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As part of a cooperative research and development agreement, the Navy, the Air Force, and Boeing are jointly working towards the development of novel processable polymer resins for structural applications requiring demanding thermal stability and hot-wet performance, targeting service temperatures in the range of 450 and 700°F. An overview of the program's approach and screening tools will be presented. Emphasis will be placed on the thermal and moisture absorption analysis techniques that are being implemented to guide resin formulation development ensuring facile liquid-molding processing, viz. resin-transfer molding (RTM) and resin film infusion (RFI). Some key findings regarding structure-property relationships are discussed.

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DEVELOPMENT OF PROCESSABLE HIGH-TEMPERATURE RESINS FOR COMPOSITE MATERIALS (PREPRINT)

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ABSTRACT

As part of a cooperative research and development agreement, the Navy, the Air Force, and Boeing are jointly working towards the development of novel processable polymer resins for structural applications requiring demanding thermal stability and hot-wet performance, targeting service temperatures in the range of 450 and 700°F. An overview of the program's approach and screening tools will be presented. Emphasis will be placed on the thermal and moisture absorption analysis techniques that are being implemented to guide resin formulation development ensuring facile liquid-molding processing, viz. resin-transfer molding (RTM) and resin film infusion (RFI). Some key findings regarding structure-property relationships are discussed.

KEY WORDS: Resins/Materials – Thermosets, Polymeric Resins/Block Copolymers/Blends, Moisture/Moisture Effects

1. INTRODUCTION

In recent years, a number of factors including the need for lighter, more energy efficient structures, increased interest in new high speed aircraft and weapons systems, and a growing desire to incorporate structures with good electrical insulating characteristics and little or no interaction with electromagnetic radiation have all contributed to renewed attention to research and development in the area of high-strength, high temperature polymer matrix composite materials. Despite the increased attention, successful development and utilization of many of these materials has been limited by, among other considerations, undesirable properties of the polymer matrix resin materials that require significant cost and complexity to mitigate. These undesirable properties include 1) toxicity of many of the chemicals used to fabricate the resins, 2) poor performance (excessive flame and smoke, dripping, and generation of hazardous substances) during fires, 3) significant absorption of water in a humid environment (which has been linked to delamination during rapid heating), and 4) in the case of many of the materials with the highest use temperatures, difficulties is fabrication, especially with newer, less expensive fabrication techniques. The second and third of the foregoing issues are of special concern to applications involving operation in a ship-board environment.

In order to address these concerns, a number of research and development efforts have recently been initiated at the Naval Air Warfare Center, the Air Force Research Laboratory's Propulsion Directorate, and BOEING Phantom Works. These efforts have thus far resulted in the creation of several new types of thermosetting polymeric resins that are potentially superior replacements for state-of-the-art materials in some applications. The following report describes these materials and their potential advantages in detail, covering two distinct classes of resin: cyanate esters and poly-p-phenylenes. In each case, the descriptions focus on the resistance to moisture uptake and thermal oxidation of the materials, with a related discussion of the processing characteristics. For both classes of resin, the newly created candidates are as easy, if not easier, than currently available materials to fabricate using simple processing techniques. Moreover, they exhibit reduced uptake of water and improvements in thermo-oxidative resistance, illustrating that the next generation of polymer composite resin materials is likely to overcome many of the current obstacles to more widespread utilization.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Toughened Cyanate Esters The di(cyanate ester) of bisphenol A (BADCy) was supplied by Lonza and used as received (HPLC indicated the monomer was 99.4% pure). Amorphous polycarbonate (APC), used as a polymeric toughening agent in this work, was supplied by Aldrich (melt flow 2.0-5.0, Aldrich grade ID 43058-7). Toughened samples were cast from a mixture formed by dissolving the toughening agent in methylene chloride and adding it to molten BADCy at 80-100°C. The toughening agent was added at 10 and 20 parts per hundred BADCy on a weight basis. In all cases the casting solution was carefully poured into 3 mm deep open molds with lateral dimensions of 10 mm x 25.4 mm and then baked according to the following schedule: 190°C (two hours), 225°C (one hour), 250°C (one hour), and lastly 300°C (one hour). Some castings were ground to powder for thermogravimetric analysis (TGA), while others were cut into sections 5 mm x 5 mm x 3 mm for thermomechanical testing. Still other samples were polished and retained for water boil testing. The chemical structures of BADCy monomer and APC are shown in Figures 1a and 1b, respectively.

2.1.2 Silane-Based Cyanate Esters The chemical synthesis of a silicon-containing analog to BADCy, the di(cyanate ester) of dimethyldi(p-phenol)silane, referred to as SiMCy) has been described previously (1). Additional physical data for this compound has also been published. The compound, which melts at 59°C, was cast from the unmodified melt using exactly the same procedures employed for the modified BADCy materials. Although the solubility of APC in BADCy and SiMCy was observed to be quite similar, a complete characterization of toughened samples made using SiMCy as a matrix has not yet been completed. The chemical structure of the SiMCy monomer is shown in Figure 1c.

