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16. Abstract
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Abstract

N-phenylnadimide modified PMR resins and composites were investigated with the objective of improving the overall flow characteristics of PMR-15 type resins without compromising composite properties. A series of N-phenylnadimide (PN) modified PMR polyimide composites reinforced with Celion 6000 graphite fibers were investigated. The improved flow matrix resins consist of N-phenylnadimide (PN), monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acide (BTDE), and 4,4'-methylenedianiline (MDA). Five modified PMR resin systems were formulated by the addition of 4 to 20 mole percent N-phenylnadimide to the standard PMR-15 composition. These formulations and the control PMR resin were evaluated for rheological characteristics. The initial thermal and mechanical properties of the PN modified PMR and the control PMR/Celion 6000 composites were determined. The elevated temperature flexural and interlaminar shear properties and the weight loss characteristics of the PMR composites isothermally exposed at 600°F in air for 1500 hours were evaluated. In addition, the effects of hydrothermal exposure on the glass transition temperatures and the elevated temperature flexural properties of the PMR composites were also investigated. The results of this study clearly showed that the addition of N-phenylnadimide to PMR-15 significantly improved the resin flow characteristics without sacrificing the composite properties. This study further revealed that concentrations of 4 and 9 mole percent PN appear to improve the thermo-oxidative stability of PMR composites.

Keywords: N-phenylnadimide Modified PMR Polyimides, PMR Polyimides, PMR Polyimide Composites, Composite Properties, Flow Properties, Thermo-oxidative Stability, Hydrothermal Exposure

1. INTRODUCTION

The "melt-flow" behavior of the resin matrix exerts considerable influence on the overall processing characteristics and properties of fiber reinforced resin matrix composites. Until the development of the class of high-temperature-resistant resins known as PMR polyimides, (1) the intractible nature of prior art high temperature resins severely restricted their use as matrix materials. Early studies (2,3) demonstrated that PMR matrix resins having a broad range of processing characteristics and properties could easily be synthesized by either varying the chemical nature or the stoichiometry of the monomer reactants. In the study (3) which investigated the resin flow characteristics of fully imidized PMR compositions ranging in formulated molecular weight (FMW) between 1000 and 1500, it was found that the lower FMW compositions exhibited increased resin flow, but with some sacrifice in elevated temperature thermo-oxidative stability. Vannucci (4) reported that the resin flow characteristics of the PMR composition having an FMW of 1500 (PMR-15) could be varied by controlling the degree of resin advancement or imidization.

This paper presents an alternative approach to achieve improved flow PMR polyimides without sacrificing the desirable thermo-oxidative characteristics. The present approach utilizes a chemically compatible flow modifying agent, viz. N-phenylnadimide (PN). The modified PMR resins consist of four monomer reactants: monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), dimethyl ester of 3,3', 4,4'-benzophenonetetracarboxylic acid (BTDE), 4,4'-methylenedianiline (MDA), and the flow modifying agent, N-phenylnadimide (PN). Table 1 shows the chemical structures of these compounds.

The purpose of this investigation was to determine the processing characteristics and properties of PN modified PMR/Celion 6000 composites. The flow properties of the PN modified PMR resins and the physical and mechanical properties of PN modified PMR/Celion 6000 composites exposed to isothermal aging in air at 600°F and humidity conditions are presented.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE, Burdick and Jackson), 4,4'-methylenedianiline (MDA, Eastman), 3,3', 4,4'-benzophenonetetracarboxylic dianhydride (BTDA, Aldrich), 5-norbornene-2,3-dicarboxylic anhydride (NA, Eastman) and aniline (Aldrich) were purchased from the commercial sources as indicated and used as received. Unsized Celion 6000 graphite fiber tows were supplied by Celanese. Dimethyl ester of 3,3', 4,4'-benzophenonetetracarboxylic acid (BTDE) in 50 weight percent methanol solution was prepared by refluxing BTDA in methanol for 2 hours. N-phenylnadimide was prepared according to the following procedure: To a stirred and warm (158°F) solution of 42.0 g (0.26 mole) of NA in 300 ml of acetonitrile was added in one portion a solution of 24 ml (0.26 mole) of aniline in 75 ml of acetonitrile. The mixture was refluxed while stirring for 94 hours. Upon cooling to room temperature, the reaction solution was washed 3 times with 200 ml of saturated potassium carbonate solution. Concentration of the organic solution using a rotary evaporator under reduced pressure afforded 55.4 g (89 percent yield) of endo-N-phenylnadimide as white crystals, m.p. 291-294°F. The spectral data supporting the chemical structure of this compound are given below: ^1H NMR ($CDCl_3$): 1.51 (singlet, 2H, $H_{7,8}$) 2.79 (singlet, 2H, $H_{1,4}$), 3.35 (singlet, 2H $H_{2,3}$), 6.29 (singlet, 2H $H_{5,6}$), 7.28-7.36 (doublet, 5H, aromatic H). IR (KBr): 2880 (C-H), 1765 and 1700 (imide carbonyl), 1592 and 1495 (aromatic), and 740 cm^{-1} (cis-olefin). A DSC scan gave the following: endotherm 292°F (melt) and endotherm 518°F (sublimations).(5)

