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Lower-Curing-Temperature PMR Polyimides

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LOWER-CURING-TEMPERATURE PMR POLYIMIDES

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INTRODUCTION

Studies conducted at NASA Lewis Research Center led to the development of a class of readily processable polyimides known as the PMR polyimides (refs. 1 and 2). The commercially available version known as PMR-15 uses an alcohol solution of three monomer reactants: 4,4'-methylenedianiline (MDA), the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) as an end-capping reagent. Because of its excellent processability and thermo-oxidative stability, PMR-15 has made it possible to design and fabricate structures for use at temperatures up to 316° C. Final curing of PMR-15 requires temperatures in the range of 288° to 316° C. These temperature requirements exceed the capabilities of many existing autoclave facilities which were originally acquired for curing of epoxy resins. A lower-curing-temperature PMR polyimide would be more compatible with existing facilities and increase the applications of PMR polyimides.

A previous study showed that the use of an alternate endcap, m-amino-styrene, lowered the final cure temperature of PMR polyimides to 260° C (ref. 3). However, the glass transition temperature of these polyimides was 270° to 280° C and limited their use to 260° C.

The purpose of this study was to investigate the effects of partial substitution of a p-aminostyrene (PAS) endcap for the norbornenyl endcap NE on the curing temperature and properties of PMR polyimide resins and graphite fiber-reinforced composites. Compression-molded neat resin specimens and Celion 6000 graphite fiber-reinforced composites were prepared from monomer solutions containing various amounts of MDA, BTDE, and equimolar amounts of the two endcaps, NE and PAS. The glass transition temperatures and weight-loss characteristics in air at 288° C and 316° C were determined for neat resin and composite specimens. The room temperature and short-time elevated temperature mechanical properties of the composites at 288° C and 316° C were determined. The mechanical property retention characteristics of the composites as a function of exposure time in air at 288° C and 316° C were also determined.

EXPERIMENTAL PROCEDURE

The monomers used in this study are shown in table I. The dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) was prepared by refluxing a suspension of the corresponding dianhydride in a calculated amount of anhydrous methanol until the solid dissolved, and then for an additional 2 hr to give a 50 wt% solution of BTDE. The remaining monomers were obtained from commercial sources.

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Molding powders were prepared by evaporating methanol solutions of the monomers in the desired stoichiometric ratios under reduced pressure, and then staging for 1 hr at 150° C. The PMR-15 control sample was staged for 1 hr at 204° C. Neat resin disks having nominal dimensions of 2.54 cm diam x 0.2 cm thickness were prepared by compression molding. The molding powders were placed in a cold circular matched metal die and heated at contact pressure to 232° C. The pressure was then increased to 17.2 MPa. The die was then heated to 260° C and held at 260° C and 17.2 MPa for 1.5 hr. A similar procedure was used for the PMR-15 sample except that final cure was conducted at 316° C. The resin moldings were subjected to a 16-hr free-standing postcure in air at 204° C. Their temperature was then increased to 316° C at about 1.5° C/min. and held for 24 hr.

Unidirectional composites were fabricated using unsized Celion 6000 as the graphite fiber reinforcement. A complete procedure for compression-molding PMR-15 composites has been published elsewhere (ref. 4). In the key step of the cure cycle for PMR-15, a pressure of 3.45 MPa is applied when the temperature is increased to 316° C and maintained for 1 to 2 hr. In this study, the prepreg prepared using the mixed endcaps was staged for 1 hr at 150° C. The mold was placed into a press preheated to 260° C, and a pressure of 8.27 MPa was applied when the temperature had reached 232° C. The temperature was increased to 260° C, and maintained for 1.5 hr. All composites were given a 24-hr free-standing postcure in air at 316° C by increasing their temperature from ambient to 316° C at about 1.5° C/min. then holding at 316° C for 24 hr.

