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1. REPORT DATE (DD-MM-YYYY) 26 May 2016		2. REPORT TYPE Conference Paper		3. DATES COVERED (From - To) 29 April 2016 – 31 May 2016	
4. TITLE AND SUBTITLE Balancing Performance and Sustainability in Next-Generation PMR Technologies for OMC Structures			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Gregory R. Yandek, Jason T. Lamb, John J. La Scala, Benjamin G. Harvey, Giuseppe R. Palmese, William S. Eck, Joshua M. Sadler, Santosh K. Yadav			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER Q16J		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQRP 10 E. Saturn Blvd Edwards AFB, CA 93524-7680			8. PERFORMING ORGANIZATION REPORT NO.		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RQR 5 Pollux Drive Edwards AFB, CA 93524-7048			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RQ-ED-TP-2016-107		
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for Public Release; Distribution Unlimited. PA Clearance Number 16222; Clearance Date 5/6/2016 The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.					
13. SUPPLEMENTARY NOTES For presentation at Society for the Advancement of Materials and Process Engineering; Long Beach, CA, USA; May 26, 2016; Prepared in collaboration with ERC. See also AD1010347, Accompanying Briefing Charts AFRL-RQ-ED-VG-2016-110					
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15. SUBJECT TERMS N/A					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 16	19a. NAME OF RESPONSIBLE PERSON A Guenther
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NO (include area code) N/A

BALANCING PERFORMANCE AND SUSTAINABILITY IN NEXT-GENERATION PMR TECHNOLOGIES FOR OMC STRUCTURES

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ABSTRACT

PMR-15, regarded as the technological foundation of “Polymerizable Monomeric Reactants”, is nearing half a century since its inception. Although it has persisted within the aerospace industry as a mid-tier performance matrix resin for organic matrix composite (OMC) structures, its continued legacy is being challenged domestically. Methylene dianiline (MDA), a principal constituent monomer in PMR-15, is recognized as biologically toxic. Attempts at identifying a suitable replacement for MDA, spanning three decades, have resulted in awareness that the balance of properties afforded by this monomer is unique. In the past two years, DoD laboratories within the Air Force, Army, and Navy have participated in a coalition, along with Drexel University, seeking to develop new monomers for PMR technologies that target high performance yet are sustainable. At the core of this effort is the spiral development of novel aniline monomers through a harmonization of chemical structure design, synthesis, resin screening, composite fabrication and testing, and monomer toxicology assessments. Notable achievements thus far are the genesis of aniline monomers derived from bio-renewable sources and a solution to the time tested problem of thermo-oxidative aging induced micro-cracking in OMCs. An overview of these results is presented.

1. INTRODUCTION

PMR-15, developed by NASA Lewis Research Center in the 1970s, is the aerospace industry’s most prolifically utilized high temperature OMC matrix resin for lightweight hot structures in

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aircraft and other applications because it offers ease of processing and good property retention in service at reasonable cost [Ref. 1-4]. Although annual consumption is variable, it is estimated that on average over 20,000 lbs of PMR-15 are consumed per year, the vast majority of which is utilized for DoD subsidized aircraft production programs [Ref. 5]. The popularity of PMR-15 is based on its unique combination of properties, including processability, service temperature (max 288 °C), long-term thermo-oxidative stability (TOS), and mechanical properties including fracture toughness and resistance to micro-cracking. However, since the early 1980s, it has been recognized that MDA, a key monomer in PMR-15, poses health risks and therefore has been intensely scrutinized. While commercial material solutions are available for lower service temperatures (epoxies and BMIs) as well as for higher service temperatures (AFR-PE), materials for mid-service temperatures, like PMR-15, are deficient. Therefore, the health effects of MDA are currently affecting design on DoD acquisition programs and a solution is needed.

The dangers associated with MDA ingestion have been studied and are well understood. In the human body, the cytochrome P450 (CYP) class of enzyme is used to oxidize organic chemicals in the body and liver [Ref. 6-7]. However, CYP bioactivates MDA and its derivatives to form nitroso compounds, via N-oxidation, that can then be converted to nitrosamines, a class of compounds known to be highly toxic [Ref. 8-9]. Additionally, the reactive intermediates can form an elimination product that conjugates with glutathione, thereby depleting the concentration of this oxygen free radical scavenger that protects against DNA degradation, which can cause cancer [Ref. 10-12]. As a consequence, the life cycle costs associated with PMR-15 have increased due to required handling measures to mitigate its health risks to humans and the environment. Furthermore, the supply chain of MDA to oligoimide prepreggers, cascading to U.S. aerospace manufacturers, has been disrupted due to the limited number of producers of the monomer, which are all in Asia. In fact, for DoD applications, MDA is solely procured from a Japanese source because the remaining manufacturers are based in China. Due to these circumstances, research and development efforts focused on alternative resin systems to replace PMR-15 have been numerous since the early 1980s. Despite the successes of many of these efforts, including the commercialization of a limited number of oligoimides developed by NASA, alternative chemistries exhibiting equivalent properties and cost have remained elusive. Of the over 50 known reported diamines studied as alternatives to MDA, including those possessing phenyl linkage groups such as ketone, sulfur, sulfone, ether, unsaturated aliphatic groups, as well as three and four-phenyl ring diamines, none have afforded the combination of T_g , >1000 hr weight loss at 288 °C, and mechanical properties that the use of MDA provides [Ref. 13]. A few notable examples which have been commercialized are AMB-21, employing 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), and LARC-RP-26, employing 3,4'-oxydianiline (ODA), feature enhanced processability, but 75 and 65 °C lower T_g s than PMR-15, respectively. Monomers imparting higher T_g s than MDA such as NASA's asymmetric class of monomers, most notably 2,2'-dimethylbenzidine (DMBZ), also recently commercialized in PMR chemistry, suffer from lower long-term TOS due to their methyl groups. MVK-16, from Maverick Corp. [Ref. 14], is claimed to be nearly equivalent to PMR-15 in delivered properties without the use of MDA.

