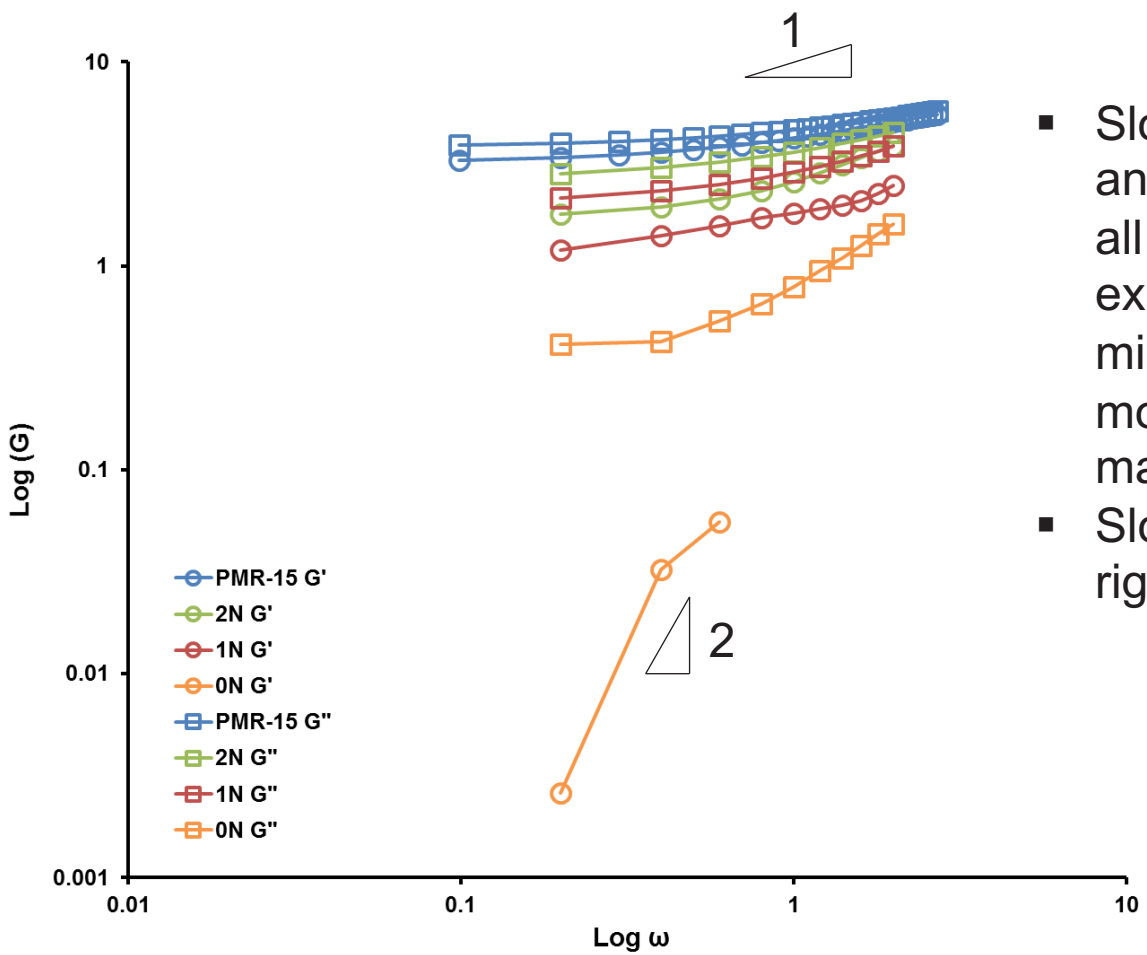
Parallel Plate Rheology (continued)



- Slopes of storage modulus G' and loss modulus G" are ~1 for all of the oligoimides with the exception of 0N, suggesting minimal interactions between molecules in 0N due to size and mass fraction of POSS groups
- Slopes for 0N are ~2, suggesting rigid rod molecular behavior

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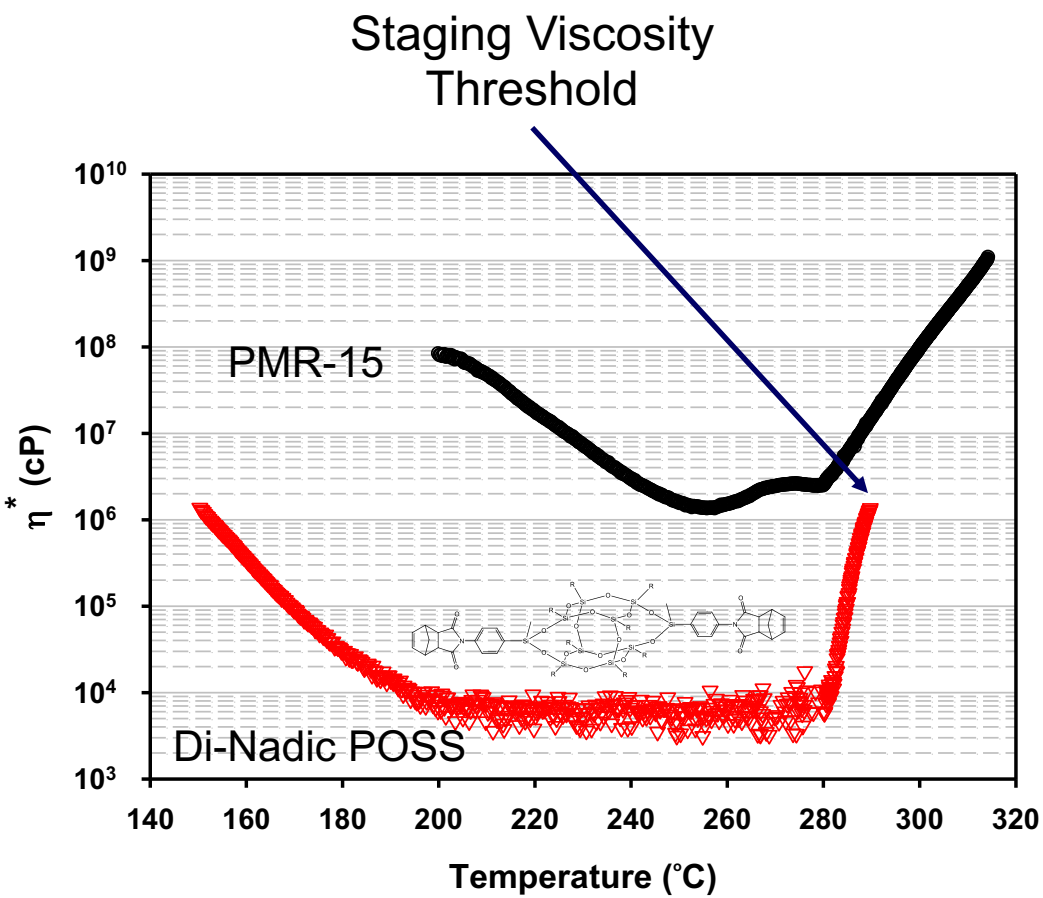
Neat Resin Specimen Molding