2.1.3 Poly-p-phenylenes The synthesis of poly-p-phenylenes through the catalytic coupling of dichlorides (and monofunctional chlorides that serve as end caps) is

described in a number of reports. Phenyl ethynyl terminated polyphenylene oligomers exhibiting the structure shown in Figure 1d (referred to as P3-2300-PE) were synthesized at the Naval Air Warfare Center and purified. Castings of P3-2300-PE were made by melting the powder in an open mold at 180°C. The castings were subsequently cured at temperatures ranging from 350-450°C by heating at 1°C/min. and holding at the temperatures and for the times indicated. In order to obtain good quality castings, the casting thickness was limited to 1 mm in thickness.

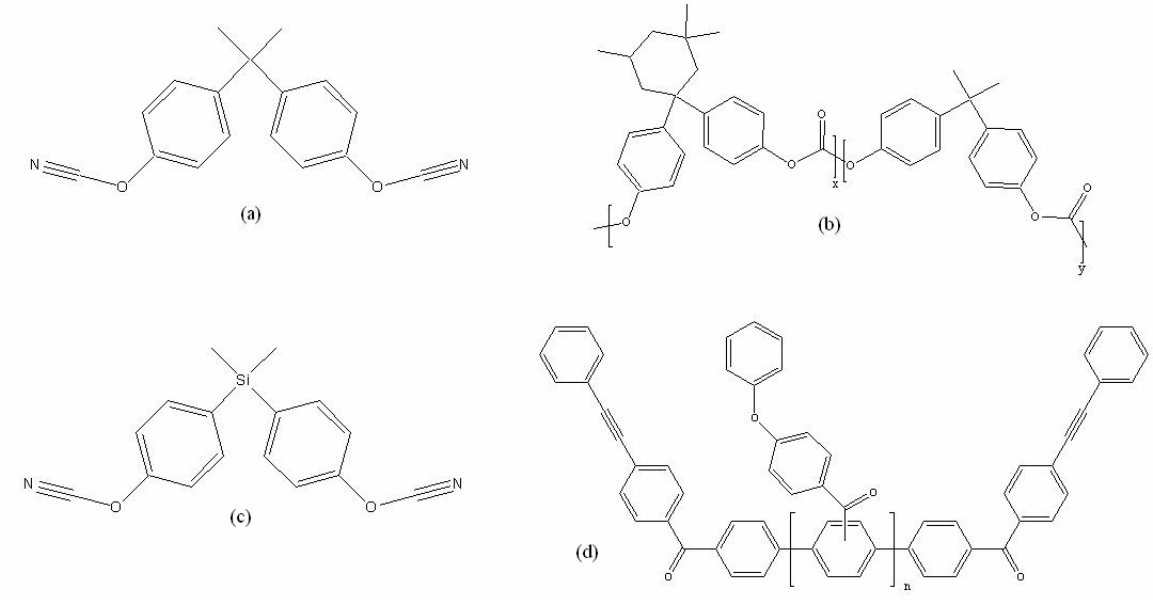

Figure 1. Chemical structures of (a) BADCy, (b) APC, (c) SiMCy, and (d) P3-2300-PE.

2.2 Methods of Analysis

2.2.1 Thermal Analysis Changes in the weight of 5 mg powdered samples of all new resin materials were monitored using a TA Instruments 2950 Hi-Res Thermogravimetric Analyzer and/or a TA Instruments Q600 Simultaneous Differential Thermal Analyzer (for simultaneous weight change in heat flow measurements). The changes were observed by heating at 10 °C / min. from room temperature to 600°C. The experiments were conducted in both nitrogen (dew point approximately -70 °C) and laboratory air atmospheres. For the cyanate ester specimens, the coefficients of linear thermal expansion were measured using a TA Instruments 2940 Thermomomechanical Analyzer (TMA). 3 mm square samples were cut from 1 mm thick castings and cycled from room temperature to 300 °C at a rate of 10 °C / min., with data from the first heating and cooling excluded from the calculation. To characterize poly-p-phenylene / carbon fiber composite panel specimens, dynamic mechanical analysis (DMA) was implemented with a TA Instruments Q800 instrument in three-point bend configuration at a frequency of 1 Hz, a strain of 0.02%, implementing a temperature scan rate of 5°C/min. in a nitrogen environment. Viscometry was performed on an Anton Paar MCR500 rheometer in parallel plate configuration with a gap spacing of 1.5 mm under a nitrogen blanket.

2.2.2 Moisture Exposure Tests Exposure of casting samples to constant humidity was accomplished by placing them in sealed chambers equilibrated with aqueous salt solutions. In addition, select samples were immersed in deionized water either at room temperature or maintained at a slight boil. Each sample was weighed twice prior to exposure and twice after exposure. When exposure involved liquid immersion, the castings were carefully patted dry with a clean laboratory cloth prior to weighing after exposure.