For this effort, alternative candidate aniline monomers to MDA were used to synthesize oligoimides based on the stoichiometric framework of PMR-15 when possible. Screening of these monomers was performed using key end-use properties as a basis for comparison,

including pre- and post-cure glass transition temperature, pre-cure flow characteristics/zero-shear viscosity, moisture uptake, and long-term thermo-oxidative stability. These properties were selectively chosen for screening because their measurements do not require significant quantities of materials (<0.5 grams per material) enabling rapid analysis of a significant number of candidates. The metrics for monomer viability were defined as those being measured within a threshold 5% of that of PMR-15 (if lower). The results to date from this characterization and screening effort are reported herein.

2. EXPERIMENTATION

2.1 Candidate Monomers

14 monomers were evaluated and compared to MDA using heritage PMR-15 chemistry as the framework for oligoimide synthesis. 11 of those monomers are difunctional in terms of amine groups like MDA, and three of the monomers are trifunctional. 5 of the monomers feature chemical structures derived from the basic framework of MDA while the others are architecturally distinct. All but one of the monomers were synthesized in the laboratory with the exception of Jeffamine D-230 which is a commercial product available from Huntsman, commonly used as an epoxy curing agent and in urethane chemistry. Monomer chemical structures and identification numbers are summarized in Table 1. Oligoimides synthesized from these monomers are identified herein as PMR-1, -2, etc.

Table 1. Numbering scheme and chemical structures for experimental monomers.

[PMR-15] MDA		[7] PACM	
[1]		[8] Derived from p-cymene	
[2]		[9]	
[3]		[10]	
[4]		[11] Derived from resveratrol	
[5]		[12] Derived from resveratrol	
[6] Jeffamine D-230			

2.2 Oligoimide Synthesis

Thermosetting oligoimides were synthesized following the conventional method developed for PMR-15. The general synthesis strategy for PMR-15 is illustrated in Figure 1, where 3,3',4,4'-

benzophenonetetracarboxylic dianhydride (BTDA) and 5-norbornene-2,3-dicarboxylic anhydride (NA) are first esterified in methanol (MeOH, or CH₃OH) and subsequently combined with methylene dianiline (MDA) to produce polyamic acid of a targeted molecular weight guided by the stoichiometric ratios of the monomers. The resultant polyamic acid, after isolation and solvent abstraction, is thermally imidized to afford the thermosetting oligoimide. To produce the experimental oligoimides, a molar substitution of the aniline monomer of interest for MDA was simply performed.

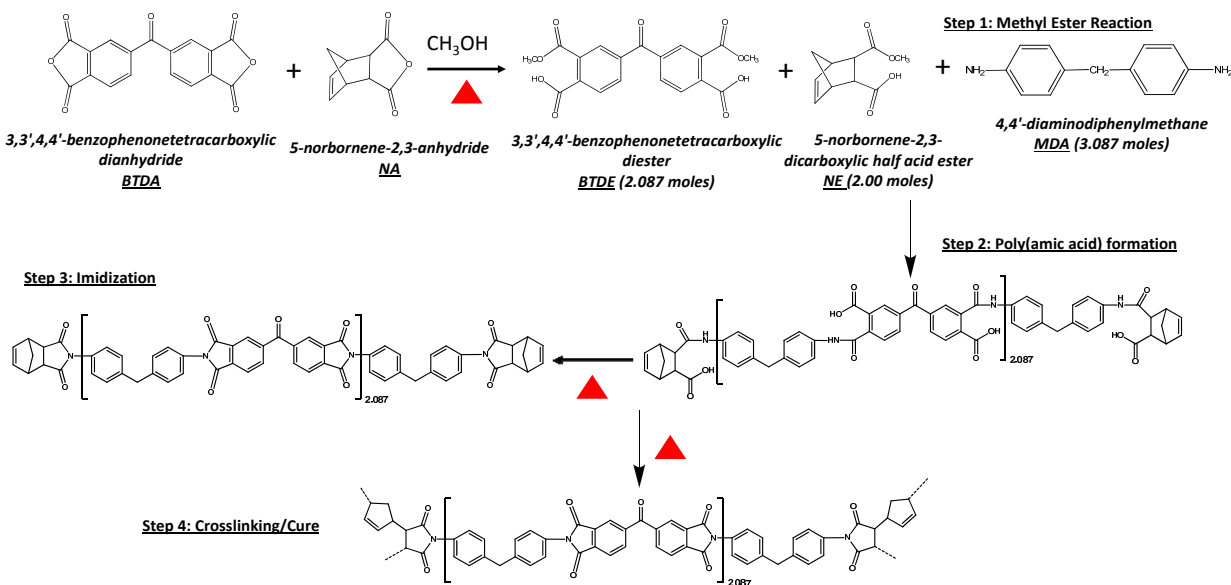


Figure 1. Synthesis strategy for PMR-15.