Weight loss of resin and composite specimens was determined in a forced-draft oven with an air-change rate of 100 cm³ per min. Flexural strength tests were performed in accordance with ASTM D-790 using a three-point loading fixture and a span of 5.08 cm. The flexural property values were normalized to 60 v/o fiber. Interlaminar shear strength tests were performed in accordance with ASTM D-2344 at a constant span/depth ratio of 5. The number of replicates for the flexural and shear tests was three. The fiber content of composites was determined by digestion with H₂SO₄/H₂O₂.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC) analysis of a 1:1 stoichiometric mixture of PMR-15 molding powder and the molding powder from the all-vinyl-endcapped analog of PMR-15 (ref. 3) established the feasibility of reducing the cure temperature by employing a mixture of norbornenyl (NE) and vinyl endcaps. The DSC scan of the mixture indicated the presence of a single reaction exotherm with its maximum centered at 285° C. This temperature is substantially lower than the cure exotherm temperature of 340° C for PMR-15 (ref. 5). A more detailed study of PMR polyimides employing mixtures of NE and vinyl endcaps was then performed.

Table II lists the monomer stoichiometry for a series of molding powders using an equimolar mixture of NE and the vinyl endcap (PAS) at three different formulated molecular weights: 1500, 1250, and 1000. These formulations were designated PMR-NV15, PMR-NV12.5, and PMR-NV10, respectively. In DSC studies, all three molding powders exhibited melt-flow endotherms at about 225° C. Excellent void-free moldings were obtained consistently when pressure was applied at 232° C, and final cure was conducted for 1.5 to 2 hr

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at 260° C. Poor consolidation was observed when the final cure temperature ranged from 204° C to 217° C. Moldings of inconsistent quality were obtained when the final cure was conducted in the temperature range of 221° C to 254° C.

The neat resin disks were subjected to the stepwise postcure schedule described in the experimental section. If the specimens were placed in an oven at 316° C without using the stepwise procedure, warping and blistering occurred in several instances. It is possible that after the cure at 260° C some residual unreacted norborenyl endcaps remain, and if the resin is exposed suddenly to 316° C, volatiles are released causing blister formation.

The density, glass transition temperature, and thermo-oxidative weight loss of the neat resins are listed in table II. All of the resins exhibited identical densities. The glass transition temperatures (T_g) of the PMR-NV15 and PMR-NV12.5 resins are lower than the T_g of PMR-15. The higher T_g of the PMR-NV10 resin is probably due to its higher crosslink density. The weight loss of the PMR-NV resins in air at 316° C shows an increase with decreasing FMW values. This is probably due to the increase in alicyclic content as the FMW is decreased.

Unidirectional composites having dimensions of 10.16 cm x 10.16 cm were fabricated from each of the resins listed in table II and Celion 6000 graphite fibers. Essentially, the same cure procedure developed for compression molding of neat resin specimens was employed for fabrication of Celion 6000 graphite fiber-reinforced composites. Pressure was applied when the temperature of the prepreg stack had reached 232° C, and final cure was conducted at 260° C for 2 hr. It needs to be emphasized that the PMR-NV systems exhibited considerably reduced resin flow compared to PMR-15 composites. Therefore, it was necessary to use a molding pressure of 8.27 MPa, compared to 3.45 MPa for PMR-15 composites. Ultrasonic C-scan examination of the composites, after postcuring, indicated that they were free of defects.

The properties of the composites are listed in table III. As in the case of neat resins, the T_g values of the PMR-NV composites are somewhat lower than that of the PMR-15 control. However, it can be seen that the short-term mechanical properties of the PMR-NV composites are equivalent to those of PMR-15 both at room temperature and 288° C. The table also lists the 288° C mechanical properties after 2016 hr of exposure in air at 288° C. All composites exhibited essentially 100 percent retention of their initial mechanical properties. This is not surprising in view of the low weight loss values after 2016 hr of exposure (2.5 to 2.9 percent).

A series of unidirectional Celion 6000 graphite fiber composites measuring 7.62 cm x 20.32 cm was compression-molded and postcured using the same procedures developed for the smaller (10.16 cm x 10.16 cm) composites. Ultrasonic C-scan examination of the postcured composites indicated that they were free of defects. The short-term 316° C mechanical properties of the composites are shown in table IV. It can be seen that the mechanical properties of the PMR-NV composites are equivalent to those of the control PMR-15 sample. The table also lists the weight loss of the composites after 1512 hr of exposure in air at 316° C. For the PMR-NV composites there appears to be a trend toward higher weight loss with decreasing FMW values. This can be attributed to the increase in alicyclic content with decreasing FMW.