3. RESULTS AND DISCUSSION

3.1 Toughened Bisphenol A Cyanate Esters Figures 2a and 2b display the comparative TGA thermograms under nitrogen (Figure 2a) and air (Figure 2b) of BADCy and BADCy modified with 10 and 20 wt% APC. APC contains both bisphenol A and aliphatic-based carbonate repeat units, with the latter exhibiting substantially inferior thermal stability. It is therefore not surprising that increasing APC content leads to increased extents of weight loss at 600°C. Even at 20 wt%, however, the magnitudes of the losses is relatively mild. It is not intuitive, however, to observe increased 5 wt% loss temperatures in the blends over the control, indicating short-time improvements in thermal stability within a certain temperature range during the non-isothermal scans.

In Figure 3, the weight gain of BADCy toughened with 10 and 20 wt% APC is compared to that of the unmodified cyanate ester as a function of exposure time in boiling water. The presence of APC results in a substantial reduction of water uptake. Since APC absorbs less than 0.2% moisture on immersion, its inclusion should lower the overall water uptake nearly in proportion to its content. The data, however, indicate an effect that is much greater than what would be expected based on the level of toughening agent, especially at 10 wt%. In light of these observations coupled with the witnessed improvements in thermal stability between 400 and 450°C, it is plausible that morphologies in the blends are achieved that reduce both thermal motion and diffusion by water and oxygen, possibly through hydrogen bonding of the oxygen atoms in the backbone of APC with hydrogen atoms of BADCy cured chemical structures and/or through a reduction in free volume. This hypothesis is supported by optical investigations of the phase morphologies of the toughened systems that demonstrated very little phase separation, even in the case of the 20 wt % APC mixture. It is conceivable that the formation of an “interpenetrating network” promoted through strong interactions between the matrix and modifier may reduce the overall crosslink density of the cyanate ester, which is currently being investigated through mechanical property evaluation.

3.2 Silane-Based Cyanate Esters Due to its low melting point, low melt viscosity, and similar curing kinetics, we observed that SiMCy could be processed readily as a drop-in replacement for BADCy. Yet in terms of performance, SiMCy exhibits two distinct advantages over BADCy. Figures 4a and 4b compare the TGA thermograms of cured SiMCy and cured BADCy in nitrogen (Figure 4a) and air (Figure 4b). SiMCy exhibits slightly lower thermal stability in nitrogen, most likely attributable to the replacement of C-C bonds with slightly weaker C-Si bonds. In air, however, the degradation of SiMCy at higher temperatures is suppressed, resulting in a char yield at 600°C that is about 50%

larger than BADCy. In SiMCy, the presence of silicon is expected to lead to the generation of non-volatile SiO_2 upon exposure to oxygen at elevated temperatures, which would account for the increased amount of material remaining after exposure to elevated temperatures.

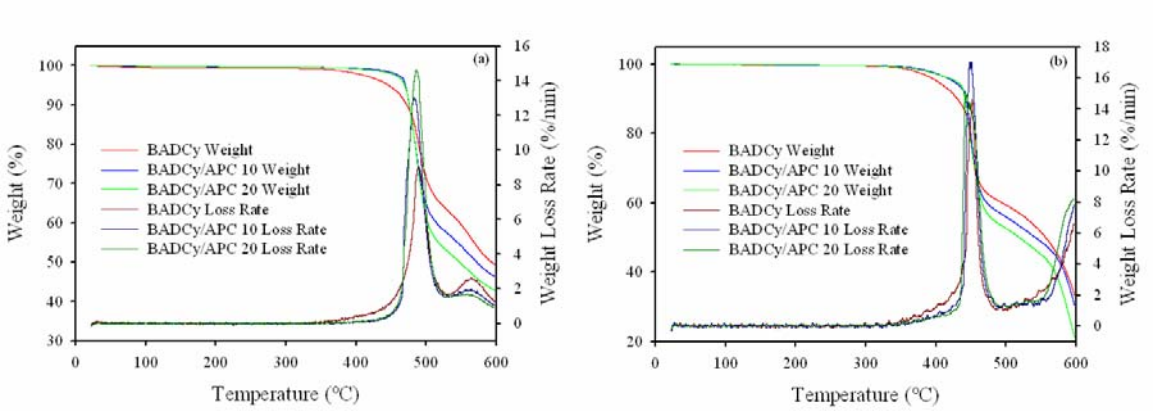

Figure 2. Thermal stability of BADCy and BADCy/APC blends via TGA in (a) nitrogen, and (b) air.

