FLAME RESISTANT PHTHALONITRILE COMPOSITES

Satya B. Sastri, James P. Armistead, and Teddy M. Keller*
Chemistry Division, Code 6120
Naval Research Laboratory
Washington, DC 20375-5320
Tel: 202-767-3095
Fax: 202-767-0594
E-Mail: keller1@ccf.nrl.navy.mil

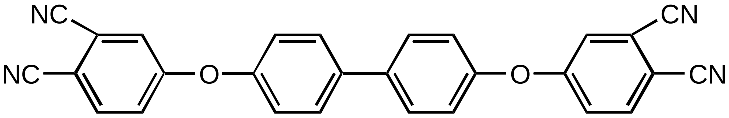
ABSTRACT

Phthalonitrile-based polymers under development at the Naval Research Laboratory (NRL) offer promise of bridging the gap between currently used high temperature polymers and ceramics/metals. Replacement of metal by fiber-reinforced phthalonitrile composites and metal foam/polymeric composites would effect substantial weight, cost, and energy savings, and improve performance. The phthalonitrile-based prepolymer exhibits unique properties not seen in other commercially available high performance materials being used for composite fabrication such as indefinite ambient stability of prepregs and ease of processability into composite components by regular prepreg consolidation, resin transfer molding (RTM), injection molding, or filament winding from the melt of the prepolymer. The phthalonitrile composite exhibits outstanding water resistance (<1 % by weight at equilibrium). Due to the superior thermal stability and the absence of a glass transition temperature (T_g) upon exposure to temperatures in excess of 450 ^oC, the phthalonitrile composites show promise for the fabrication of primary structural components. Moreover, the phthalonitrile-based composites show superior flammability properties. The relative concentration of toxic gas such as carbon monoxide (CO) is extremely low when compared to other high performance composites at a heat source of 100 kW/m^2. The unique properties exhibited by phthalonitrile composites are being exploited in planned development activities to expand our composite development activities and to quickly transfer the phthalonitrile technology into applied Navy programs and to industry. Our current research activities are concerned with the optimization of processing parameters and expansion of the database. The phthalonitrile monomer can be purchased from two commercial sources.

INTRODUCTION

The aircraft industry is utilizing structural composites in airframes and skins to reduce weight and to improve fuel efficiency (1). With an increase in composite usage in future aircraft, materials with low flammability and high strength will be needed to maintain airframe loads in advanced subsonic and supersonic aircraft. Boeing plans to expand the structural weight fraction of polymeric composites in subsonic commercial aircraft from about seven percent currently to about twenty percent over the next fifteen years. Polymer-based materials are currently being used in non-structural and semi-structural applications in cabin interiors. The materials are fairly flammable and/or generate copious amounts of smoke in a fire scenario and do not meet the FAA goal of generating survivable aircraft cabin conditions for 15 minutes in post-crash fuel fire. Fiber-reinforced composites utilizing high temperature polymers are more resistant to ignition but can suffer from poor processing characteristics and mechanical properties. Increased usage of polymers and composites by the aircraft industry will demand materials with better fire performance, structural integrity, and ease of processability.

Phthalonitrile-based composites under development at the NRL show excellent flame resistant properties and thermo-oxidative stability (2) approaching 375 ^{0}C. The phthalonitrile cure reaction is not accompanied by evolution of volatile by-products. Therefore, void-free components can be made easily from this resin system. The advantages and versatility of the phthalonitrile polymer may be realized in terms of ease of processing and superior properties. The phthalonitrile monomer can be cured into a thermoset resin using a wide variety of curing additives (2-5). Additionally, a prepolymer (B-staged resin) or prepolymerization composition may be prepared and stored for later usage with an indefinite shelf life under ambient conditions. The polymerization rate is also easily controllable as a function of curing additive and processing temperature for thick section composite fabrication. With regard to the thermal properties, the fully cured resins do not show a glass transition temperature up to 450 ^{0}C and exhibit good mechanical property retention at elevated temperatures. The current state-of-the-art high temperature resin based on PMR polyimide, designated as PMR-15, shows promise up to 316 ^{0}C but is accompanied by processing problems such as volatiles from residual solvent and a short processing or reaction time (6,7). The short reaction time translates to inadequate resin flow for fabricating thick and complicated composite structures. In light of these drawbacks with existing resin systems, phthalonitrile matrices show promise and may help further the usage of polymeric composites in frontiers that need high temperature and flame resistant capabilities.