2.2 Rheological Characterization

Table 2 shows the five PN modified PMR and the control PMR resin compositions used in this study. The molding powders of the six resin systems were prepared by the general procedures given below: A 50 weight percent solution of the monomer mixture in methanol was stirred at room temperature for 1/2 hour to give a clear dark brown solution. The solution was concentrated using a rotary evaporator under reduced pressure first at 122°F for 45 minutes and then at 194°F for 15 minutes. This yielded a brown powder containing traces of solvent. The brown powder was then staged in an air-circulating oven at 400°F for 1 hour to give a brown molding powder which was used for the rheological and DSC studies. The rheological behavior of the molding powders were determined using a Rheometrics Dynamic Spectrometer, Model 7700. Approximately 1 g of each molding powder was placed between parallel plates having 1 inch diameter. The temperature was raised at 7°F/minute to 460°F at which point the sample softened and the gap between the platens was set to 0.055 inch. Immediately, the sample was subjected to torsional shear at a constant frequency of 10 radians/second and 10 percent strain. The sample was heated at 7°F/minute and the shear viscosity was measured and recorded at 2 minute intervals over the temperature range of 460-590°F.

2.3 Thermal Characterization

For the DSC scans, approximately 8 mg of each molding powder was studied at a heating rate of 18°F/minute under a static N_2 atmosphere at 60 psi.

2.4 Resin Flow

The resin flow for each composite system was determined under identical cure parameters as described below. Twelve plies of four-inch square prepreg were stacked unidirectionally in a mold. The stacked plies were staged at 400°F for 1 hour in an air-circulating oven, placed in a cold matched metal die, and then placed in a preheated 600°F press. When the temperature of the mold reached 450°F, 500 psi pressure was applied. The temperature was raised to 600°F at 7°F/minute and the composite system was cured at 600°F under 500 psi pressure for 2 hours. The resin material which flowed as a result of this cure process was determined according to the following equation

$$F = \frac{W_2}{W_1 + W_2} \times 100 \qquad (1)$$

where

F = resin flow, weight percent

W_1 = weight of resin in molded composite sample as determined by acid digestion method

W_2 = weight of staged prepreg - weight of molded composite after removal of resin flash

2.5 Composite Fabrication

The prepreg was prepared by drum winding the Celion 600 graphite yarn followed by brush application of a quantity of a 50 weight percent methanol solution of resin components calculated to yield finished composites containing 60 volume percent fiber. The tapes were dried on the rotating drum at room temperature for 16 hours, removed from the drum, cut into 3-inch by 8-inch plies, stacked unidirectionally to 12 plies, and then staged at 400°F for 1 hour in an air-circulating oven. The staged lay-up was placed in a cold matched metal die. This was then inserted into a preheated 600°F press. A thermocouple was attached to the matched die to follow the temperature. In order to obtain the molded composites having similar resin contents, the pressurization temperatures for the composites were progressively increased as the concentration of PN increased. For the control sample, 500 psi pressure was applied when the die temperature reached 450°F. For PMR-P1, PMR-P2, PMR-P3, PMR-P4, and PMR-P5, the pressure was applied when the die temperature reached 540°F, 550°F, 560°F, 570°F, and 580°F, respectively. The temperature was then raised to 600°F at 7°F/minute and all of the composites were cured at 600°F under 500 psi pressure for 2 hours and removed from the press when the die temperature reached 350°F. Composites were given a free standing post-cure at 600°F for 16 hours in an air-circulating oven.

2.6 Composite Characterization

The laminates were examined by ultrasonic C-scan for voids and defects prior to testing. The laminates showed essentially void-free scans, and thus were accepted for test specimen preparation. Flexural tests were performed in accordance with ASTM D790 using a three point loading fixture and at a center loading rate of 0.05 inch/minute. Specimen thickness, which ranged between 0.084 and 0.087 inch, resulted in span-to-depth ratios of 23 to 24. Interlaminar shear strengths were measured following ASTM D2344 specifications at a constant span-to-depth ratio of 5. Elevated temperature mechanical tests on dry samples were performed in an environmental heating chamber after the chamber had equilibrated at the test temperature for 15 minutes prior to applying the load. A 15 minute equilibration period was not employed for testing of humidity exposed (wet) specimens. The load was applied to the wet specimens immediately after they had been placed in the loading fixture. This type of test is referred to as a temperature spike test.(6) For the thermo-oxidative stability study, a series of precut flexural and interlaminar shear specimens were exposed at 600°F in air for various time intervals and then tested. The weight loss data were obtained from the precut flexural specimens. The fiber-resin compositions of the composites were determined by the H_2SO_4/H_2O_2 digestion method, and the densities of the composites were measured using the liquid displacement method.