- Compression molding neat resin disks of PMR-15 was found to be trivial; initial attempts at di-Nadic POSS failed due to the resin wicking the piston (due to very low viscosity and metal affinity)
- The cure behavior of the two materials was examined by oscillatory rheology
- Both materials cure reaction initiates at the same temperature; di-Nadic POSS viscosity development much more rapid due to higher nadic concentration
- Successful di-Nadic POSS disks were fabricated by staging material to above 10^6 cP prior to application of compression

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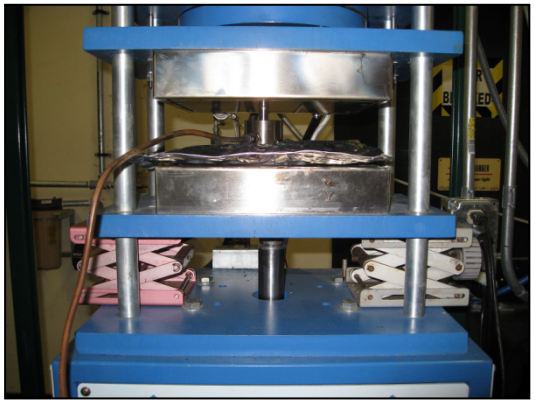
Neat Resin Disk Fabrication and Density Measurements



- Neat resin disks fabricated by compression molding in a cylindrical mold using a programmable heated press
- Densities measured using alcohol immersion method
- Cured resin densities found to decrease with increasing POSS mass fraction
- Likely due to increasing free volume in network structures

Material	Average Density (g/cm^3)	Standard Deviation
PMR-15	1.284	0.0121
2N	1.268	0.0184
1N	1.253	0.0140
0N	1.238	0.0028

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Thermal Mechanical Analysis (TMA)

- Complex thermal mechanical analysis (TMA) performed on neat resin disks to assess viscoelastic behavior and coefficients of thermal expansion
- 2N, 1N, and 0N all have 0.80 mass fraction POSS, but differ in crosslink densities due to relative concentrations of nadic endcap groups
- Tan delta is below 0.2 for all materials, suggesting high degrees of cross-linking
- Co-oligomerization with POSS decreases glass transition temperatures as witnessed in DSC measurements

	Tg (°C)			
	Storage Modulus	**Loss Modulus**	**Tan Delta**	**Dimension Change**
PMR-15	343	366	374	319
2N	288	303	312	274
1N	301	315	321	265
0N	304	315	326	293

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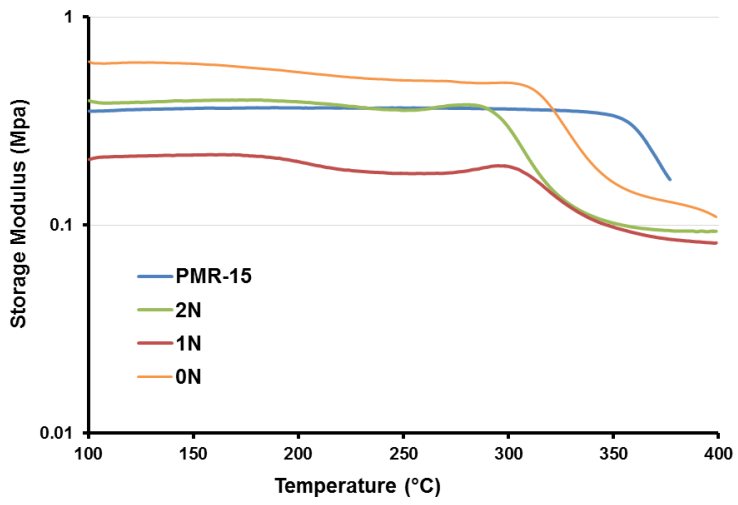
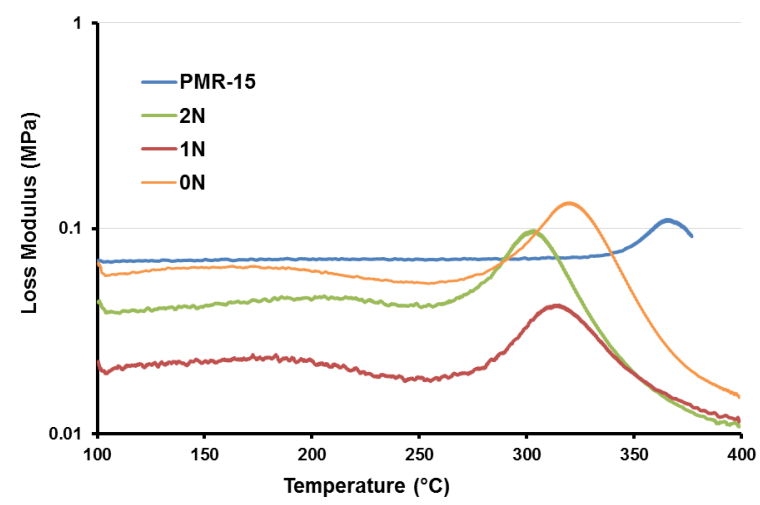
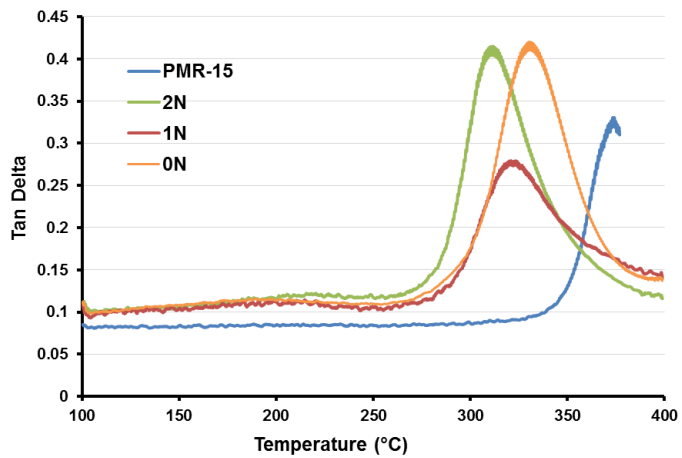
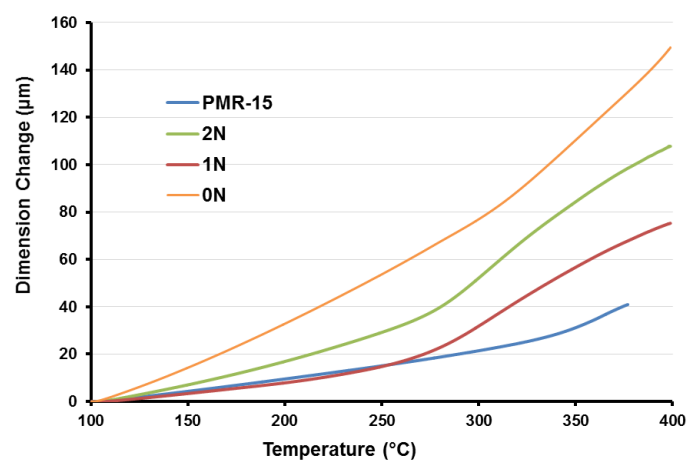
Thermal Mechanical Analysis (TMA) Data