Phthalonitrile Monomer

Phthalonitrile monomer [4,4'-Bis(3,4-dicyanophenoxy)biphenyl] has been effectively used as a matrix resin for composite formulations. Composite panels have been processed by conventional prepreg consolidation and by resin infusion and filament winding methods using carbon tape (8), carbon fabric and glass fabric (9, 10) as reinforcements. Since the initial resin melt viscosity is low (100-200 cp) and can be controlled by the proper selection of curing additive and curing temperature, the phthalonitrile composites are amenable to processing by more cost effective methods such as resin transfer molding and resin infusion molding. Mechanical properties and thermal and oxidative stability of phthalonitrile-based composites are superior to that of many state-of-the-art high temperature composites. With regard to fire performance, phthalonitrile composites excel over other polymeric composites. The phthalonitrile composites are the only materials that meet the Navy's stringent requirements of MIL-STD-2031 (11) for use of polymeric composites aboard Navy submarines. The specification contains test methods and requirements for flammability characteristics such as flame spread index, specific optical density, heat release, time to ignition, oxygen-temperature index, combustion gas generation, etc. A large fraction of our current efforts at NRL are targeted toward the optimization of curing parameters, property determination, and working with industry and other research organizations to further develop these new composite materials for marine and aerospace applications.

PROCESSABILITY

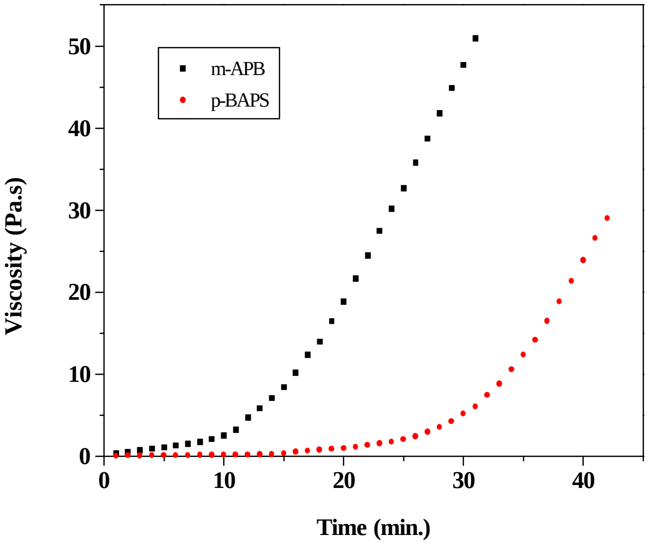
Most of our composite efforts have involved using aromatic diamines with ether linkages connecting the terminal aromatic amine moieties as curing additives. The amount of aromatic amine that can be used to form a prepolymer is limited due to the reactivity of the amine toward the phthalonitrile monomer. A prepolymer is defined as a low molecular weight B-staged polymeric composition, which is formed from reaction of the amine with the melt of the monomer. Upon cooling, the B-staged prepolymer is a frangible solid, which can be pulverized into a powder. In contrast to prepolymers from other resin systems, the phthalonitrile prepolymer can be stored indefinitely at room temperature. In the fabrication of thick composite components from either a prepreg, by resin infusion molding, or by resin transfer molding (RTM), processing difficulties may arise if the polymerization proceeds too rapidly. This is not a problem in the phthalonitrile systems due to the low cure exotherm.

An improved, more cost effective processing method, which involves a prepolymerization composition formed from mixing various amounts of phthalonitrile monomer and aromatic amine curing additive at room temperature, is under development at the NRL. Upon melting, the polymerization rate depends on the composition of the mixture and melt temperature. These phthalonitrile/curing additive prepolymerization compositions are especially useful for fabrication of composite components by resin transfer molding (RTM), filament winding, injection molding, or prepreg formulation from the melt in the absence of solvent. The composition is completely stable under ambient conditions before melting occurs. Any amine curing additive that is stable and shows non-volatility at the processing or polymerization temperatures can be used to polymerize phthalonitrile monomers. The prepolymerization composition is heated until complete melting occurs, which depends on the melting point of the phthalonitrile monomer. In the melt stage, the curing additive reacts with the phthalonitrile monomer. The viscosity of the resulting B-staged prepolymer at a given temperature and time depends on the amount and reactivity of curing additive in the composition. The composition can be used upon melting (B-stage) in the fabrication of composite components.

$$\text{Phthalonitrile Monomer + Curing Additive} \xrightarrow{\text{mix}} \text{Prepolymerization Composition}$$