The foundation of PMR-15 material technology is that it affords the beneficial thermal and thermomechanical properties of polyimides, but due to its truncated molecular weight, is processable, thus enabling the fabrication of fiber reinforced polymer matrix composites via conventional tooling and manufacturing methods. In general, this technology is harnessed by coating fibrous fabric and unidirectional tape with a solution of PMR-15 amic acid dissolved in methanol, and most of the carrier solvent is driven off through drying processes. The resultant product is laid up in molds and on tools and cured through the controlled application of pressure and heat. The thermally precipitated crosslinking reaction for PMR-15 occurs through the nadic endcap as also illustrated in Figure 1, in simplified form, as network formation is not ideal in that several crosslinking products are formed, but the principal product is shown.

2.3 Characterization Methods

2.3.1 Differential Scanning Calorimetry

DSC experiments were carried out on a TA Instruments Q200 DSC. T-Zero DSC pans were loaded with 10-20mg of imide powder. The experiments were performed under a nitrogen environment at a purge rate of 50 mL/min. An initial ramp of 10 °C/min to 250 °C from RT was implemented to eliminate any residual solvent or water and to allow the powder to flow to form good contact with the bottom of the pan. The samples were then equilibrated at 40 °C and

ramped again at 10 °/min to 315 °C. The material was then held at this temperature for 2 hours to promote curing and subsequently equilibrated at 40 °C. The final temperature ramp was performed at 10 °C/min to 400°C.

2.3.2 Thermal Gravimetric Analysis (TGA)

TGA experiments were performed on a TA Instruments Q5000. Experiments were conducted under both air and nitrogen atmospheres. Temperature ramps were implemented between 25°C and 600°C at a rate of 1 °C/min, and the 5% mass loss temperature was utilized as a point of comparison between the materials. 5% mass loss was interpreted after the first mass loss event where species are lost during crosslinking.

2.3.3 Rheology

Rheological experiments were carried out on a TA Instruments Discover DHR3. The samples were loaded onto 25mm stainless steel parallel plates with a gap of 0.75 mm. Oscillatory experiments were performed at strain amplitude of 1% and the angular frequency was ramped from 0.1 to 100 rad/s. All experiments were carried out at 250°C.

2.3.4 Thermomechanical Analysis (TMA)

TMA experiments were conducted using a TA Instruments Q400. A quartz expansion-type probe was used and the furnace was purged with a nitrogen atmosphere. Initially, a force of 0.20N was implemented and the temperature was equilibrated at 100°C. Force was modulated at 0.05Hz and amplitude of 0.10N. The temperature was then cycled between 200 °C and 100 °C for two iterations. The temperature was then ramped at 5 °C/min to 350 °C, cooled at 5 °C/min to 100 °C, and again ramped at 5 °C/min to 360-400 °C. The cured glass transition temperature was ascertained from the last temperature ramp.

2.3.5 Density

Density measurements were performed using a Mettler-Toledo Density Kit for an MS-S Analytical Balance, in ethanol. Three measurements were taken and the average is presented.

2.3.6 Moisture Uptake

A 2L Erlenmeyer flask was filled with approximately 1750mL of de-ionized water and heated until boiling. Specimen discs were thoroughly dried in a vacuum oven for 3 days or until weight stabilization occurred. All specimens were weighed and then placed into the flask. At approximately 1 hour intervals, the samples were removed from the boiling water, blotted dry with paper media, blown dry with nitrogen, and weighed. The samples were then placed back into the boiling water and the process was repeated until the eighth interval at which time the samples were left overnight in boiling water before the final weight measurement.

2.3.7 Long-Term Thermal Oxidative Stability (TOS)

Long-term isothermal TOS experiments were conducted in a Lindberg Blue M tube furnace, at 316 °C. An air-generator fitted with a flow meter was connected to the tube such that a continuous flow of 100ml/min of air occurred across the samples. The cured discs were placed onto a graphite boat which was wrapped in an aluminum mesh to provide support to the discs

and to facilitate gas flow above and below the samples. Disk mass measurements were taken at 3-4 day intervals.

3. RESULTS

3.1 Analysis of Glass Transition Temperatures

The glass transition temperature, or T_g , can be determined from the inflection point of the transition from the “glassy” to “rubbery” state as measured by DSC. For PMR-15, the pre-cure glass transition temperature is clearly visible at 200 °C, after which an exotherm appears at ~260 °C, indicative of nadic endcap crosslinking. After cure for two hours at 315 °C, the T_g evolved to 339 °C. These T_g values are consistent with those reported in the literature for PMR-15. Immediately following the cured T_g , another exotherm is evident, this time caused by network degradation.

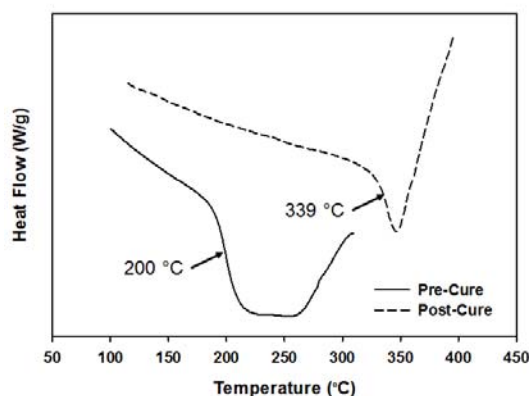


Figure 2. DSC traces for PMR-15 in the uncured and cured states.