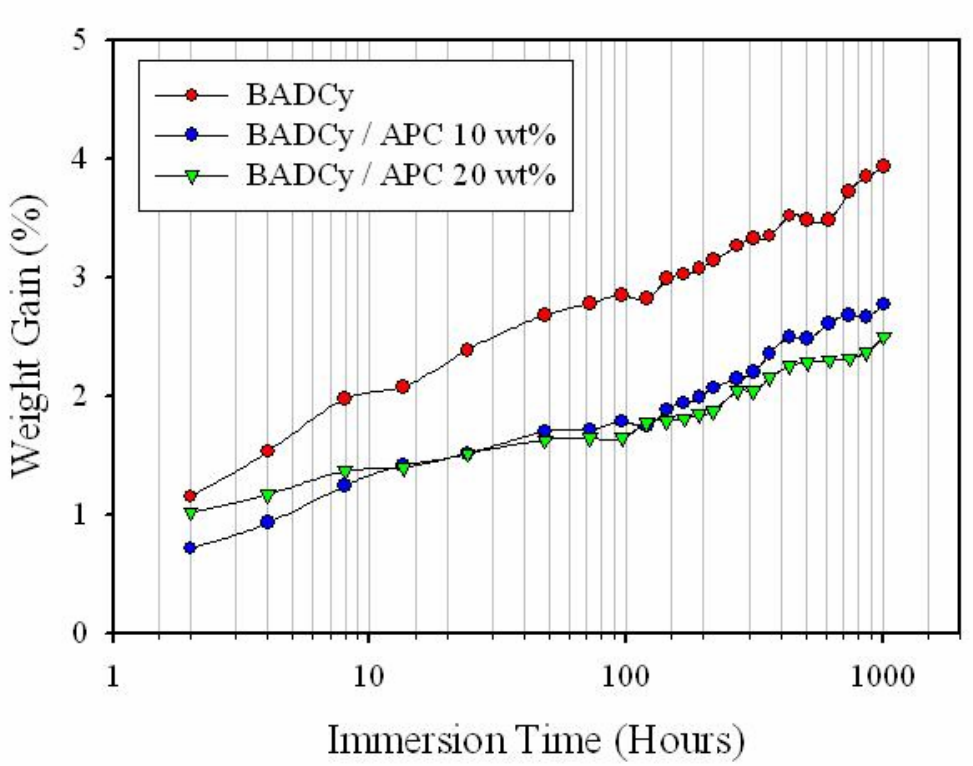

Figure 3. Weight gain of BADCy and APC blends during water boil immersion.

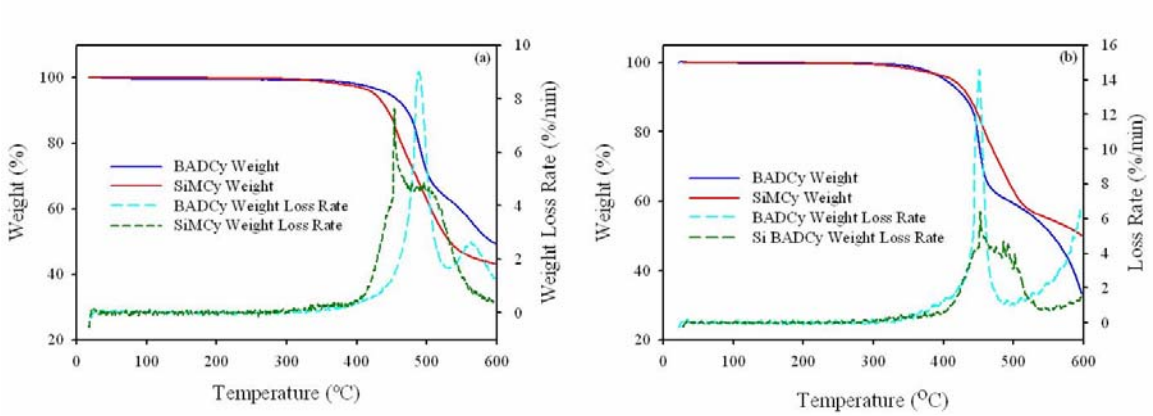

Figure 4. Thermal stability of BADCy and SiMCy via TGA in (a) nitrogen, and (b) air.

Although the foregoing result is in line with expectations, the data in Figure 5 reveal a more surprising result, illustrating that the amount of water absorbed by SiMCy over the course of 1000 hrs of exposure to boiling water is about 50% less than in BADCy. The amount of water absorbed by cyanate ester resins varies considerably as a function of monomer chemistry and extent of pre-polymerization, yet in most cases there is a well-understood mechanism to explain the difference (for instance, the replacement of $–CH_3$ groups with more hydrophobic $–CF_3$ groups decreases moisture uptake.) It is worth noting that adding ortho-substituted methyl groups to the phenyl rings adjacent to the cyanate ester linkages (in AroCy L10) also results in substantially decreased water uptake. These groups may lower moisture uptake by disrupting a network of hydrogen bonds that can form among the ether cyanurate linkages in the polymer. It is hypothesized that in SiMCy, differences in local molecular packing in the amorphous polymer may similarly alter the distribution of hydrogen bonding, resulting in lower moisture uptake. Such differences are hinted at by the remarkably different crystal structures of SiMCy and BADCy, as well as by the fact that the molar volumes of SiMCy and BADCy are demonstrably different in polymers with a high degree of cure.