Rheometric studies on phthalonitrile prepolymers with the same molar concentrations of 1,3-bis(3-aminophenoxy)benzene (APB) and bis[4-(4-aminophenoxyphenyl) phenyl] sulfone (BAPS) as curing agents (8.55 mmoles of diamine per 227 mmoles of monomer) were conducted to monitor the viscosity changes accompanying the cure reaction. Figure 1 shows the melt viscosities as a function of reaction time at 260 ^{0}C. The initial melt viscosities are low and range between 50-300 cp. From the plots, it is evident that the melt viscosities of prepolymers containing APB increase at a faster rate

Figure 1. Viscosity vs.Time Plots for Phthalonitrile Cure with Two Different Amines at 260 ^{0}C



than the BAPS-containing compositions. Differential scanning calorimetry (DSC) analyses show that both curing additives react readily with the monomer between 250-260 ^{0}C. The difference in the reactivities of APB and BAPS toward the phthalonitrile monomer is attributed to the differences in the basicities of the two amines. The basicity of the BAPS is lower due to the presence of the electron withdrawing sulfone group when compared to APB that has an electron donating phenoxy group. Based on this study, cure of the phthalonitrile monomer with BAPS may be advantageous to slow down the polymerization and thus broaden the processing window. Previous cure studies with APB (8) have indicated that melt viscosities are very sensitive to small changes in the diamine concentration used to make the prepolymer. The preferred amount of APB for composite component fabrication is 1.5-2.3 weight percent. When larger amounts are used, the viscosity of the prepolymer advances too rapidly to consolidate a quality composite panel or component. Given the lower reactivity and a higher molecular mass of BAPS, the amine concentration range for prepolymer formulations can be broadened to 2-4 weight percent.

COMPOSITE FABRICATION

Phthalonitrile composite panels have been fabricated by consolidation of prepreg (undirectional carbon, woven glass and carbon) and by resin infusion molding (woven glass and carbon) techniques for testing in a research size United McGill Corporation autoclave at the National Institute of Standards and Technology (NIST). The resin infusion process is similar to the prepregging process in that the resin flows over the surface of dry fibers. Resin infusion may be viewed as similar to the cure and consolidation process since the viscosity of the resin changes with time and temperature due to the cure process. In this process, the melt viscosity, which controls the resin flow, is of paramount importance. Resin infusion simplifies the composite manufacturing process where impregnation and consolidation are combined in a single step. In this process, unlike with prepregs, each ply is made up of dry fibers and the matrix resin is placed at the top or bottom. A mold is formed from sealant tape and bagging materials and the matrix resin may be in the form of a film, powder, pellet or viscous liquid. This processing technique is particularly attractive for resins that can realize very low viscosity values. Regardless of the technique used to fabricate the phthalonitrile panels, consolidation is accomplished by heating for 1h at 250°C and 3h at 325°C under 200 psi pressure (1.3 MPa). Heating and cooling rates are at 4°C/min and high vacuum is applied at the start of the cycle. After a dwell at 250°C for 0-60 min., pressure is applied, which is completed within 1/2h, followed by the cessation of vacuum.

Table 1. Mechanical Properties of Unidirectional Composite Panels (*Denotes Values Measured for A Panel Made from Different Batch of Prepreg)

Property	Phthalonitrile/IM7	PMR-15/IM7
0° Tension		
Strength, MPa (±%)	2000 [2400]* (1)	2500 (7)
Modulus, GPa (±%)	183 [162]* (2)	146 (3)
Strain, % (±%)	1.0 [1.36]* (7)	1.6 (4)
90° Tension		
Strength, MPa (±%)	41 (10)	29 (7)
Modulus, GPa (±%)	10 (8)	9 (3)
Strain, % (±%)	0.4 (12)	0.5 (30)
0° Flexure		
Strength, MPa (±%)	2350 (2)	1530 (5)
Modulus, GPa (±%)	174 (2)	122 (4)
Strain, % (±%)	1.3 (18)	1.3 (6)
90° Flexure		
Strength, MPa (±%)	80 (1.3)	
Modulus, GPa (±%)	11 (9)	
Strain, % (±%)	0.6 (4)	
Short Beam Shear		
Strength, MPa (±%)	85 (2)	105 (2)

The glass transition temperature (T_g) of the panels is estimated from the modulus vs. temperature plots obtained by dynamic mechanical analysis (DMA). A carbon reinforced panel that had been fabricated from a prepreg and cured for 1h at 250°C and 3h at 325°C exhibited a glass transition temperature in excess of 350°C and maintained 75% of the initial modulus at 400°C. With an additional postcure for 2h at 350°C, the T_g is shifted to temperatures above 400°C. Specimens that are postcured at 375°C for 2, 4 and 6h do not exhibit a T_g in the measurement range (<450°C) and appear to retain about 73, 75 and 83%, respectively, of their storage modulus at 450°C. With an even longer postcure cycle of 8h each at 350 and 375°C, approximately 90% of the room temperature modulus is maintained at 450°C.