3. RESULTS AND DISCUSSION

3.1 Processing Characteristics

Figure 1 shows the rheological behavior of the PN modified and unmodified PMR-15 molding powders which had been imidized at 400°F for one hour. It is evident that the PN modified PMR samples exhibited lower shear viscosities over the temperature range 460 to 577°F when compared to PMR-15. The minimum viscosity of the control (PMR-15) was found to be 2940 poise at 550°F while the minimum viscosities of the PN modified PMR samples varied from 1769 for 4 mole percent PN to 884 poise for 20 mole percent PN. This represents a decrease in the minimum shear viscosity ranging from 40 to 70 percent of the minimum viscosity for PMR-15 control. Also, the minimum viscosities of the PN modified PMR resins occurred at lower temperatures than for the PMR-15 control. At 579°F the viscosities of PN modified PMR and PMR-15 were equal.

The minimum viscosity as a function of mole percent N-phenylnadimide is plotted in Fig. 2. This figure shows that the addition of 4 mole percent PN to PMR-15 significantly reduces its viscosity. The figure also reveals that in the PN concentration range of 4 to 20 mole percent a linear relationship holds. A linear relationship between resin flow and mole percent PN was also found in the composite fabrication studies in which the composites were fabricated under identical condition. As indicated in Fig. 3, the resin flow of the composites increased from 3 to 20 percent, when the PN mole percent was increased from 0 to 12 percent. Thus, it is clear that PN is an effective flow modifying agent for PMR-15. This suggests that the melt-flow properties of PMR polyimides can be tailored to meet specific processing requirements by a simple variation of the PN concentration.

In addition to varying the PN concentrations as mentioned above, changing composite pressurization temperatures in the cure cycle can provide an additional method to control the flow properties of the PN modified PMR polyimide composites. As described in Section 2.5, the pressurization temperatures for the control composite and PMR-P1 through PMR-P5 were progressively increased from 450 to 580°F. This was done to allow the PN modified PMR polyimide resins to advance to completely imidized prepolymers. As a result of delaying the application of pressure to higher temperatures in the cure cycle, each of the PN modified PMR polyimide composites exhibited resin flow equal to that of the control system. This is indicated by the resin content of each composite molded (Table 3). This finding suggests that the PN modified PMR polyimides also offer versatility in selecting processing parameters, such as PN concentrations and pressurization temperatures. It is expected that cure pressure can also be varied, but this parameter was not investigated in this study.

The thermal characteristics of the molding powders which had been treated at 400°F for 1 hour are shown in Fig. 4. This figure shows that the thermal behavior of PMR-P1 (curve a) closely resembles that of the control PMR-15 (curve b), suggesting that both resins undergo the same cure characteristics. This is expected since PN and PMR-15 imide prepolymers contain a common crosslinker, viz. the nadic end-group and, thus, the crosslinking reactivity of PN is expected to be the same as that of PMR-15 imide prepolymer. Other PN modified PMR molding powders exhibited similar DSC thermal behavior as PMR-15. The PN modified resins exhibited on-set exotherms near 600°F. This is the temperature at which the crosslinking reaction of the nadic end groups occurs. The endotherm centered around 392°F is assigned to the melt-flow of the imide prepolymers.(7)

The endotherm near 482°F has not been observed in the work published previously.(7) This thermal transition may be ascribed to the melting of polyamic acids, which are precursors of imide prepolymers. The reasons for this suggestion are based on the following observations: (1) this endotherm disappeared from the DSC thermogram of the control sample after additional treatment at 500 F for 1/2 hour; (2) the disappearance of this endotherm occurs with the concomitant enlargement of the endothermic peak near 400°F which is assigned to imide prepolymer. This is evident from a comparison of curve c with curve b shown in Fig. 4. (3) The infrared spectrum of the control sample showed an absorption band around 1650 cm^{-1} assignable to carbonyl stretching vibration of an amide. Because the presence of polyamic acids depends on the extent of staging the molding powders, it appears that the molding powders prepared according to the procedure described in Section 2.4 afforded both polyamic acids and imide prepolymers. This seems to suggest that staging of the PMR monomer mixtures at 400°F for one hour may not result in complete imidization. However, when the mixtures are further treated at 500°F for 1/2 hour, complete conversion of residual polyamic acids to imide prepolymers seems to occur. Polyamic acids in the control PMR-15 polyimide system had not been observed. Although the presence of polyamic acid intermediates in the PN modified PMR and the control (PMR-15) resins investigated in this study appears well founded, additional studies need to be carried out to verify their existence.

3.2 Composite Properties

3.2.1 "As Fabricated" Composites. Table 3 shows the physical properties of the PN modified and unmodified composites. By delaying the application of cure pressure to higher temperatures in the cure cycle, essentially void free PN modified PMR composites were produced as determined by ultrasonic C-scan and by the resin digestion technique. The PN modified and unmodified PMR-15 composites showed only small variations (57 to 59 mole percent) in fiber content. Thus, the fiber contents of the PN modified PMR can be controlled in the same fashion as PMR-15 even though these resins have much higher flow characteristics. The Tg of the modified PMR composites was about 18°F lower than the Tg of the PMR-15 (control) composite. After isothermal aging for 1000 hours, the Tg's of all composites increased by about 36°F. In addition, each of the aged composites invariably exhibited a second glass transition temperature which was found to be approximately 36°F higher than its first glass transition temperature. The presence of two distinctive glass transition temperatures suggests that at least two chemically distinctive polyimides may be formed in the course of the long term thermo-oxidative exposure.