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The mechanical property retention characteristics of the composites after exposure in air at 316° C are compared in figures 1 to 3. Figure 1 shows that all composites exhibited excellent retention of their interlaminar shear strength (ILSS). It appears that the PMR-NV composites exhibit higher ILSS values throughout the 1512 hr of exposure at 316° C. There is more scatter in the flexural strength (shown in fig. 2) and flexural modulus (shown in fig. 3) values of the PMR-NV composites. The important point to note is that the PMR-NV composites exhibited mechanical properties equivalent to or higher than those of the PMR-15 control sample.

CONCLUSIONS

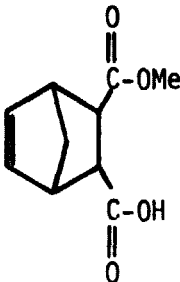
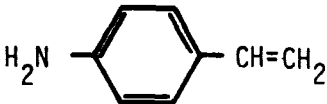
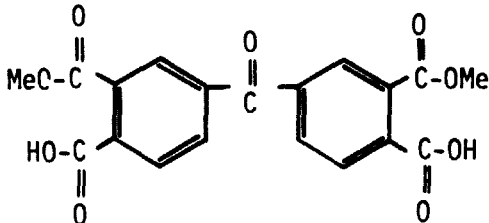
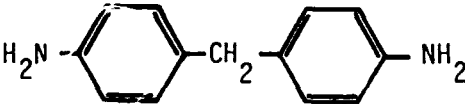
Based on the results of this investigation, several conclusions can be drawn: (1) PMR polyimides prepared from monomer solutions containing equimolar amounts of norbornenyl and vinyl endcaps (designated PMR-NV polyimides) can be cured at 260° C (500° F), compared to 316° C (600° F) for state-of-the-art PMR-15 polyimides; (2) Compared to PMR-15, the PMR-NV polyimides exhibit reduced resin flow. Void-free resin moldings and composites can be fabricated by using higher pressure during compression molding; (3) The PMR-NV composites exhibit short-term mechanical properties equivalent to those of PMR-15 composites; and (4) The PMR-NV composites exhibit mechanical property retention characteristics equivalent to those of PMR-15 after exposure in air at 288° C and higher than those of PMR-15 after exposure in air at 316° C.

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TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

Structure	Name	Abbreviation
	Monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid	NE
	p-Aminostyrene	PAS
	Dimethyl ester of 3,3', 4,4'- benzophenonetetracarboxylic acid	BTDE
	4,4'-Methylenedianiline	MDA

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TABLE II. - PROPERTIES OF NEAT PMR POLYIMIDE RESINS^a

Resin	Monomer stoichiometry	Density, g/cm ³	T _g , °C	Weight loss, percent ^b
PMR-15	2NE/3.087MDA/2.087BTDE	1.287	332	16.3
PMR-NV15	1PAS/1NE/2.5MDA/2.5BTDE	1.289	320	16.1
PMR-NV12.5	1PAS/1NE/2MDA/2BTDE	1.288	326	16.5
PMR-NV10	1PAS/1NE/1.5MDA/1.5BTDE	1.287	349	17.5

^a Postcured 16 hr in air at 204° C plus 24 hr in air at 316° C.

^b After 151½ hr in air at 316° C.

TABLE III. - PROPERTIES OF PMR POLYIMIDE/CELION 6000 GRAPHITE FIBER COMPOSITES^a

Resin	Fiber V/O	T _g , °C	Interlaminar shear strength, MPa			Flexural strength, ^b MPa			Flexural modulus, ^b GPa			Weight ^c loss, percent
			25° C	288° C	288° C ^c	25° C	288° C	288° C ^c	25° C	288° C	288° C ^c	
PMR-15	58.2	342	113	54.3	57.1	1830	1060	1110	120	117	118	2.6
PMR-NV15	58.6	324	106	54.1	57.9	1750	970	1130	130	113	114	2.5
PMR-NV12.5	56.7	333	107	55.1	60.1	1860	1110	1100	121	118	117	2.6
PMR-NV10	55.7	341	118	56.5	60.6	1810	1140	1220	120	119	120	2.9

^a Postcured 24 hr in air at 316° C.

^b Normalized to 60 V/O fiber.

^c After 2016 hr in air at 288° C.