Since polymer matrix composite components are often mated with metallic parts in a variety of structures, novel resin development is driven in part by tailoring coefficients of thermal expansion (CTE). The CTE's of BADCy and its blends with APC, in addition to that of SiMCy, are shown in Table 1. The replacement of C – C bonds with C – Si bonds in SiMCy is accompanied by a doubling in CTE in comparison with that of BADCy, likely due to the increased length of the C – Si bond causing elevated expansion with temperature. The addition of APC to BADCy also increases the observed CTE's, an expected result, since in general thermoplastics exhibit greater thermal expansions than thermosets. The presence of APC may also reduce the effective crosslink density of BADCy, especially in the case of interpenetrating network formation.

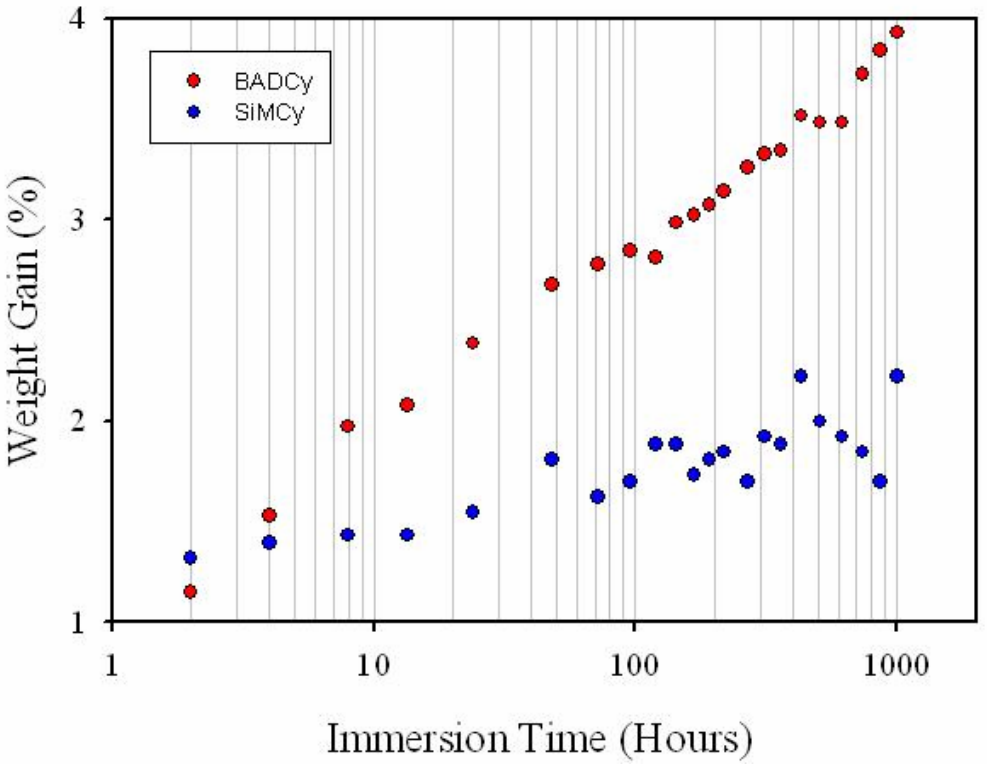

Figure 5. Weight gain of BADCy and SiMCy during water boil immersion.

Sample	CTE mm/(mm•K)
BADCy	5.00×10^{-5}
SiMCy	9.34×10^{-5}
BADCy / APC 10 wt%	6.82×10^{-5}
BADCy / APC 20 wt%	9.29×10^{-5}

Table 1. Coefficients of thermal expansion of SiMCy and BADCy and its blends with APC as measured by TMA.

3.3 Poly-p-phenylene Resins Polyphenylene thermoplastics, which have recently become commercially available, are noted for their outstanding fire resistance and low moisture absorption. In Figure 6, the weight loss rate of cured poly-p-phenylene is compared with those of other state-of-the-art high temperature polymeric materials, namely polyetherimide (Ultem 1000), novolac-type cyanate ester Primaset PT-30, APC, and an anthracene-containing copolyimide (a-cPI). As shown by the traces, polyphenylenes demonstrate outstanding thermal stability in comparison with the other materials, with noticeable weight loss commencing in the vicinity of 500°C but markedly less in magnitude than most polyimides. As a general observation, the extent of the weight loss of polyphenylene in TGA experiments under nitrogen usually appears to be proportional to the molecular weight of the chemical groups pendant to (but not including) the ketone linkage to the phenylene backbone. The observed benefits in thermal stability manifest in remarkable flame retardant properties, where like their

thermoplastic analogues, the phenyl ethynyl terminated Navy P3 thermosets have been shown to be self-extinguishing when infused into a carbon fiber cloth and cured to form a 2” x 2” composite panel.