Table 4 summarizes the mechanical properties of the "as fabricated" composites. Although the initial elevated temperature properties of the modified composites were slightly lower than those of the control, the room temperature properties of the modified PMR composites were equal to or superior to the room temperature properties of the control PMR-15 composites. Thus, it may be concluded that quality composites were fabricated from higher flow PN modified PMR prepreg with no sacrifice in the mechanical properties of the composites. The high value of RT flexural strength for the PMR-P5 composite is not readily explainable at this time.

3.2.2 Isothermally Aged Composites - Thermo-Oxidative Behavior. Table 5 summarizes the elevated temperature mechanical properties of the composites exposed and tested at 600°F in air, using precut flexural and interlaminar shear specimens. Table 5 shows that PN modified and PMR-15 composites exhibited excellent strength properties at 600°F after 1000 hours aging at 600°F in air. It is significant that as a result of 360 hours of exposure all of the composites showed a significant improvement in 600°F flexural and interlaminar shear strengths, but no change in flexural modulus. Furthermore, even after 1000 hours, the composites maintained this improvement. Thus, the PN modified PMR composites exhibited a level of thermo-oxidative stability at least equivalent to the unmodified PMR-15. This is significant in that a high flow PMR has been developed with no compromise in the thermo-oxidative stability of the polyimide system.

The 1500 hour isothermal aging data gave some rather unexpected results. Namely, PMR composites containing 4 and 9 mole percent PN (i.e., PMR-P1 and -P2, respectively) exhibited superior thermo-oxidative stability than did PMR-15 and the higher mole percent PN containing composites. This is further illustrated by their superior flexural strength, interlaminar shear strength, and flexural modulus retention (Figs. 5, 6, and 7) and their significantly lower weight loss (Fig. 8) relative to PMR-15 and PMR-P3, -P4, and -P5 composites. Furthermore, the greater thermo-oxidative resistance of the 4 and 9 mole percent PN containing PMR composites is shown in their fiber retention characteristics. As seen in Fig. 9, the PMR-15 control composite revealed many loose surface fibers after the isothermal exposure at 600°F in air for 1500 hours (Fig. 9a). In striking contrast, the PMR-P1 composite contained no loose surface fibers after the same thermo-oxidative exposure as that of the control (Fig. 9b). Thus, it appears that 4 and 9 mole percent PN in PMR-15 have improved the thermo-oxidative stability of PMR-15, and the useful lifetimes of PMR-15/Celion 6000 composites at 600°F in air have been extended by approximately 500 hours.(8)

3.2.3 Hydrothermally Exposed Composites. A series of precut flexural specimens of the PN modified and unmodified PMR-15 composites were exposed to 95 percent relative humidity at 180°F for 360 hours. Table 6 lists the glass transition temperatures and the elevated temperature flexural strengths of the hydrothermally exposed composites. The composites exhibited 1.3 percent equilibrium moisture absorption except for PMR-P1 sample, which absorbed 1.1 percent moisture. Moisture caused a considerable decrease in the glass transition temperature, ranging from 18°F to 54°F. A slower heat-up rate of 18°F/minute compared to 90°F/minute give higher Tg values, indicating that greater drying occurs at the lower heating rate. This is further substantiated by the Tg's of the samples after drying for 15 minutes at 473°F. The Tg's of the dried samples were nearly equal to the Tg's of the composites in the dry as-fabricated condition except for PMR-P1 and -P5. The data demonstrate the reversibility of moisutre effect on the Tg of PMR-15.(6) The moisture resistance of PMR-P1 and -P2 was comparable to that of the control PMR-15 (600°F flexural strengths of about 71.5 and 63 ksi for PMR-P1 and -P2, respectively, compared to about 65 ksi for PMR-15 sample).

These values are approximately 50 percent of the 600°F dry strengths. The other PN modified PMR composites exhibited lower flexural strengths than the above mentioned composite systems. These results are in agreement with the isothermal aging results which showed that PMR composites containing 4 and 9 mole percent PN demonstrated higher composite properties.

It was expected that lower flexural strengths would be obtained for the wet samples because the flexural strengths were measured at a temperature approaching the Tg of wet specimens using a temperature spike test.(6) This method minimizes the drying of the composites. Conventional testing of wet PMR-15 composites usually includes a 15 minute equilibration period at the test temperature. Serafini and Hanson(6) showed that this allows the composite to dry out and does not provide a realistic assessment of effect of moisture. Therefore, the flexural strengths obtained in this study reflect more closely the actual flexural strengths of the wet samples than the values obtained by the conventional testing method.

4. CONCLUSIONS

The processing and properties of N-phenylnadimide modified PMR polyimide/Celion 6000 graphite composites were investigated. On the basis of these results, it is concluded that:

1) higher flow N-phenylnadimide (PN) modified PMR matrix resins have been developed which show no compromise in the elevated temperature properties of Celion 6000/polyimide composites, compared to the control PMR-15.

2) Concentrations of 4 and 9 mole percent PN improve the thermooxidative behavior of the PMR-15 composite systems.