MECHANICAL PROPERTIES

Composite mechanical properties, in general, are governed by many factors including processing parameters (time, temperature and pressure), type of fibers and fiber orientation, prepreg quality, post-curing environment (e.g., air or nitrogen), specimen size and configuration, and composite composition (fiber, resin and void content). At this stage, many of these variables remain to be assessed for the phthalonitrile-based composite system. Preliminary data on the mechanical properties of carbon-based phthalonitrile (8) and PMR-15 composites (12) are summarized in Table 1. These results reveal that some of the mechanical properties of phthalonitrile-based composites are superior while others are comparable to PMR-15. For instance, the flexural strength of the phthalonitrile composite is substantially higher than that for the PMR-15 analog (2350 MPa vs. 1530 MPa). Similarly, the transverse tensile strength of the phthalonitrile composite is 41 MPa, which is higher than the corresponding PMR-15 composite value by about 40%. Although the measured longitudinal tensile strength for the phthalonitrile system is low (2010 MPa), panels fabricated from a different batch of prepreg and processed by a different method yield a strength value (2400 MPa) comparable to that of the PMR-15 composite (2500 MPa). This improvement suggests that there is additional room for property improvement with optimization of the prepregging and consolidation processes. The measured tensile and flexural modulii of the phthalonitrile composite are also superior to those of the PMR-15 composite. However, the short beam shear strength of the phthalonitrile composite is slightly lower than that of the PMR-15 system. This test is particularly sensitive to relative sample and fixture dimensions and specimen surface preparation.

Mechanical properties of the phthalonitrile carbon composite were also evaluated for two different post-cure conditions (Table 2). Panels that were subjected to a short post-cure cycle of 8h at 325°C have properties almost comparable to those post-cured at elevated temperatures of 350°C for 8h and 375°C for 8h. This latter post-cure cycle was chosen essentially to enable comparison with earlier work performed in this laboratory. Our studies suggest that shorter post-cure times (2-8h) at 375°C may be adequate to substantially improve the thermal and mechanical properties.

Table 2. Influence of Postcure Conditions on Mechanical Properties

Property	Phthalonitrile/IM7 Postcure Cycle: 8H-350°, 8H-375°C	Phthalonitrile/IM7 Postcure Cycle: 8H-325°C

0° Tension		
Strength, MPa (±%)	2000 (2)	2100 (2)
Modulus, GPa (±%)	183 (2)	172 (2)
Strain, % (±%)	1 (7)	1.14 (0.2)
90° Tension		
Strength, MPa (±%)	41 (10)	33 (6)
Modulus, GPa (±%)	10 (8)	10 (1)
Strain, % (±%)	0.4 (12)	0.33 (8)
0° Flexure		
Strength, MPa (±%)	2350 (2)	2380 (8)
Modulus, GPa (±%)	174 (2)	183 (4)
Strain, % (±%)	1.3 (18)	1.3 (0.2)
90° Flexure		
Strength, MPa (±%)	80 (1)	79 (10)
Modulus, GPa (±%)	11 (9)	10 (1)
Strain, % (±%)	0.6 (4)	0.5 (3)
Short Beam Shear		
Strength, MPa (±%)	85 (2)	80 (3)

WATER ABSORPTION AND FLAMMABILITY CHARACTERIZATION

To be considered for advanced aircraft applications, a polymeric composite should have low water absorption. Phthalonitrile based glass and carbon reinforced composites readily satisfy this requirement with their water uptake level remaining <1% after immersion in water for over 30 months. The composite should also exhibit good flame resistant properties. Tables 3 and 4 present heat release and ignitable data of phthalonitrile/glass and phthalonitrile/carbon composites. Pertinentdata for other state-of-the-art polymeric composites and the Navy specification (MIL-STD-2031) are also presented in these tables for comparison. Heat release is defined as the heat generated in a fire due to various chemical reactions occurring within a given weight or volume of the material. This characteristic provides a relative fire hazard assessment in that the material with low heat release rate per unit weight or volume will do less damage to the surroundings than the one with a high heat release rate. It has been suggested that the heat release rate of a material measured in a small scale test under simulated radiant exposure conditions is the single most important parameter in characterizing the hazardous nature of a material in a fire (13). The peak heat release (PHR) and time to ignition (T_{ig}), which serve as a measure of resistance of a material to participate in fire, are very impressive for carbon and glass reinforced phthalonitrile composites.