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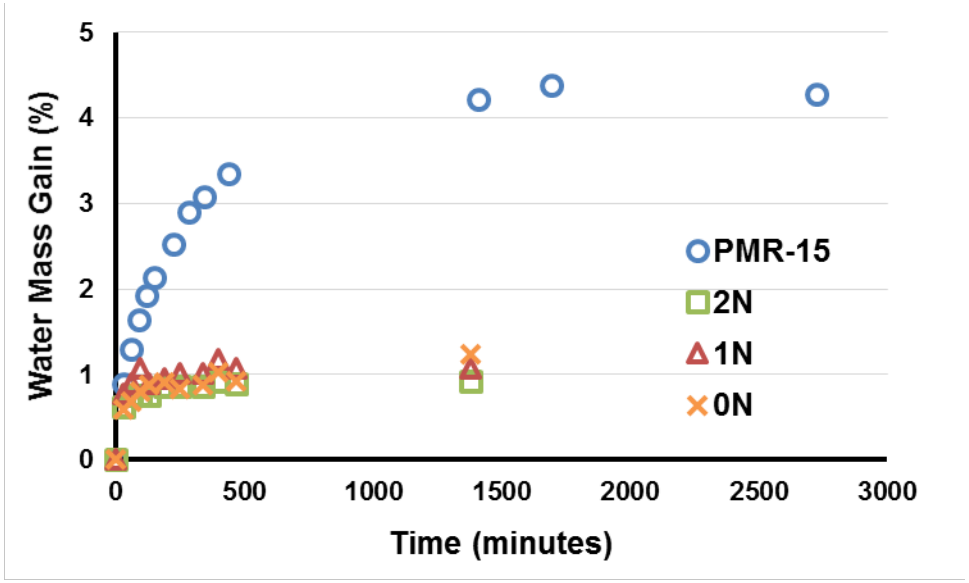
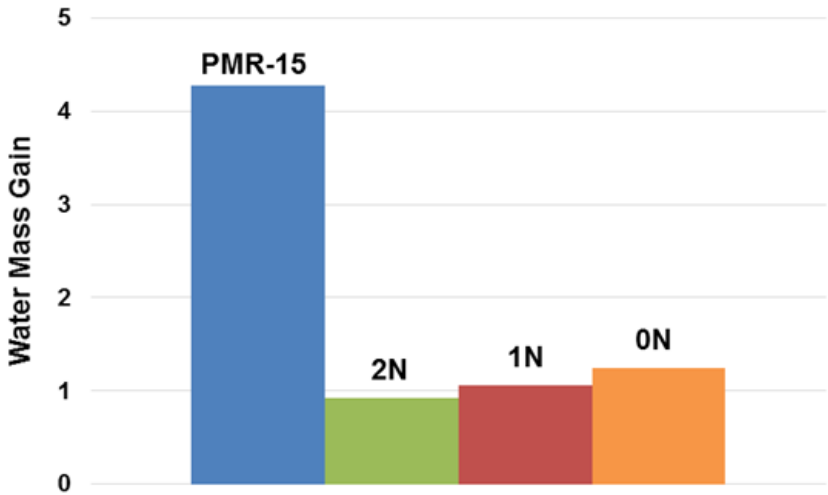
Water Uptake





- Neat cured resin disks immersed in boiling deionized water and periodically weighed to assess water ingress
- Saturation for the POSS-containing materials occurs within 1 hour of exposure, much faster than in PMR-15
- Level of saturated moisture uptake reduced significantly with POSS incorporation
- Imide and carbonyl groups in PMR-15 are known to hydrogen bond with water; these chemical groups may be shielded by large POSS molecules

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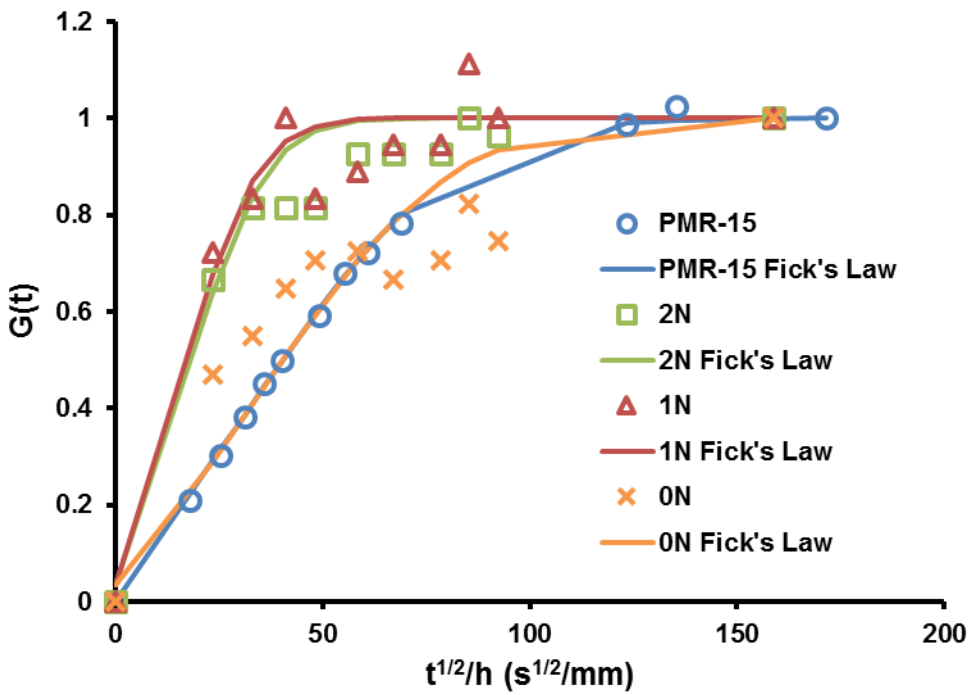
Quantification of Water Diffusion Coefficients