3) Melt-flow properties of PN modified PMR polyimides can be tailored to meet specific applications by either varying the concentrations of PN or the composite pressurization temperatures.

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Table I Monomers used for modified PMR polyimides

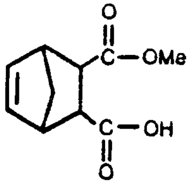
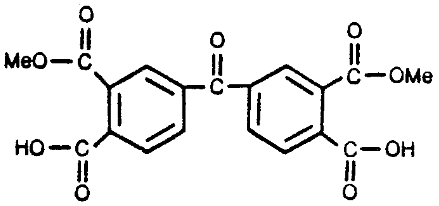
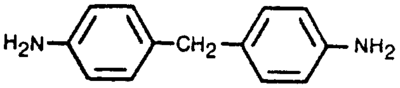
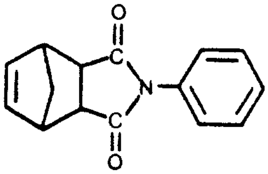
STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF 5-NORBORNENE- 2, 3-DICARBOXYLIC ACID	NE
	DIMETHYL ESTER OF 3, 3', 4, 4'- BENZOPHENONETETRA-CARBOXYLIC ACID	BTDE
	4, 4'-METHYLENEDIANILINE	MDA
	N-PHENYLNADIMIDE	PN

TABLE 2. COMPOSITIONS OF MODIFIED PMR POLYIMIDES

Resin System	PMR-15/PN Mole Percent	PMR-15/PN Weight Percent	Monomer (Mole) NE	MDA	BTDE	PN
PMR-15 (Control)	100/0.0	100/0.0	2	3.087	2.087	0.0
PMR-P1	96/4	99.33/0.67	2	3.087	2.087	0.041
PMR-P2	91/9	98.47/1.53	2	3.087	2.087	0.099
PMR-P3	88/12	97.86/2.14	2	3.087	2.087	0.136
PMR-P4	85/15	97.20/2.80	2	3.087	2.087	0.177
PMR-P5	80/20	96.2 /3.80	2	3.087	2.087	0.251

TABLE 3. PHYSICAL PROPERTIES OF MODIFIED PMR POLYIMIDE/CELION 6000 COMPOSITES

Resin System	Density g/cc[a]	Glass Transition Temperature, °F[b]			Composition Volume Percent[a]		
		As Fabricated[c]	1000 hours aged[d]				
			First	Second	Fiber	Resin	Void
PMR-15 (Control)	1.58	666	698	739	59.2	40.2	0.6
PMR-P1	1.56	644	680	707	58.1	41.3	0.6
PMR-P2	1.55	644	680	709	58.8	41.1	0.1
PMR-P3	1.55	644	685	716	57.3	42.2	0.5
PMR-P4	1.55	626	680	707	57.9	41.6	0.5
PMR-P5	1.55	653	680	711	57.1	42.5	0.4

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[a] average of three determinations
[b] determined by thermomechanical analysis heating rate of 18°F/minute
[c] post cured for 16 hours at 600°F in air
[d] aged at 600°F in air

TABLE 4. MECHANICAL PROPERTIES OF MODIFIED PMR POLYIMIDE/ CELION 6000 COMPOSITES AS FABRICATED

Composite Property	Resin System					
	PMR-15 (Control)	PMR-P1	PMR-P2	PMR-P3	PMR-P4	PMR-P5
Flexural Strength, ksi[a]						
Room Temperature	231.1	227.1	230.9	235.5	240.9	268.7
600°F	133.9	112.7	118.4	127.5	126.4	129.6
Flexural Modulus, psi x 10^6 [a]						
Room Temperature	16.17	15.66	17.19	15.64	16.62	17.66
600°F	14.58	13.12	13.21	14.26	14.65	13.61
Interlaminar Shear Strength, ksi						
Room Temperature[b]	14.19	17.06	14.04	15.89	16.76	16.09
600°F [c]	6.46	6.13	5.94	6.78	7.53	6.58
Tensile Strength, ksi[b] 10° off axis						
Room Temperature	63.50	64.16	59.36	62.20	64.19	64.22
Tensile Modulus, psi x 10^6 [d]						
Room Temperature[d]	9.14	8.76	8.99	8.64	7.83	10.12
Elongation, Percent[d]	1.07	1.18	1.21	1.45	1.53	1.17

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[a] average of three determinations; normalized to 60 volume percent fiber
[b] average of five determinations
[c] average of three determinations
[d] average of four determinations