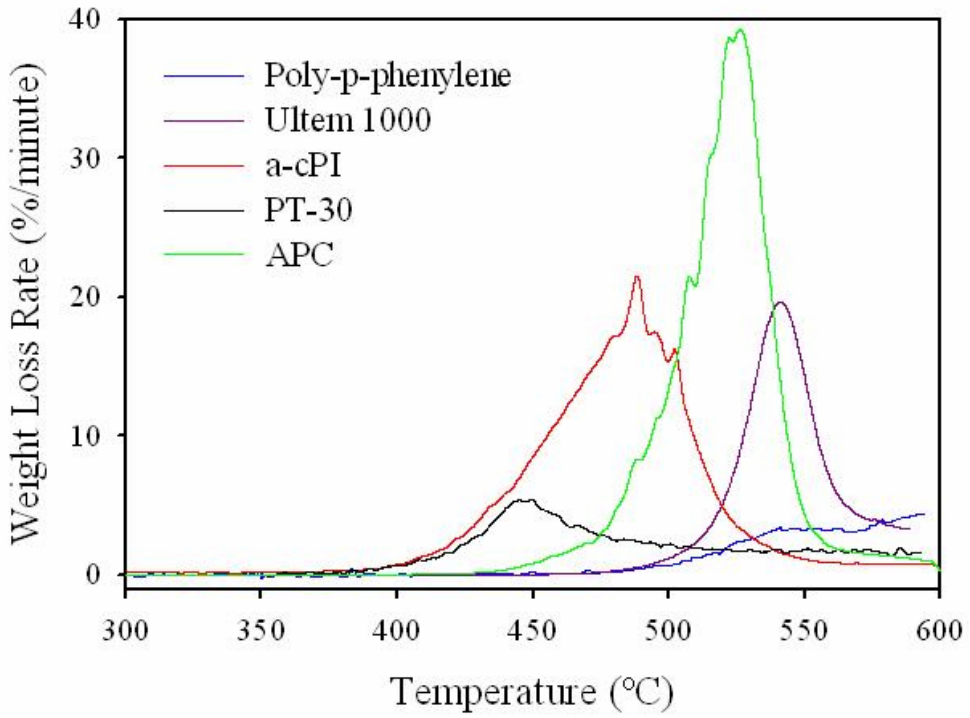

Figure 6. Comparison of rates of weight loss via TGA (nitrogen) amongst various high temperature polymers.

The incentive to develop reduced molecular weight yet reactive polyphenylene resins is rooted in generating materials that are suitable for composites processing. Although there are commercially available versions of polyphenylenes, they are currently high molecular weight thermoplastics that generally require high tonnage injection molding machines to fabricate void-free parts. These high viscosity materials would undoubtedly damage the structural integrity of fiber mats in conventional resin transfer molding (RTM) processes leaving them unsuitable for carbon fiber infiltration. To investigate the processing viscosities of P3-2300-PE, variable shear parallel plate rheometry was employed, utilizing disks formed by sintering the polymer powder at 180°C in free standing molds devoid of pressure (a disk fabricated via this methodology is depicted in Figure 7(a)). RTM processing requires resins to have viscosities in the range of 10 – 100 Poise, which are achieved at all of the investigated shear rates in the temperature range 280 – 300°C as shown in Figure 7(b). In addition, an isothermal experiment was conducted at 300°C to evaluate the pot-life of the resin. Owing to the activation energy of the phenyl ethynyl end-caps, the viscosity of P3-2300-PE did not exceed 100 Poise during an exposure time of 1.5 hours (results not shown).

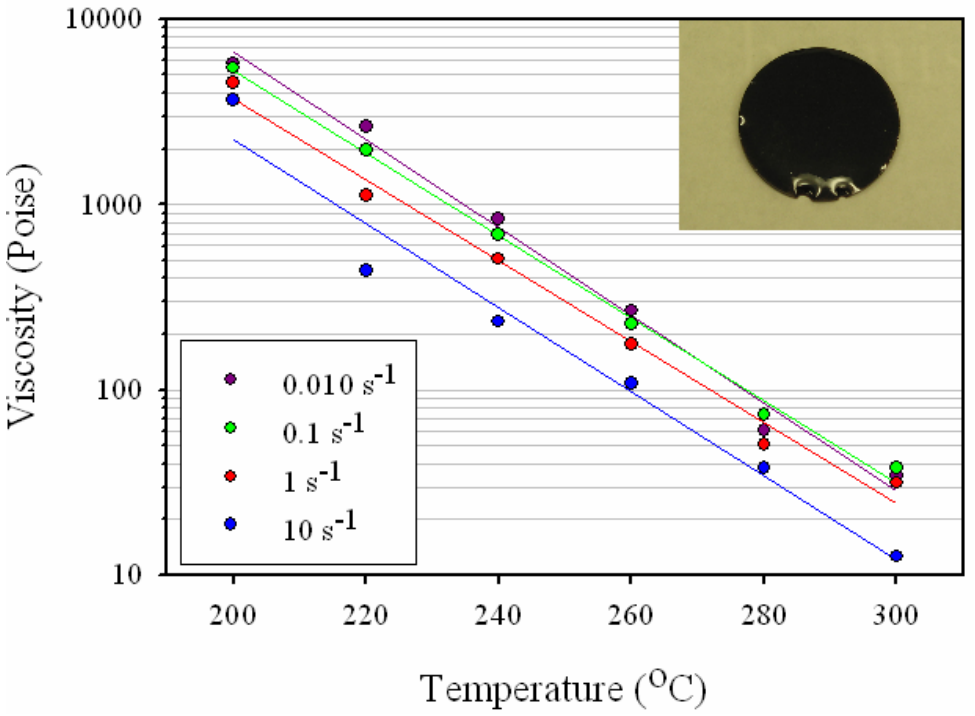

Figure 7. (a) P3-2300-PE disk formed by pressure free sintering process, and (b) viscosities of P3-2300-PE at various temperatures and shear rates.