The uncured and cured T_g s of the experimental oligoimides are tabulated in Table 2, in comparison with PMR-15. PMR-3, -8, -10, and -12 exhibit cured T_g s in the vicinity of that of PMR-15. The anilines used to synthesize these oligoimides are either similar to MDA (3 and 8), but possessing aliphatic moieties on the phenyl rings, or are tris-anilines (10 and 12), offering the possibility of a higher degree of crosslinking in the cured state.

Table 2. Measured uncured and cured glass transition temperatures for oligoimides.

Oligoimide	Uncured T_g (°C)	Cured T_g (°C)
PMR-15	200	339
PMR-1	151	240
PMR-2	168	283
PMR-3	203	320
PMR-4	173	277
PMR-5	181	270
PMR-6	57	95
PMR-7	199	271
PMR-8	192	323

PMR-9	186	294
PMR-10	167	324
PMR-12	244	347

3.2 Rheology and Viscosity Characterization

The dependence of oligoimide complex viscosity on angular frequency was investigated at strain amplitude of 1% and at 250 °C. This temperature was chosen as a comparison point because it is above all uncured T_g s as determined by DSC, and the reactivity of the nadic endcaps at this temperature was found to be low enough to not affect measurements within the timespan of this experiment. The results of this analysis are plotted in Figure 3. The majority of the oligoimides demonstrate lower complex viscosities than PMR-15 with the exception of PMR-3, -7, and -8. PMR-8 exhibits a very similar viscosity profile in comparison to that of PMR-15. The highly aliphatic structure of Jeffamine D-230 results in the lowest oligoimide complex viscosity of 30 Pa·s at 0.1 rad/sec, almost three orders of magnitude lower than PMR-15.

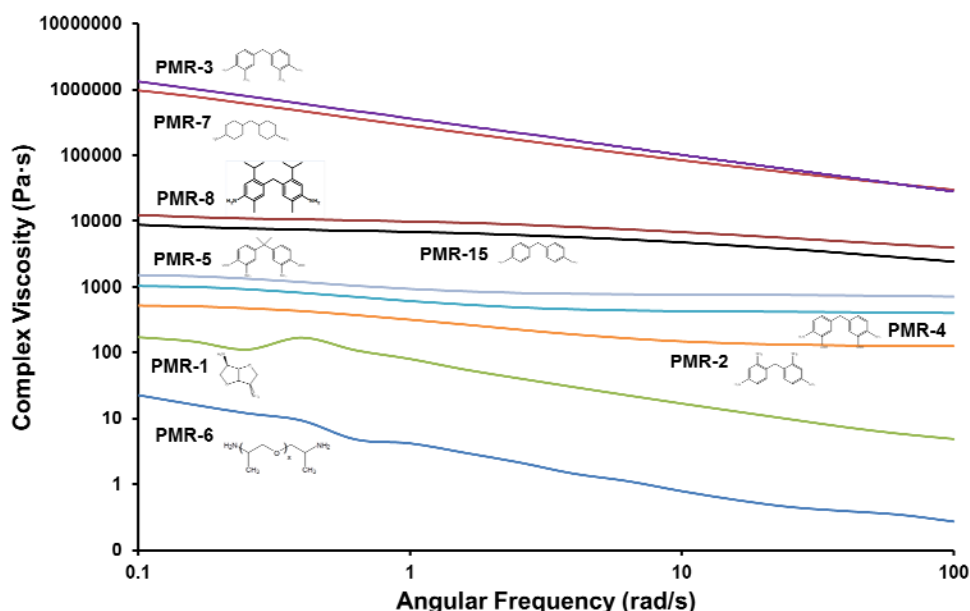


Figure 3. Complex viscosity as a function of angular frequency at 1% strain amplitude and 250 °C for several experimental oligoimides, in comparison with PMR-15.

3.3 Thermal Stability by TGA

The mass loss profiles for PMR-15 oligoamic acid in nitrogen and air are shown in Figure 4 (left), at a heating rate of 10 °C/min, to magnify events. Three distinct events are distinguished, clarified by the appearance of peaks in the derivative mass loss datasets. In the first event (~18% loss), the amic acid groups are converted to imides through ring closure and release of methanol and water. During the second mass loss event, much weaker than the first, nadic crosslinking occurs, and material response is dependent on atmosphere. Greater mass loss occurs in nitrogen in comparison with air, and this is known to be due to the release of cyclopentadiene. In the final

event, cured polyimide network degradation occurs. As expected, complete oxidation transpires in air and considerable char forms and subsists in inert conditions. TGA experiments were conducted on the experimental oligoimides, at a heating rate of 1 °C/min in two different purge atmospheres (air-oxidizing and nitrogen-inert), in a screening attempt because long-term weight loss experiments are prohibitively long duration. From the weight loss data, 5% mass loss temperatures after cure were quantified. Mass loss for PMR-15 initiates slowly at ~300 °C followed by intense mass loss occurring above 400 °C, peaking at ~460 °C (data not shown). The thermally induced degradation of PMR-15 occurs first by a breakdown of the aliphatic crosslinked species, followed by the methylene bridge in MDA, and lastly degradation of the remaining polymer. The oligomers possessing anilines with a higher degree of aliphatic character (PMR-1, -6, and -7), exhibit significant mass loss events at lower temperatures (commencing between 150 – 250 °C) and thus lower intensity higher temperature mass loss peaks, suggesting that the lower temperature mass loss events are due to premature aniline degradation, with respect to MDA in PMR-15. The addition of methyl groups to the basic MDA framework on the aromatic rings and at the methylene bridge catalyzes a higher degree of mass loss just above 300 °C in comparison with PMR-15. The 5% mass loss temperatures after oligoimide cure in both air and nitrogen are shown in Figure 4 (right), quantifying the general behavior of the mass loss rate data sets. As expected, the 5% mass loss temperatures are higher in an inert atmosphere due to the absence of oxidation. The PMR oligomers containing trisanilines perform best by this metric, most likely a result of a higher number of bonds to be broken [REF]. Also, PMR-3 behaves similarly to PMR-15, owing to the chemical similarity between the two monomers (aniline [3] features methyl groups meta to the anilines).