For usage of organic polymeric composites inside of a submarine, Navy specification MIL-STD-2031 requires a maximum peak heat release (PHR) of 150 kW/m^2 and a minimum time to ignition (T_{ig}) of

60 sec. at a radiant heat flux of 100 kW/m^2. When compared with other high temperature, high performance composites, cone calorimetric studies have shown that a phthalonitrile carbon composite (8) is the only polymeric material that satisfies the Navy's flame retardant specification (PHR and T_{ig}) for using lightweight, polymeric composites for submarine applications (Table 4). At 100 kW/m^2 irradiance heat treatment, phthalonitrile carbon composites meet the requirement and exhibit PHR and T_{ig} values of 118 and 75, respectively. This is an important finding given the fact that high performance composites that meet the Navy's flammability specification have not been available. Preliminary cone calorimetric data has also been obtained on a phthalonitrile glass composite panel (9) containing a fiber volume fraction of 54. The PHR and T_{ig} values are 106 and 59, respectively (Table 3). This study will be repeated on a panel containing a higher volume fraction of fiber.

Table 3: Summary of Heat Release Data for Phthalonitrile and Other Polymeric Composites. *NI Stands for No Ignition

Composite	Time to Ignition (s) at Heat Flux (kW/m^2) of				Peak Heat Release at Heat Flux (kW/m^2) of			
	25	50	75	100	25	50	75	100
MIL-STD-2031	300	150	90	60	50	65	100	150
Gl/Phthalonitrile	NI	NI	84	59	NI	NI	98	106
Gl/Vinyl Ester	278	74	34	20	188	199	300	256
Gl/Epoxy	535	105	60	40	39	178	217	232
Gl/Bismaleimide	503	141	60	38	128	176	245	285
Gl//Phenolic	NI	214	57	25	NI	47	97	133
Gl/Polyimide	NI	175	75	55	NI	40	78	85

Table 5 shows the relative concentrations of combustion gases and specific optical density data measured during the smoke density test for various glass reinforced composites. Smoke affects visibility and hinders the ability of the occupants to escape fire. Specific optical density measurements serve as useful criteria in assessing this imminent problem due to smoke. The specific optical density at 300s (Ds) and maximum specific optical density (D_{max}) for phthalonitrile/glass composite are both 1, which is substantially lower than other tested polymeric composites. Another desirable feature of the phthalonitrile/glass composite is that the concentration of toxic gas (carbon monoxide) evolved during combustion is low (40 ppm) relative to glass reinforced polyimide (200 ppm), phenolic (300 ppm), BMI (300 ppm), epoxy (283 ppm) and vinyl ester (230 ppm) composites.

The superior flame resistance of the phthalonitrile/carbon composite also meets the FAA requirement (no flammability at 35 kW/m^2 irradiance) for composite usage in an aircraft cabin. The flammability parameters derived from micro-scale calorimetric measurements (16) are the char yield at 650 ^{o}C, the peak rate of heat release, and the total heat release at 900 °C. The peak heat release rate is originally measured in W/g but is subsequently normalized by dividing with the heating rate to obtain the heat release with units of J/g-K. The total heat release in KJ/g is obtained from a numerical integration of the heat release rate curve and the char yield from the residual mass after the test. The char yield and total heat release of the phthalonitrile polymer are 87% and 2.1 kJ/g, respectively. The char yield and the total heat release values for the phthalonitrile polymers are far

Table 4. Flammability Results for Carbon Fiber-Reinforced Composites

Composite	**Time to Ignition (sec.)**	**Peak Heat Release (kW/m^2)**
Carbon/Phthalonitrile	75	118
Carbon/PMR-15	55	85
Carbon/BMI	22	270
Carbon/PEEK	42	85
Carbon/Epoxy	28	232
Carbon/Phenolic	25	96

Table 5. Smoke and Combustion Data. *Trace Amount. **Not Detected

Composite	Ds (300 s)	D_{max}	CO (ppm)	CO_2 (%V)	HCN (ppm)	HCl (ppm)
Gl/Phthalonitrile	1	1	40	0.5	tr*	ND**
Gl/Vinyl Ester	463	576	230	0.3	ND	ND
Gl/Epoxy	56	165	283	1.5	5	ND
Gl/Bismaleimide	40	130	300	0.1	7	tr
Gl/Phenolic	7	20	300	1.0	1	1
Gl/Polyimide	3	15	200	1.0	tr	2

superior to those of other polymers such as polyimide (kapton), polybenzimidazole (PBI), phenolic triazine (PT-30), etc. (17).