A 100 mm x 100 mm x 3 mm stitched AS4 carbon fiber composite panel was fabricated by resin infusion molding PE-2300-PE and was cured for 4 hours at 370°C. To evaluate the glass transition temperature of the matrix resin in the composite and to offer an indication of the associated loss in mechanical properties beyond the glass – rubber transition, non-isothermal DMA scans were conducted on a section of the panel, the results of which are shown in Figure 8. The composite demonstrates a broad glass transition marked by the appearance of a peak in the damping factor at approximately 270°C, far surpassing the T_g of the uncured resin (154°C) suggesting substantial phenyl ethynyl consumption through crosslinking. The first scan was commenced with a 30 minute isothermal anneal at 450°C, during which time a second glass transition develops associated with a rise in the storage modulus terminating surprisingly close to its initial value. This behavior is indicative of the occurrence of additional crosslinking at 450°C, likely through a graphetization mechanism occurring along the polymer backbones. A second DMA scan of the annealed specimen revealed a higher value of storage modulus leading into the glass transition that occurs at nearly the same temperature as the first observed T_g. The damping factor is greatly reduced in comparison with the first scan associated with less dominant values of the loss moduli in this regime. A second anneal at 450°C revealed a further increase in the storage modulus and the appearance of another glass transition. The mechanisms of chemical reaction occurring at 450°C are currently being investigated coupled with changes in the mechanical properties to determine if the resin is experiencing embrittlement during the elevated heat treatment.

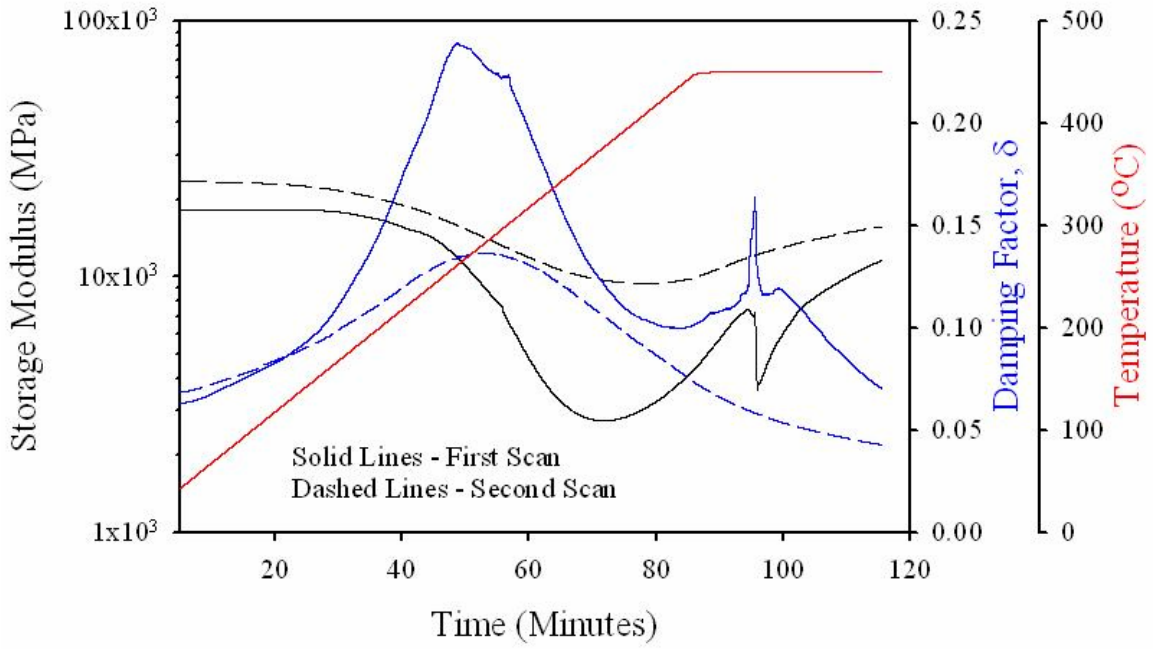

Figure 8. DMA analysis of PE-2300-PE / AS4 composite panel.

Table 2 presents a comparison of weight gain upon immersion in water for 24 hours for Navy P3-2300-PE cured under differing conditions, along with reported values for polyphenylene thermoplastics, polyimide, and polybismaleimide. There is no significant difference between the P3-2300-PE thermoset and the thermoplastic versions of the polyphenylene. The reported values are far less than comparable values for the other fire-resistant materials. The weight gain of 25 mm x 25 mm specimens cut from the composite panel cured for 4 hours at 370°C as a function of relative humidity revealed that the presence of the graphite fibers, which are generally impermeable to moisture, reduces the water uptake compared to the pure resin. Immersion tests with the same specimens show an uptake of 1-1.5% by weight, with all but about 0.4% of the added moisture evaporating in a few minutes as shown in Figure 9. Such behavior is consistent with the infiltration of water into voids in the composite, which accounts for the excess water uptake in relation to the saturation value indicated by exposure to variable relative humidity.