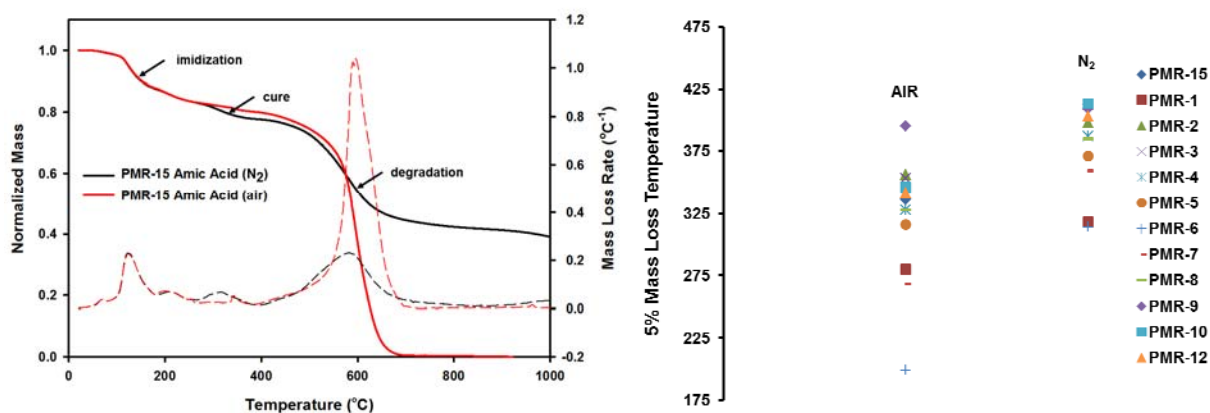


Figure 4. Mass loss profiles (solid lines) and their first derivatives (dashed) for PMR-15 oligoamic acid in nitrogen (black) and air (red) at 10 °C/min (left); 5% mass loss temperatures in nitrogen and air after oligoimide cure at a scan rate of 1 °C/min (right).

3.4 Neat Resin Disk Specimen Fabrication

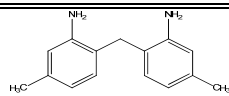
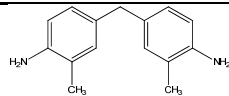
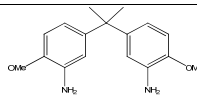
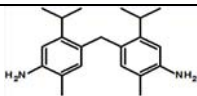
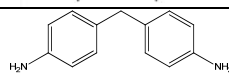
0.5 inch diameter disks, approximately 1-2 mm thick, served as specimens from which the most critical screening tests were performed, including moisture uptake, viscoelastic analyses by TMA, moisture uptake, and long-term TOS. Density measurements were also performed. TOS was the last test to be performed on a disk due to its irreversibly destructive nature. Specimens were fabricated via heated compression molding to varying degrees of success and based on the availability of material. Successful specimens were fabricated from PMR-2, -3, -5, -8, and -15.

The remaining materials required processing modifications and a viable disk could not be fabricated on the first attempt, and subsequent attempts are currently being made.

3.5 Density

Densities of the cured neat resin discs are given in Table 3. Most of the disks exhibited lower densities than PMR-15, with the exception of PMR-2. In general, the addition of isopropyl, methyl, and methoxy groups on the phenyl rings increase free volume of the cured network, resulting in lower cured densities. For PMR-2, the expected effect of additional methyl groups appears to be countered by the change in location of the amines.

Table 3. Density measurements of cured neat resin discs and the corresponding chemical structures of the aniline monomers used in their syntheses.

Material	Density (g/cm ³)	Aniline Structure
PMR-2	1.27	
PMR-3	1.23	
PMR-5	1.19	
PMR-8	1.15	
PMR-15	1.27	

3.5 Thermomechanical Analysis (TMA)

From modulated TMA, the viscoelastic properties of materials including the elastic and viscous components are readily decoupled. The T_g of a polymer can be ascertained from the onset of loss in elasticity (storage modulus), the peak temperature of the viscous (loss) modulus, and the temperature peak in tan delta, as well as from the change in the coefficient of thermal expansion. These values are presented in Table 4, for all of the cured disk specimens that could be fabricated. From an engineering perspective, the storage modulus method yields the most meaningful results as this represents the temperature at which a polymer will typically begin to yield under stress at elevated temperature. While all four methods yield different results, the trends across methods and materials is consistent.