METAL FOAM/PHTHALONITRILE COMPOSITES

Metal/organic polymer composites have been made by impregnating porous metals/alloys having isotropic properties with elastomers (silicon rubber), acrylic, phenolic, epoxies, and with high temperature, flame resistant phthalonitrile-based polymers developed at the Naval Research Laboratory. Any porous metal with various percent density can be used. Phthalonitrile/Al composites were made from high temperature phthalonitrile resin and porous Al (6-8% density, 40 ppi). The phthalonitrile monomer was first melted at 250 ^{0}C and degassed for about an hour to remove trace amounts of volatiles trapped in the monomer. The monomer was then converted to a prepolymer by adding 1.8 % by weight of a curing additive [1,3-bis(3-aminophenoxy)benzene] and stirring for 15 min. The prepolymer melt was poured into steel molds that contained the porous Al sample and degassed for an additional 30 min. at 250 ^{0}C. Small weights on a teflon film were placed on top of the Al block to keep it submerged in the resin. Composite samples were then cured in an air circulating oven for various times at 2, 9 and 18h at 280 ^{0}C. Samples were then post-cured by heating in sequence at 325 ^{0}C for 4h, at 350 ^{0}C for 4h, and at 375 ^{0}C for 4h under an inert atmosphere (argon). The resulting light weight composite exhibited high damping capacity, outstanding fire resistance, and high isotropic mechanical properties. The acoustic behavior exhibited by the phthalonitrile/Al composite is far superior to that of current state-of-the-art (SOA) damping materials.

Metals and alloys that possess a large inherent damping capacity have been extensively sought for many domestic and military applications. Components, fabricated from the metal foam/polymer composites, will be affordable and lightweight, exhibit outstanding fire resistance, display outstanding mechanical properties, and provide high damping capacity. The metal component will provide isotropic mechanical strength and the polymeric phase will produce the attenuation attributed to the softening effect above the glass transition temperature or by relative motion or deformation at the interface between the two phases.

CONCLUSION

The use of polymeric composite materials for aircraft cabin applications offers benefits in a variety of areas such as improvements in weight, maintenance, corrosion control, and lower thermal conductivity. High performance composites that fit the Navy's flammability requirements of MIL-STD-2031 for application in hull, machinery and structural applications inside naval submarines have not been available. The superior performance of phthalonitrile-based composites on exposure to a flame should enhance their importance for consideration by the aircraft industry in the design of a totally fire resistant cabin for future commercial aircraft.

The phthalonitrile polymer offers many advantages as flame resistant and high temperature matrix materials for composite applications. The mixed prepolymerization composition and B-staged prepolymer are completely stable under ambient conditions and below the melt temperature. These compositions are especially useful in the fabrication of fiber reinforced composite by RTM, filament winding, resin infusion molding, injection molding, and prepreg formulation from the melt in the absence of solvent. Metal foam/phthalonitrile composites can be easily fabricated by resin injection molding or resin infusion molding. A user can readily make changes in the phthalonitrile/curing additive prepolymerization composition to meet the processing needs. No reaction occurs between the monomer and curing additive until melting commences. Conventional resins such as epoxies and polyimides must be stored under freezer conditions and used in a short time frame upon addition of curing additive. The phthalonitrile resin can be easily processed into void-free composite components. Preliminary data reveal that the phthalonitrile composites exhibit mechanical properties that are either superior or comparable to the state-of-the-art high temperature PMR-15 composites. Panels post-cured at 375°C do not exhibit a glass transition temperature up to 450°C and retain about 90% of their initial modulus. Based on the excellent physical properties and ease of processability, phthalonitrile composites are finding uses in both marine and aerospace applications.

ACKNOWLEDGEMENT

The authors wish to thank the Office of Naval Research for financial support of this work and NIST Polymer Composite Group for the autoclave facility. The authors also want to thank Dr. Ashraf Imam of the Materials Division, Code 6320, Naval Research Laboratory, for the preliminary damping studies on the metal foam/phthalonitrile composite.

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