- Water diffusion coefficients calculated from mass gain experiments
- Diffusion coefficients for 1N and 2N polyimides much higher than PMR-15
- Diffusion coefficients for PMR-15 and 0N very similar

	Density (g/cm^3)	D (mm^2/s)	Water Mass Gain (%)
PMR-15	1.284	0.000029	4.27
2N	1.268	0.0001	0.93
1N	1.253	0.00017	1.07
0N	1.238	0.00003	1.24

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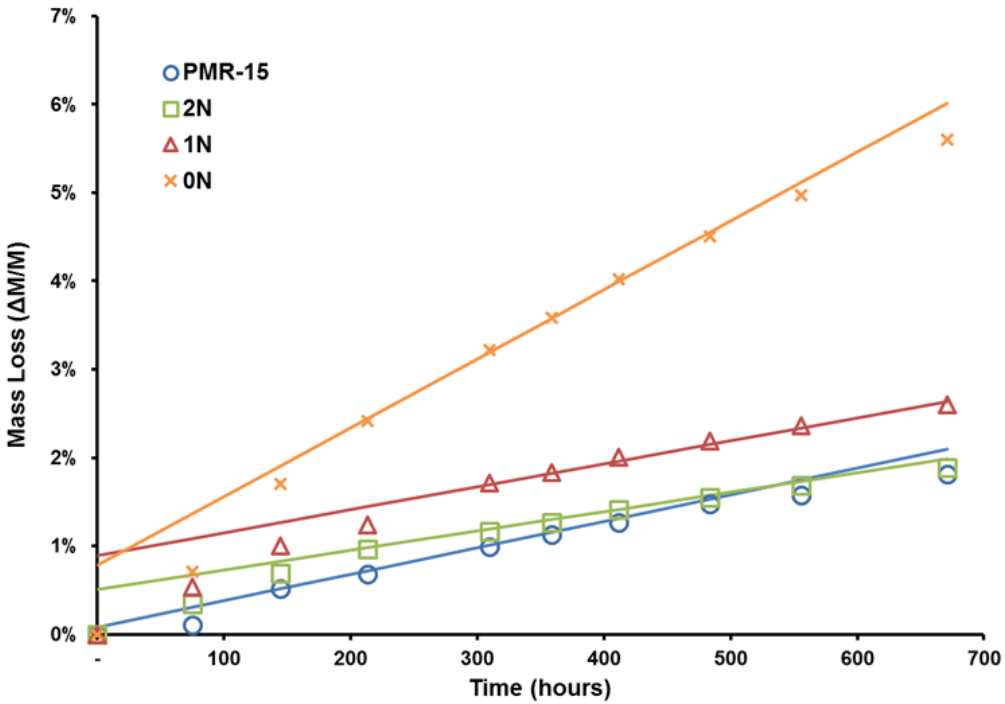
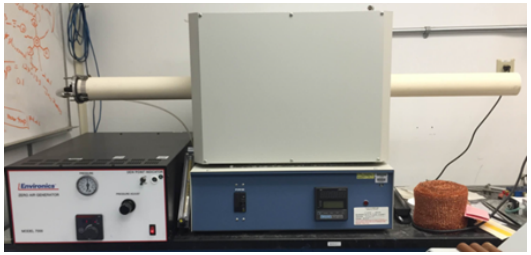
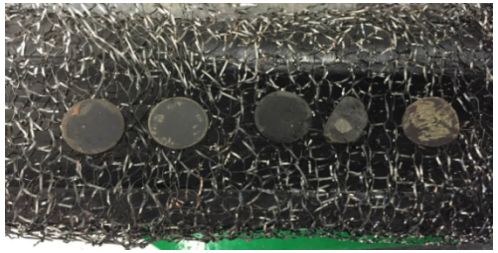
Long-Term Thermo-Oxidative Stability



Increasing nadic dianhydride concentration reduces long-term TOS





- Long-term thermal stability of cured resin disks quantified
- Tests conducted in tube furnace at 316 °C, 30 mL/min air flow rate
- Sample specimens are 0.5 inch diameter neat resin disks
- Suspended using a graphite boat covered with copper mesh such that both sides of disks exposed to hot gas

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Tabulated Summary of Resin Properties

Property	PMR-15	2N	1N	0N
Zero Shear Viscosity (@ 150 °C, P)	1.16×10^6	-	-	-
Zero Shear Viscosity (@ 250 °C, P)	**100688**	**4978**	**1047**	**139**
T_g (°C, no postcure) – measured by TMA (Storage Modulus)	299 (**343**)	**288**	**301**	**304**
T_g (°C, postcured in air at 316 °C for 24 hrs)	333	-	-	-
Weight Loss (% @ 316 °C/400 hrs in air)	1.88 (**1.3**)	**1.4**	**1.9**	**3.9**
Weight Loss (% @ 316 °C/500 hrs in air)	4.97 (**1.6**)	**1.6**	**2.2**	**4.7**
5% Weight Loss Temperature (°C, 1 °C/min ramp, N_2 purge	440 (461)	**520**	**512**	**488**
Coefficient of Thermal Expansion (µm/mm·°C)	55 (**121**)	-	-	-
Moisture Uptake (100 hrs, 80 °C/80 RH)	4.0 (1.6)	**0.8**	**1.1**	**0.8**