TABLE 5. MECHANICAL PROPERTIES OF MODIFIED PMR POLYIMIDE/ CELION 6000 COMPOSITES EXPOSED AND TESTED IN AIR AT 600°F

600°F Composite Property		Resin System					
		PMR-15 (Control)	PMR-P1	PMR-P2	PMR-P3	PMR-P4	PMR-P5
Flexural Strength, ksi[a]							
After exposure for	0 Hour	133.9	112.7	118.4	127.5	126.4	129.6
	360 Hours	143.6	143.7	140.9	153.7	161.4	148.0
	600 Hours	145.1	151.2	152.6	151.7	164.6	143.9
	1000 Hours	146.5	153.5	150.4	154.4	163.1	154.8
	1500 Hours	115.6	137.2	137.0	138.2	117.9	121.7
Flexural Modulus, psi x 10^6 [a]							
After exposure for	0 Hour	14.58	13.12	13.21	14.26	14.65	13.61
	360 Hours	15.54	15.96	14.79	15.16	15.2	14.77
	600 Hours	15.71	14.71	14.23	15.14	15.11	14.01
	1000 Hours	12.32	13.00	12.33	12.32	13.48	12.64
	1500 Hours	8.29	11.53	11.04	9.53	8.15	7.09
Interlaminar Shear Strength, ksi[b]							
After exposure for	0 Hour	6.46	6.13	5.94	6.78	7.53	6.58
	360 Hours	6.83	6.67	6.59	7.02	7.90	6.91
	600 Hours	6.72	6.64	6.76	7.10	7.81	7.24
	1000 Hours	6.54	6.59	6.64	7.02	7.98	7.33
	1500 Hours	4.40	5.58	6.19	6.13	5.48	5.55

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[a] average of three determinations; normalized to 60 volume percent fiber
[b] average of three determinations

TABLE 6. HYDROTHERMAL EFFECTS ON PROPERTIES OF MODIFIED PMR POLYIMIDE/ CELION 6000 COMPOSITES EXPOSED FOR 360 HOURS AT 180°F AND 95 PERCENT RELATIVE HUMIDITY

Resin System	Moisture Absorbed Wt Percent [a]	Glass Transition Temp., °F				600°F Flexural Strength, ksi[f]
			Wet			
		Dry[b]	A[c]	B[d]	C[e]	
PMR-15 (Control)	1.3	666	617	658	658	65.05
PMR-P1	1.1	644	599	626	613	71.46
PMR-P2	1.3	644	599	621	642	62.94
PMR-P3	1.3	644	621	640	622	56.94
PMR-P4	1.3	626	608	622	622	55.05
PMR-P5	1.3	653	617	630	617	54.40

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[a] average of three determinations
[b] dry as fabricated composites tested at a heating rate of 18°F/minute
[c] tested at a heating rate of 90°F/minute
[d] tested at a heating rate of 18°F/minute
[e] after drying for 15 minutes at 473°F and then tested at 18°F/minute
[f] temperature spike tested, average of five determinations, and normalized to 60 volume percent fiber

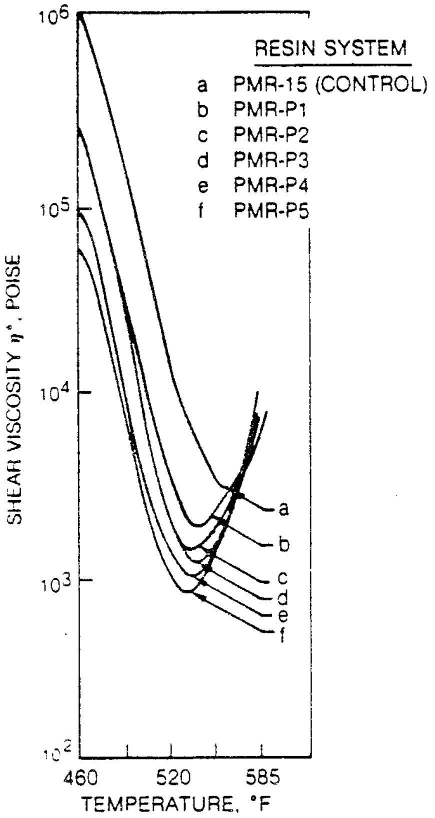


Figure 1 Shear viscosity as a function of temperature for modified PMR polyimide molding powders

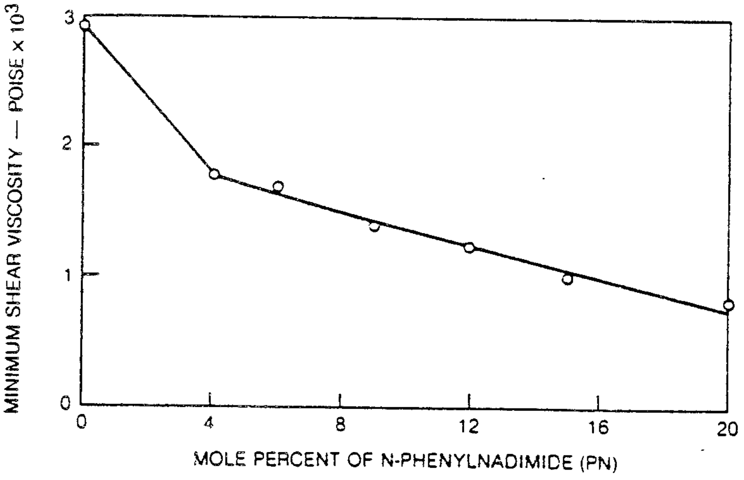


Figure 2 Minimum shear viscosity as a function of concentration of N-phenylnadimide for modified PMR polyimide molding powders