The T_g values from storage modulus for PMR-2, -4, and -8 are all within 5% of PMR-15, in contrast to the DSC data. PMR-5, modified with methyl and methoxy groups, exhibits the lowest T_g among the materials tested. Discrepancies between the two methods is likely due to the different thermal histories of the materials at the time of measurement: DSC measurement of the T_g was performed after a 315 °C isothermal cure for two hours, while TMA measurement of the

T_g was performed after ramping the specimens to 360 – 400 °C, which could precipitate some degradation or further cure of the networks.

Table 4. T_g values as determined from various TMA measurements.

	T _g (°C) based on:			
	Storage Modulus	Loss Modulus	Tan Delta	Dimension Change
PMR-2	326.96	334.96	345.05	315.1
PMR-4	334.76	362.93	372.9	316.41
PMR-5	288.91	300.58	305.63	278.35
PMR-8	330.39	338.3	343.22	315.92
PMR-15	343.04	365.9	374.17	319.37

3.6 Moisture Uptake

Moisture uptake as a function of time in boiling water, depicted in Figure 5, shows that both PMR-15 and PMR-8 absorb water at approximately the same rate during the first 3 hours. After that period, PMR-8 slows in terms of water absorption and levels out at 3.2%, saturating at 3.4% after 23 hours. PMR-15 does not equilibrate until reaching approximately 4%, saturating at 4.5% after 23 hours. PMR-8 therefore exhibits a 24% decrease in saturated water absorption. PMR-3 and PMR-5 both demonstrate decreases in ultimate absorption at near 4%. In general, the addition of substituent groups to the phenyl rings or central quaternary carbon of MDA evidently occupy volume in the cured network that would otherwise be available space for water molecules.

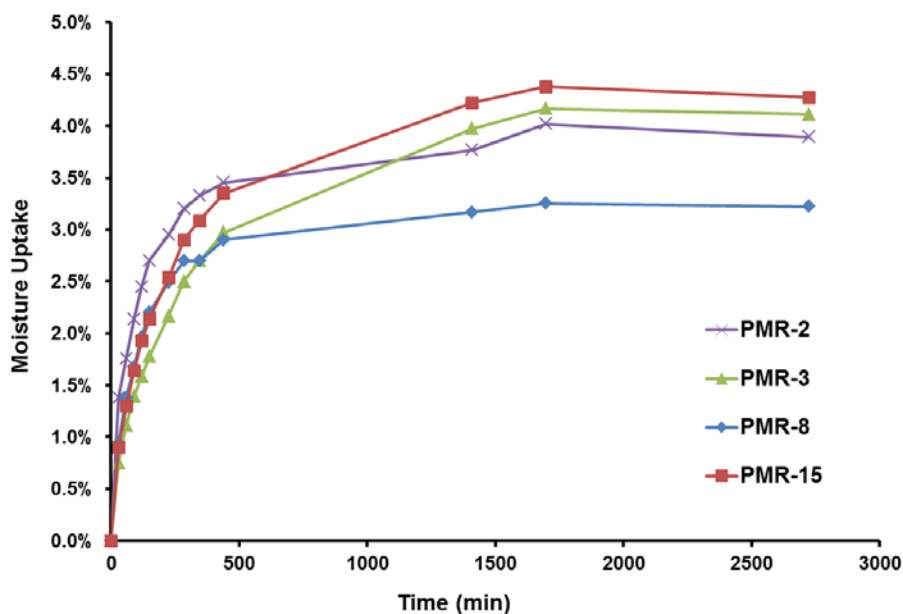


Figure 5. Moisture mass uptake over time of cured neat resin discs in boiling deionized water.

3.7 Long Term Isothermal Thermo-Oxidative Stability (TOS)

Figure 6 presents the mass loss as a percentage of initial mass of each cured neat resin disc over time at 316°C in the presence of an air purge. Surprisingly, PMR-8 exhibits the best TOS performance in comparison with PMR-15, despite aniline [8] having the highest degree of aliphatic substituents on its phenyl rings. At over 650 hours, its mass loss is almost 3.5% compared to approximately 1.7% for PMR-15. PMR-3 and PMR-2 lose 3.9% and 4.7% of mass, respectively, at 675 hours.

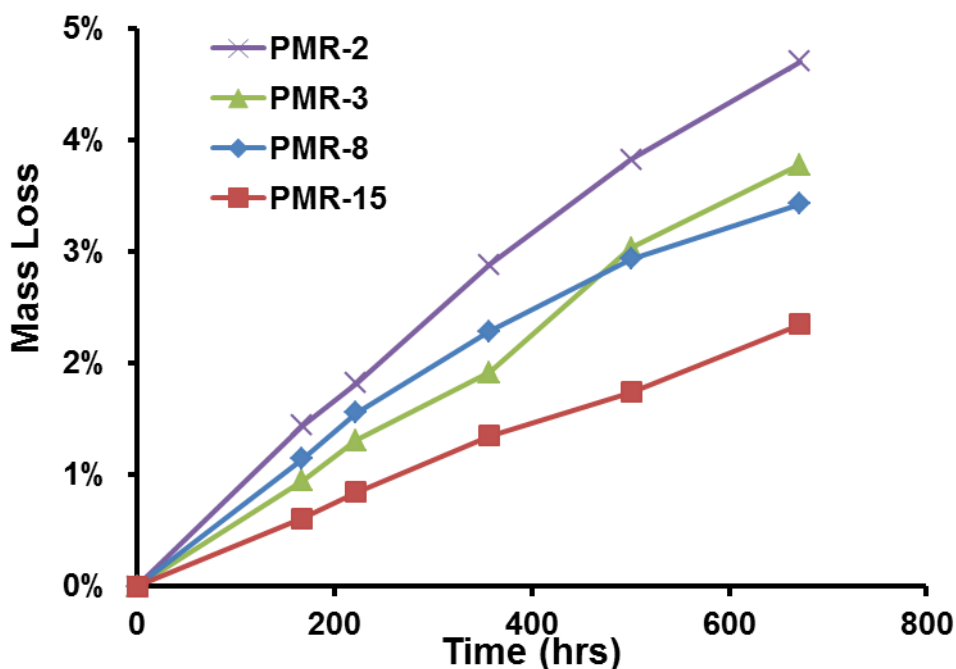


Figure 6. Mass loss as a percentage of initial mass of cured neat resin discs at 316 °C over time in air.