No cured POSS oligoimide found to match combination of properties of PMR-15, but 0N chosen for synthesis scaleup to facilitate composite fabrication and testing because it features the highest softening temperature and unusually low viscosity

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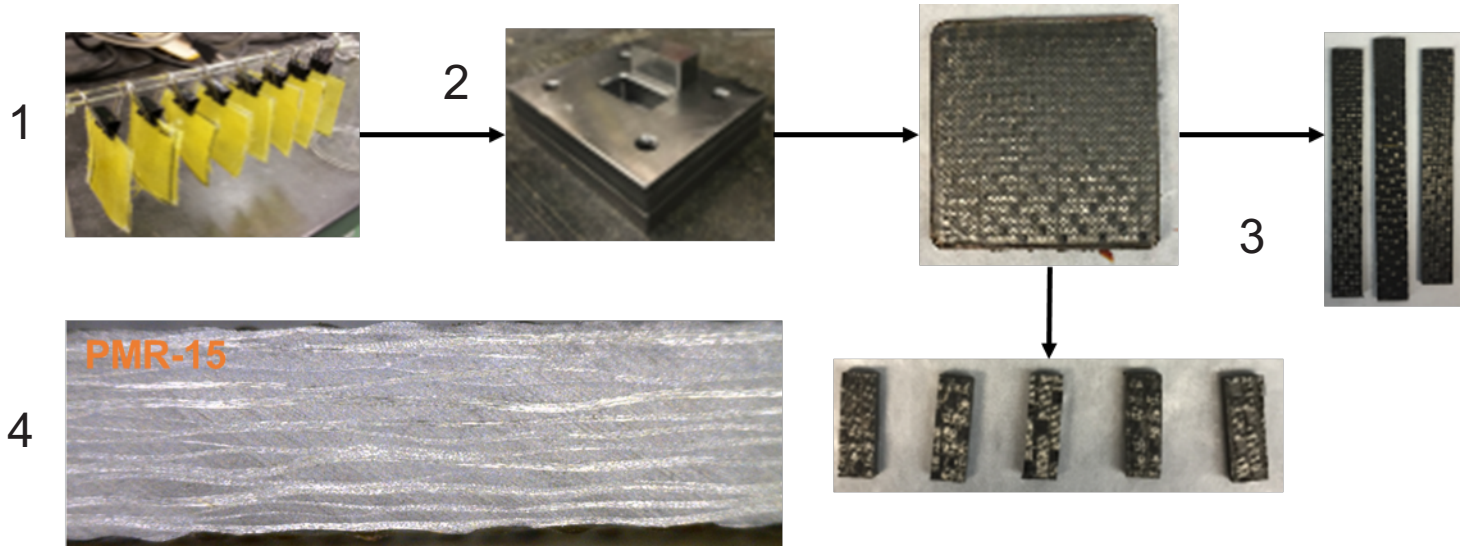
PMR-15 Composite Fabrication



To fabricate PMR-15/carbon fiber composites:

1. Dip coated 8×8 inch IM7 4 harness satin weave fabric plies in PMR-15/methanol solution (60% solute concentration), and most of solvent removed in drying oven
2. 14 plies placed compression molded to form a 0.1 inch thick panel
3. Panel sectioned into specimens for mechanical testing and void quantification
4. Very good laminate quality observed by microscopy with low void content

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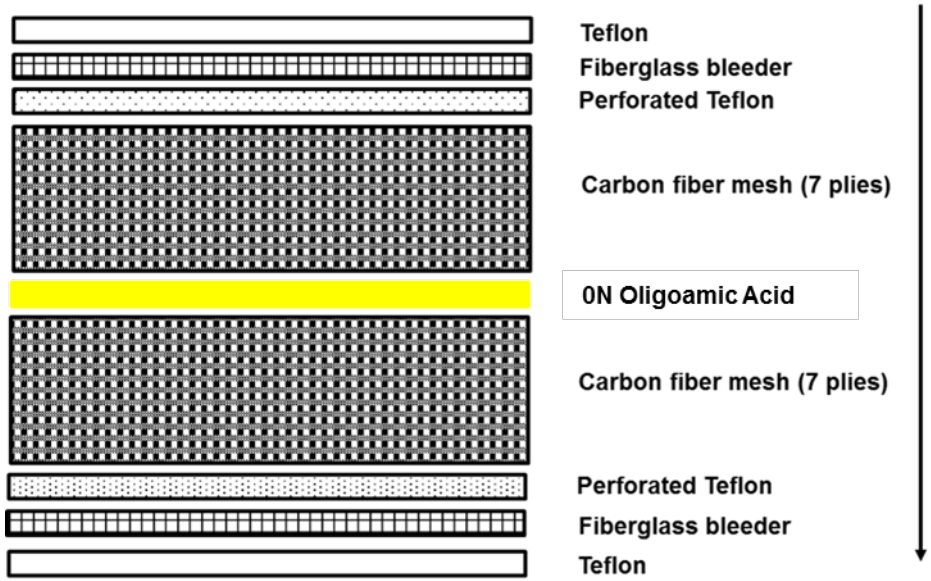
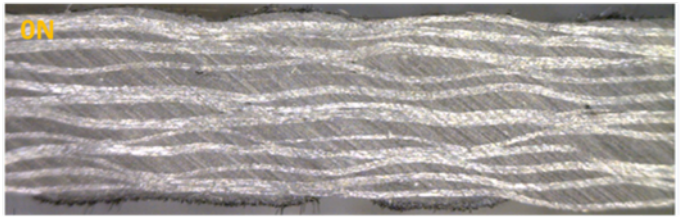
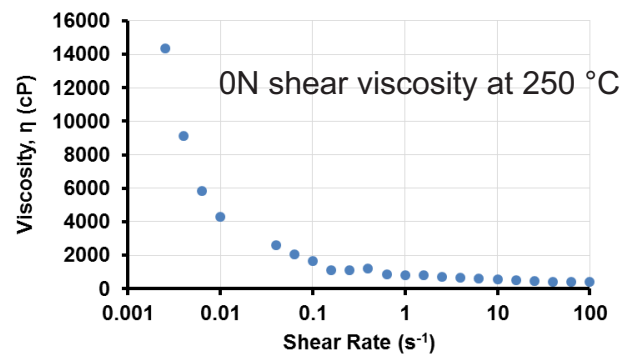
0N Composite Fabrication