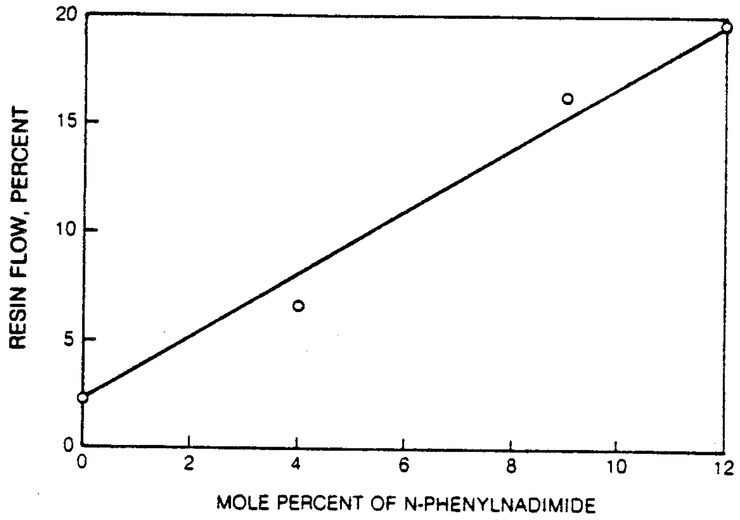


Figure 3 Resin flow as a function of concentration of N-phenylnadimide for modified PMR polyimide/Celion 6000 composites

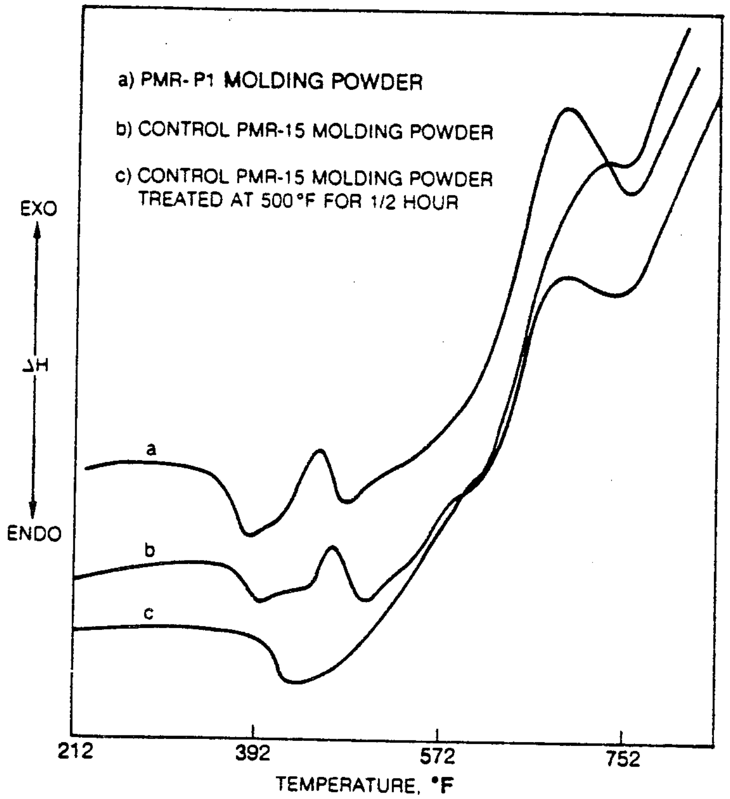


Figure 4 Differential calorimeter scans of PMR-P1 and PMR-15 molding powders

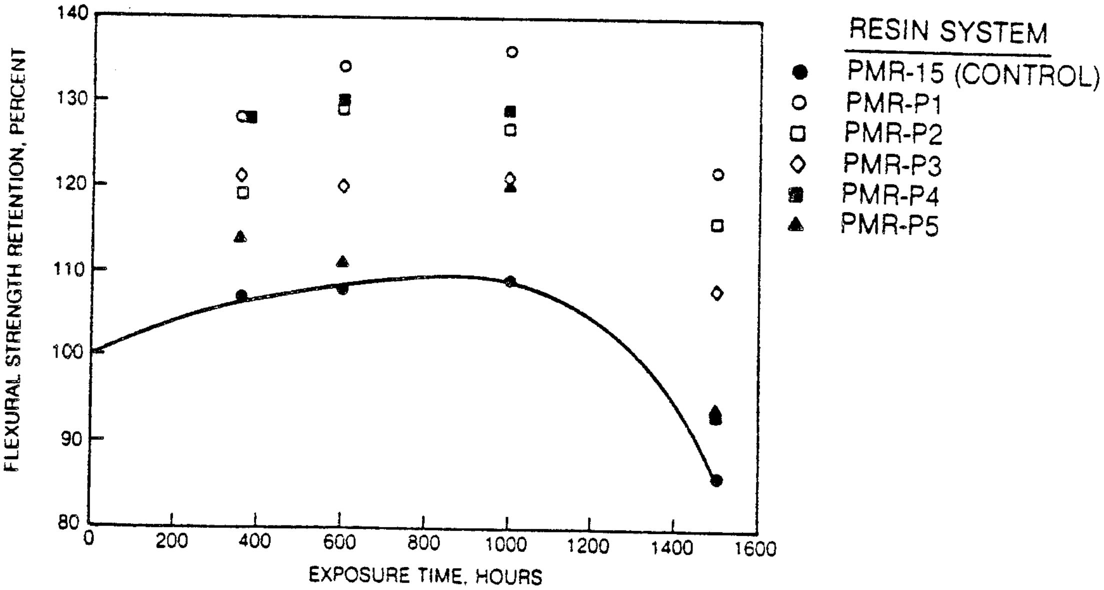


Figure 5 Flexural strength retention of modified PMR polyimide/Celion 6000 composites exposed and tested at 600° F in air