3.8 Hybrid (Organic/Inorganic) Resins

A polyhedral oligomeric silsesquioxane (POSS) dianiline was analyzed for its properties when oligomerized with BTDA and NA. Shown in Figure 7, this monomer features a silsesquioxane core with an aryl periphery to maximize thermal stability. Three ratios of monomers were successfully oligomerized: BTDA/POSS/NA 0/1/2, referred to here as Di-Nadic POSS, 1/2/2 (oligomer 1), and 2/3/2 (oligomer 2). Oligomer 2 is analogous to PMR-15 in terms of molar stoichiometry.

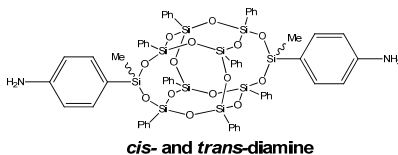


Figure 7. Chemical structure of silsesquioxane (POSS) diamine. Ph represents phenyl group.

The POSS dianiline was found to significantly reduce processing viscosity. To illustrate this effect, oscillatory rheology experiments were conducted on PMR-15 and di-nadic POSS, shown in Figure 8. The latter demonstrates at the lowest point a complex viscosity that is two orders of magnitude lower than PMR-15. This presented difficulties in processing neat resin disks and composites from di-nadic POSS, eventually overcome through institution of a staging cycle, devoid of pressure, to increase the complex viscosity to that of PMR-15 prior to the application of pressure.

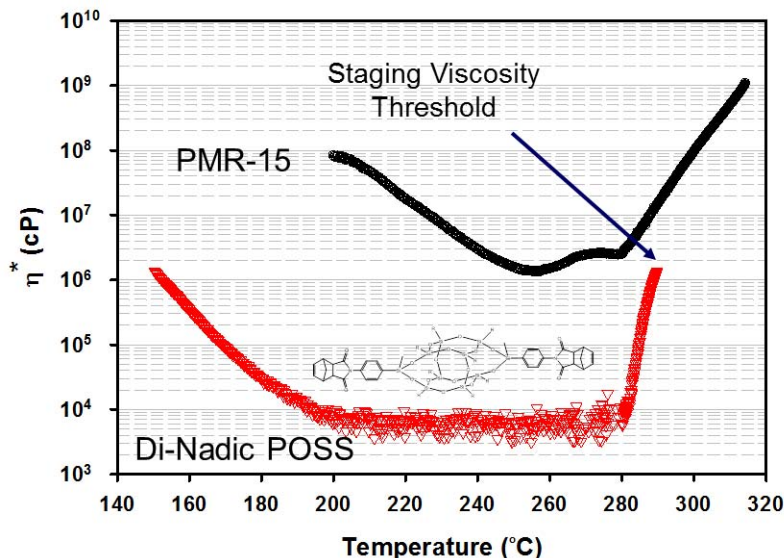


Figure 8. Non-isothermal oscillatory rheology experiments conducted on PMR-15 and Di-Nadic POSS.

Substitution of the POSS dianiline for MDA reduces pre- and post-cured T_g , due to its large size, which effectively decreases inter-chain interactions in the uncured state and the distance between crosslinks in the cured states. The cured T_g s for oligomers 1, 2, and Di-Nadic POSS were measured to be 230, 253, and 343 °C, respectively, in comparison with 330 °C for PMR-15. The relatively high T_g of Di-Nadic POSS is a consequence of its high concentration of nadic endcap and resultant crosslink density. Although this property was found to be favorable, the high nadic crosslink density was found to be detrimental to long-term TOS, as the products of nadic group crosslinking are weakest in terms of stability, and flexural strength due to resin embrittlement. POSS oligomerization was found to greatly enhance moisture resistance, where saturated moisture uptake for the cured resins was measured to range from 0.5-1% in comparison with over 4.5% for PMR-15, despite the presence of POSS reducing cured network density and increasing the water molecule diffusion rate.

Flat laminate composites were fabricated from both PMR-15 and Di-Nadic POSS using Hexcel IM7 4 harness satin weave, GP sized. Mechanical and long-term TOS characterization was performed on these laminates. The POSS Di-Nadic composite's resin dominated mechanical properties including flexural and interlaminar shear did not compare favorably with PMR-15. Also, the POSS Di-Nadic composite lost more mass during isothermal TOS in air at 316 °C, but

showed no signs of micro-cracking after 450 hours, in contrast to the PMR-15 composite that exhibited significant matrix micro-cracking, as shown in Figure 9.