- Due to very low melt viscosity at 250 °C, 0N powder situated between carbon fiber plies in mold and heated
- Resin found to flow through carbon fiber plies (not possible for PMR-15 without solvent)
- High quality laminates formed



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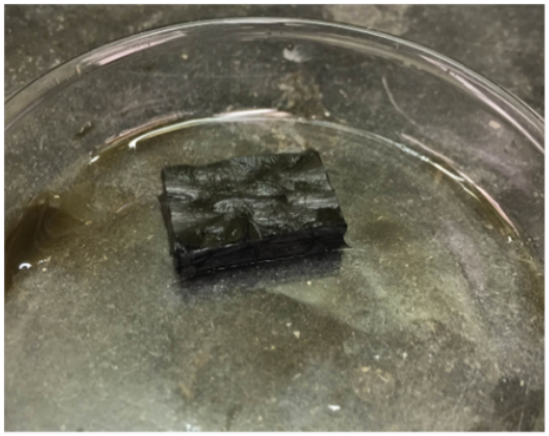
Composite Laminate Void Content

PMR-15

Acid Digestion:
Boiling H_2SO_4

1 Week

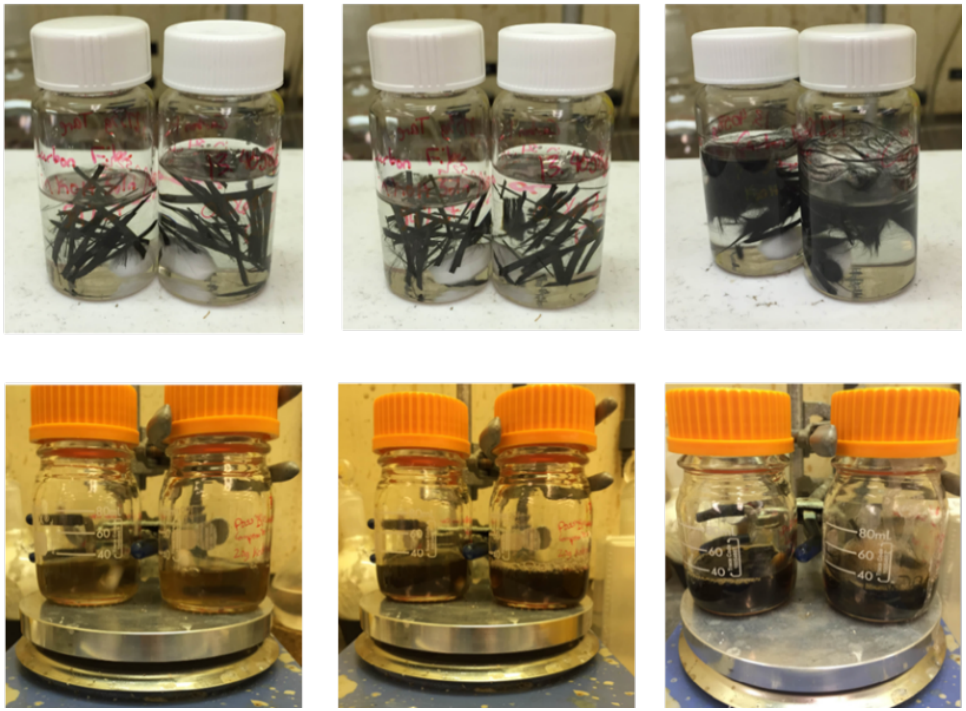


Resin System	Resin Content (wt%)	Fiber Content (vol%)	Void Content (vol%)
PMR-15	29.84	61.97	1.88
0N	28.68	62.19	3.53

0N

Base Digestion:
55wt% KOH in H_2O

4 Hours | 1 Day | 2 Days



- PMR-15 and 0N composite void content quantified using acid and base digestion methods, respectively
- 0N composite possesses 2X higher void content than PMR-15 composite

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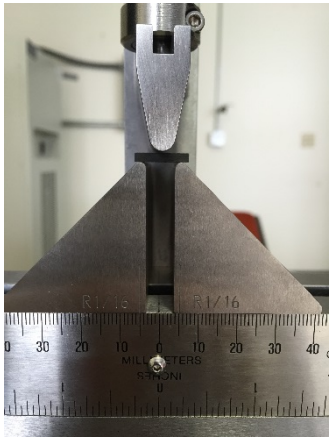
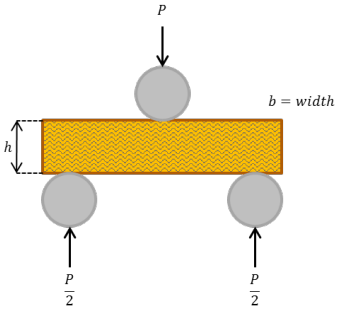
Composite Mechanical Properties Interlaminar Shear Strength

ASTM D2344

Thickness (h)		Width (b)		Max Force (Pm)		**Short Beam Strength (Fsbs)**	
mm	in	mm	in	lbf	N	**Kpsi**	**MPA**
2.59	0.101968559	5.39	0.212204839	326	1450.048	11.3	77.9
2.51	0.098818951	5.5	0.21653555	323	1436.704	11.3	78.1
2.62	0.103149662	5.47	0.215354447	326	1450.048	11.0	75.9
2.56	0.100787456	5.25	0.206693025	306	1361.088	11.0	76.0
2.5	0.09842525	5.13	0.201968613	293	1303.264	11.1	76.2
					Average	**11.1**	**76.8**
					StDev	**0.2**	**1.1**



Thickness (h)		Width (b)		Max Force (Pm)		**Short Beam Strength (Fsbs)**	
mm	in	mm	in	lbf	N	**Kpsi**	**MPA**
2.53	0.099606353	5.27	0.207480427	87.3	388.3104	3.2	21.8
2.48	0.097637848	5.19	0.204330819	91.5	406.992	3.4	23.7
2.57	0.101181157	5.4	0.21259854	80.3	357.1744	2.8	19.3
2.52	0.099212652	5.09	0.200393809	86.9	386.5312	3.3	22.6
2.44	0.096063044	5.15	0.202756015	90.6	402.9888	3.5	24.1
					Average	**3.2**	**22.3**
					StDev	**0.3**	**1.9**