Material (Condition)	Weight Gain
P3-2300-PE uncured (consolidated at 180°C)	0.4 %
P3-2300-PE cured (390°C for 60 minutes)	0.5 %
TECAMAX™ SRP (commercial PPP thermoplastic)	0.5 % [2]
Kapton 500 HN® (commercial polyimide)	3.0 % [3]
Poly(bismaleimide) (BMI)	1.0 – 4.8 % [4]

Table 2. Weight gain comparison of various high temperature polymeric materials after a 24 hour water immersion.

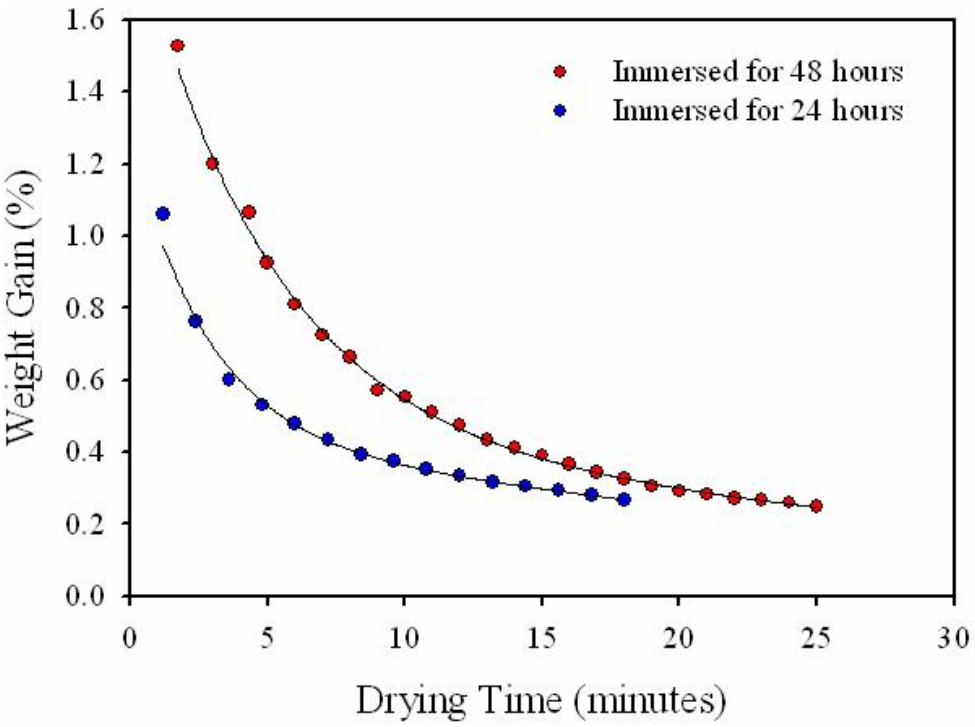

Figure 9. Weight loss of sections of the P3-2300-PE / AS4 composite panel during drying following water immersion.

4. CONCLUSIONS

New cyanate ester and polyphenylene thermoset resins developed at the Naval Air Warfare Center, in collaboration with the Air Force Research Laboratory and Boeing Phantom Works, have exhibited improved thermo-oxidative stability and reduced moisture uptake compared to state of the art materials. Significant decreases in moisture absorption were observed when the dicyanate ester of Bisphenol A (BADCy) was cured with both amorphous polycarbonate (APC) added at 10 to 20 wt% as toughening agents. A silane-based cyanate ester, referred to as SiMCy, showed a 50% reduction in moisture uptake compared to BADCy. Moreover, the presence of silicon in the SiMCy imparted increased char yield when heated to elevated temperatures in air, most likely due to the formation of SiO_2 at high temperatures. The physical characteristics of SiMCy make it a suitable drop-in replacement for other cyanate esters in composite applications.

Even more impressive thermal stability and low moisture uptake have been demonstrated in new poly-p-phenylene (P3) thermoset resins. These resins, which have been successfully infused into carbon fiber cloths and mats, have exhibited thermal stability and flame resistance characteristics of the same caliber as polyphenylene thermoplastics. In addition, the P3 resins absorb around 0.5% moisture on immersion, a level that is virtually identical to the polyphenylene thermoplastics and significantly lower than many state-of-the-art high-temperature thermosetting polymer materials.

The development of these new thermosetting polymers demonstrates that the design of novel resins for polymer matrix composites at the molecular level is capable of producing a new generation of processable materials that exhibit improved fire resistance and reduced moisture uptake, thereby overcoming many of the obstacles to more widespread adoption of composites structures in maritime operating environments.

5. ACKNOWLEDGEMENTS

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