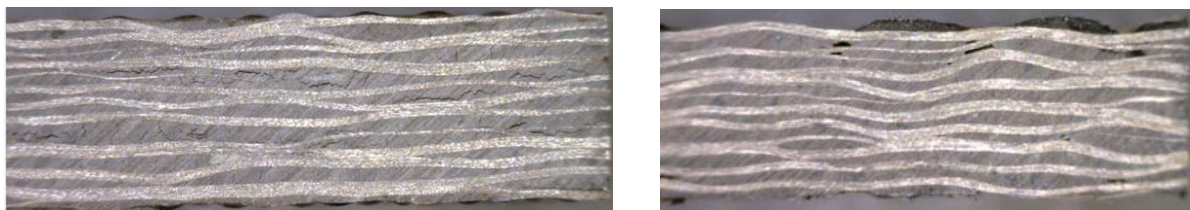


Figure 9. Micrographs of PMR-15/IM7 (left) and Di-Nadic POSS/IM7 (right) composites after 450 hours aging in air at 316 °C.

4. CONCLUSIONS

A number of thermosetting oligoimides were synthesized from novel aniline monomers, affording the opportunity to screen the key properties of those materials using PMR-15 as the benchmark. Cured glass transition temperatures, short- and long-term thermal stability, processing viscosities, moisture uptake, cured densities, and cured viscoelastic properties were measured. Some of these properties could be determined simply from imidized powder, but the majority required analyses on cured neat resin disks. In some cases, difficulties were encountered during disk fabrication attempts, either due to very low oligoimide viscosity, or due to premature reaction/degradation events. The latter condition resulted in porous disks that could not be characterized. Nevertheless, disks from some materials were successfully fabricated.

The metric of success for a given property is, if that property is lower than that of PMR-15, it is to be within 5%. Characterization activities have thus far revealed that no difunctional aniline monomer provides the same combination of properties that MDA affords, in that not all properties measured for a particular material were found to be within 5% of that of PMR-15. Cured glass transition temperatures and long-term TOS are clearly the most difficult properties to achieve, especially in the context of having to meet bio-compatibility goals. Nevertheless, a few monomers demonstrate properties that are worthy of further investigation, PMR-3 (MDA with methyl groups meta to the anilines) and PMR-8 (MDA with meta isopropyl and ortho methyl groups). Both monomers exhibit cured glass transition temperatures within 6% of that of PMR-15 (based on a 0 °C scale), and approximately twice the mass loss during long-term TOS in air. However, it remains a possibility that the cured glass transition temperatures resulting from the use of these monomers may be raised by modifying the cure cycle, but network degradation must be avoided. Furthermore, since only ~40% of a composite is resin by volume, the observed increases in mass loss during TOS experiments could be within acceptable boundaries in composite form. PMR-8 is currently being scaled up to facilitate composite fabrication and characterization.

Promising cured glass transition temperatures and short-term thermal stability have been observed from trifunctional monomers (trisanilines), including PMR-10 and hydrogenated resveratrol (PMR-12). Issues with fractionation and inconsistent synthesis product have lingered.

Hybrid oligoimides synthesized from a POSS dianiline afforded mixed results. The POSS monomer significantly reduces processing viscosity which could expand the use of high

temperature polyimides to resin infusion composite manufacturing techniques. The POSS monomer itself is sufficiently thermally stable and imparts notable moisture resistance, but significantly reduces cured network T_g . This effect can be countered by increasing crosslink density, although this is to the detriment of those resin properties affected by toughness.

New anilines will continue to be explored as they are available. The current experimental framework for the screening of materials is largely predicated on the success of small cured neat resin specimen fabrication, of which varying degrees of success have been experienced, due to premature reactions (likely due to chemical degradation) and prohibitively low viscosities. Low viscosity is an issue that is difficult to overcome when utilizing compression molding as a fabrication technique. Nevertheless, although cured glass transition temperature can be measured by DSC without fabricating a cured, void-free specimen, it is unclear as of yet whether TGA is an effective screening experiment, based solely on the availability of comparable data, as only a few disks have been fabricated thus far. For materials PMR-2, PMR-3, PMR-8, and PMR-15, TGA experiments performed at 1 °C/min in air correlate very well with long-term TOS, however they only reveal trends but no quantitative information on how materials perform during isothermal aging.

Lastly, quantitative Structure-Activity Relationship (QSAR) models were used to predict the physical characteristics and toxicity of alternative anilines. QSAR methods start with a group of chemical structures whose properties are known (the “training set”), classify the structures using various chemical descriptors (sub-elements of chemical structures and functional groups), and extrapolate the toxicological properties of new, unknown compounds (the “test set”). The more closely the test set compound conforms to the descriptors of the training set, the more accurate the prediction. Even in the absence of good conformation with the training set, in the hands of an experienced evaluator, the QSAR prediction can often provide useful information indicating what toxicity effects can be expected from a novel compound. While not all chemical substances can be modeled using QSAR techniques, organic, organometallic, and organic salts can often be adequately assessed. Agreement for MDA between model predictions and experimental data was found for the following parameters: skin sensitization, ocular irritation, mutagenicity, and carcinogenicity. Of the experimental monomers evaluated by QSAR, monomer [8] was found to be non-toxic, and this compound was recently experimentally confirmed to be non-mutagenic (and therefore likely non-carcinogenic) by the Ames test. The POSS dianiline has not been evaluated by QSAR.

5. ACKNOWLEDGEMENTS

We gratefully acknowledge financial support from the Strategic Environmental Research and Development Program (Dr. Robin Nissan) for programs WP 2402 and 2403.

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