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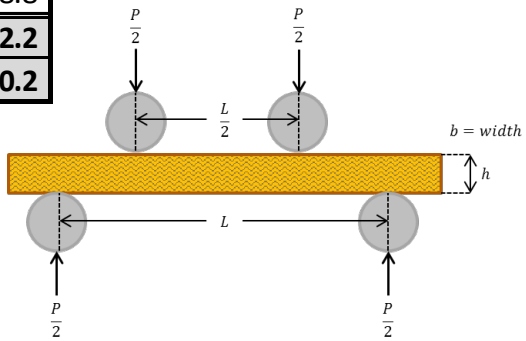
Composite Mechanical Properties Flexural Strength

Sample	Thickness (h)		Width (b)		Span (L)		Fracture Stress (σ)		Modulus	
PMR-15	mm	in	mm	in	mm	in	MPA	Kpsi	MPA	KPSI
1	2.4765	0.0975	10.51052	0.4138	79.375	3.125	1569.2	227.6	435.1	63.1
2	2.67462	0.1053	9.08558	0.3577	85.725	3.375	1601.7	232.3	806.0	116.9
3	2.58572	0.1018	12.11072	0.4768	82.55	3.25	2375.2	344.5	1068.2	154.9
						Average	**1848.7**	**268.1**	**769.8**	**111.6**
						StDev	**456.3**	**66.2**	**318.1**	**46.1**

ASTM D 7264

Sample	Thickness (h)		Width (b)		Span (L)		Fracture Stress (σ)		Modulus	
POSS diNadic	mm	in	mm	in	mm	in	MPA	Kpsi	MPA	KPSI
4	2.5908	0.102	13.12418	0.5167	82.55	3.25	486.8	70.6	342.7	49.7
5	2.87528	0.1132	13.0302	0.513	92.075	3.625	335.1	48.6	538.5	78.1
8	2.63398	0.1037	12.9921	0.5115	85.725	3.375	394.4	57.2	612.3	88.8
						Average	**405.4**	**58.8**	**497.8**	**72.2**
						StDev	**76.4**	**11.1**	**139.3**	**20.2**



Interlaminar shear and flexural strengths of 0N composite significantly inferior to those of PMR-15

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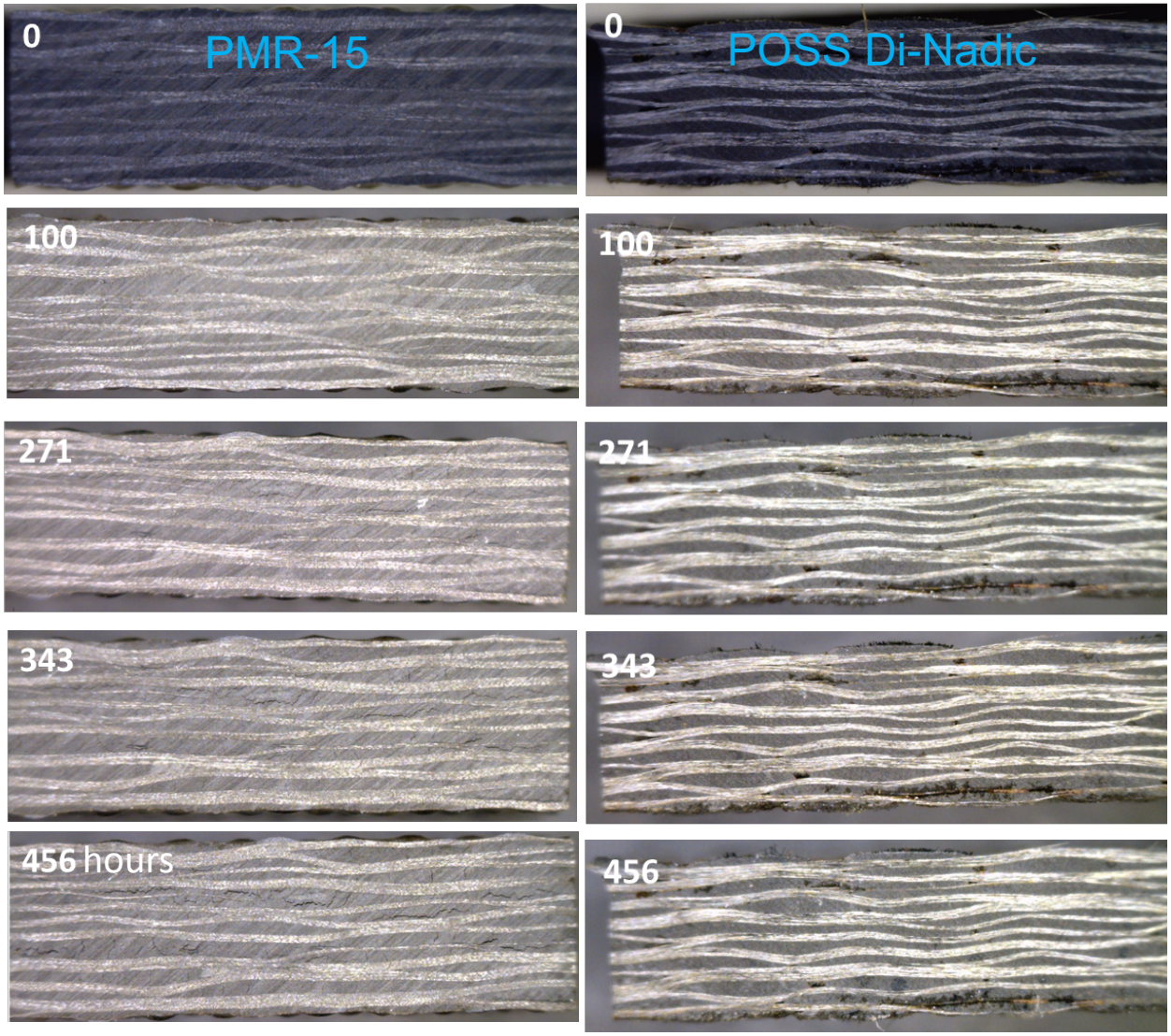
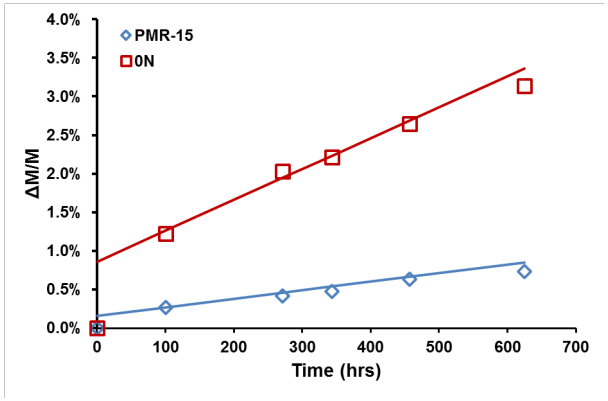
Long-Term Thermo-oxidative Stability of Composite Laminates