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TABLE IV. - PROPERTIES OF PMR POLYIMIDE/CELION 6000
GRAPHITE FIBER COMPOSITES^a

Resin	Fiber	T _g , ° C	Mechanical properties at 316° C			Weight ^c loss, percent
			Interlaminar shear strength, MPa	Flexural ^b strength, MPa	Flexural ^b modulus, GPa	
PMR-15	60.2	341	50.7	896	112	7.4
PMR-NV15	57.7	327	50.6	882	112	6.3
PMR-NV12.5	57.3	335	51.0	875	111	8.1
PMR-NV10	58.1	340	51.8	937	113	10.3

^a Postcured 24 hr in air at 316° C.

^b Normalized to 60 V/O fiber.

^c After 1512 hr in air at 316° C.

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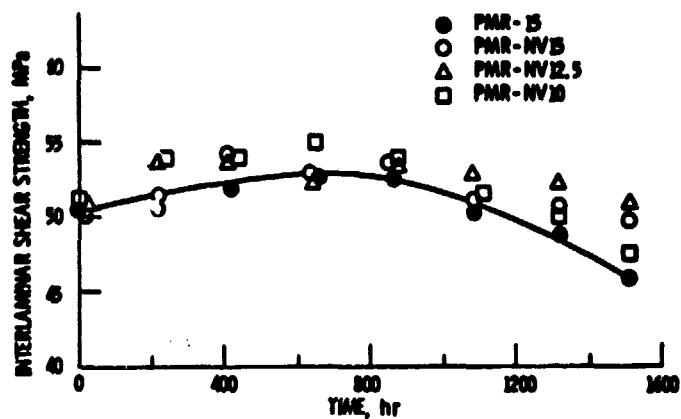


Figure 1. - Interlaminar shear strength of PMR polyimide/Celion 6000 graphite fiber composites exposed and tested in air at 316° C.

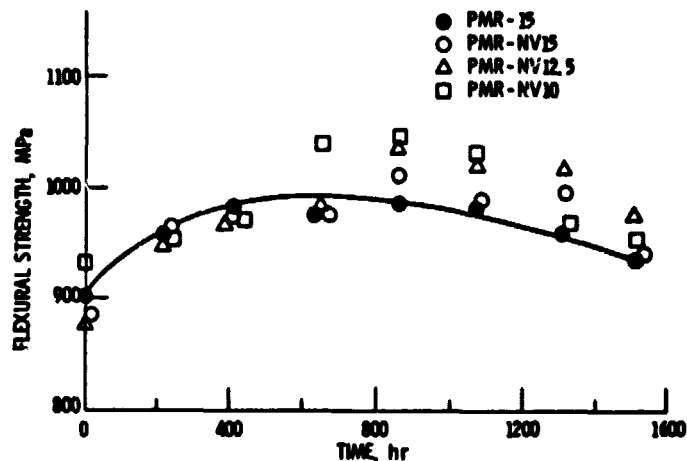


Figure 2. - Flexural strength of PMR polyimide/Celion 6000 graphite fiber composites exposed and tested in air at 316° C.

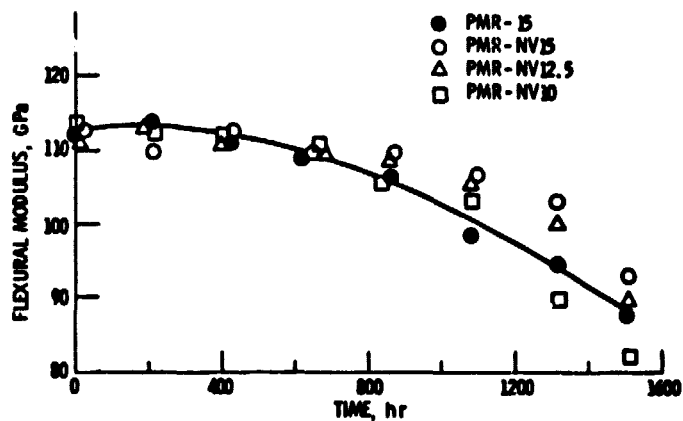


Figure 3. - Flexural modulus of PMR polyimide/Celion 6000 graphite fiber composites exposed and tested in air at 316° C.