- IM7 4 Harness Satin Weave Fabric – 16 plies
- 316 °C in air
- Micro-cracks witnessed in PMR-15 composite at 271 hrs
- No micro-cracks development in POSS Di-Nadic composite at 456 hrs



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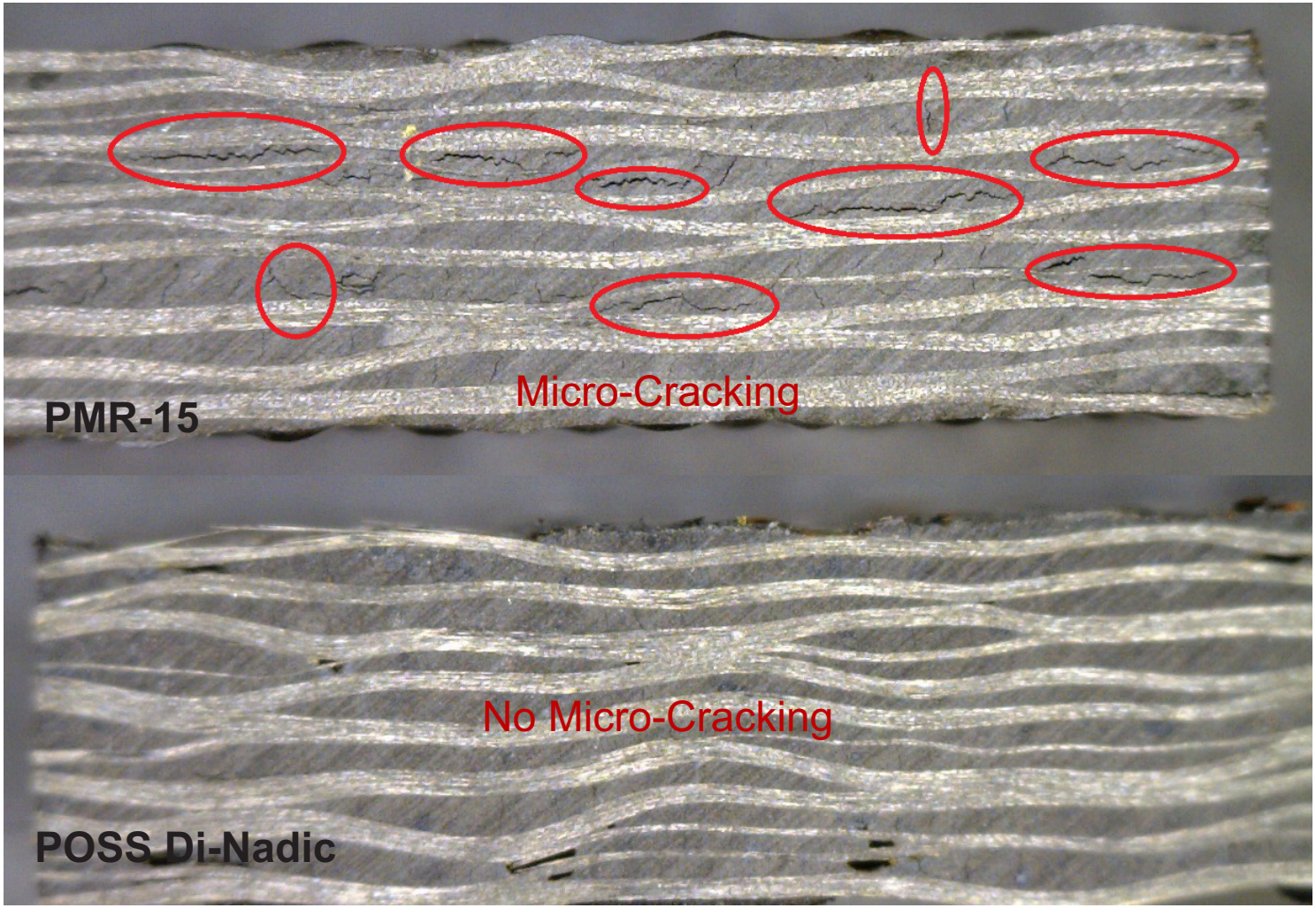
456 Hours of Aging at 316 °C in Air



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Summary and Conclusions

Summary

- Synthesis of POSS oligoimides was not possible in methanol due to insolubility of POSS monomer; synthesis in THF successfully rendered target theoretical products
- Although POSS imparts unique property characteristics such as lower viscosity and improved water resistance, it also lowers use (softening) temperature
- 0N oligoimide chosen for scaleup synthesis due to its unusually low viscosity and highest softening temperature amongst POSS oligoimides synthesized
- 0N composite could be fabricated without the use of solvent by a simulated resin transfer molding (RTM) method
- The long-term thermal stability of 0N in air was found to be poor, attributed to relatively high concentration of nadic crosslinking groups
- 0N/carbon fiber composite resin dominated mechanical properties (interlaminar shear and flexural sttrengths) were found to be poor in comparison with those of PMR-15

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Conclusions

- Substitution of MDA with POSS dianiline into heritage PMR-15 chemistry improves resin flow viscosity and resistance to water
- Although beyond the scope of this project, the POSS dianiline is expected to be benign to humans
- The POSS dianiline provides an opportunity to eliminate the use of solvents in composite processing
- Most notably, the POSS dianiline appears to eliminate micro-cracking during long term exposure of composites to oxygen at elevated temperature, an issue that PMR-15 suffers
- POSS dianiline is costly in comparison with MDA
- Crosslink density must be increased to offset the effects of POSS size in terms of lowering resin softening temperature – crosslinking group must be judiciously chosen as nadic anhydride does not have the best thermal stability amongst crosslinking group chemistries
- Further oligoimide molecular design is required to best exploit the benefits of POSS but achieve a better balance of properties
- POSS is not a suitable drop-in replacement for MDA in heritage PMR-15 chemistry

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