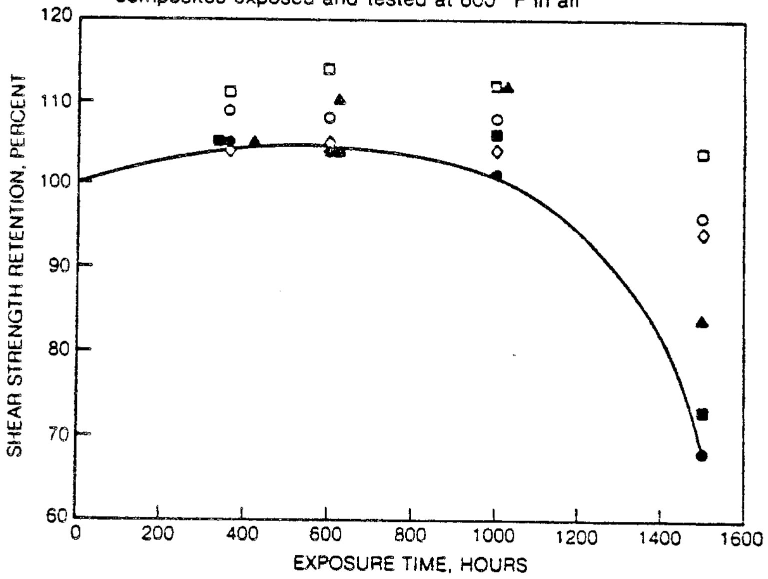


Figure 6 Interlaminar shear strength retention of modified PMR polyimide/Celion 6000 composites exposed and tested at 600° F in air

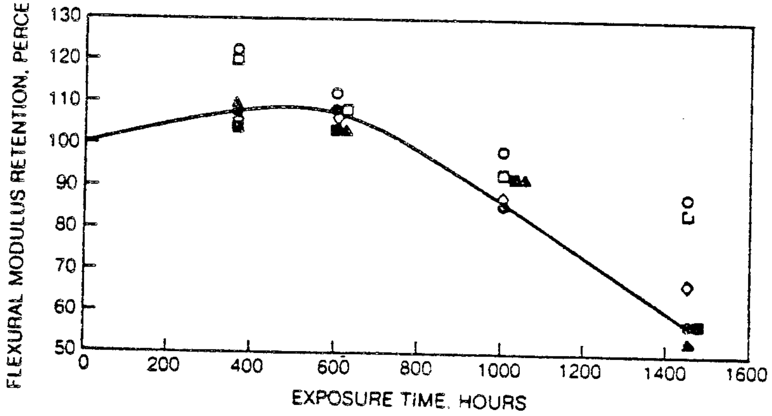


Figure 7 Flexural modulus retention of modified PMR polyimide/Celion 6000 composites exposed and tested at 600° F in air

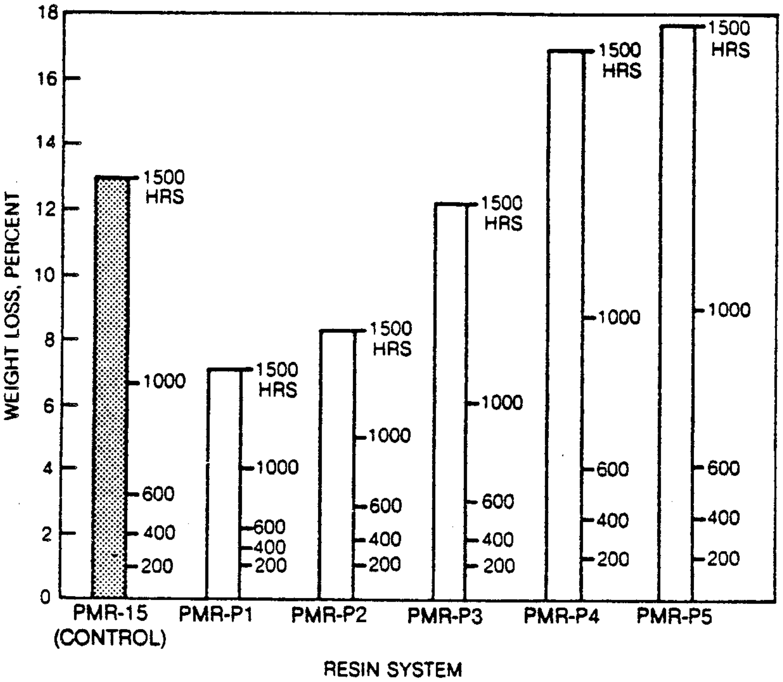
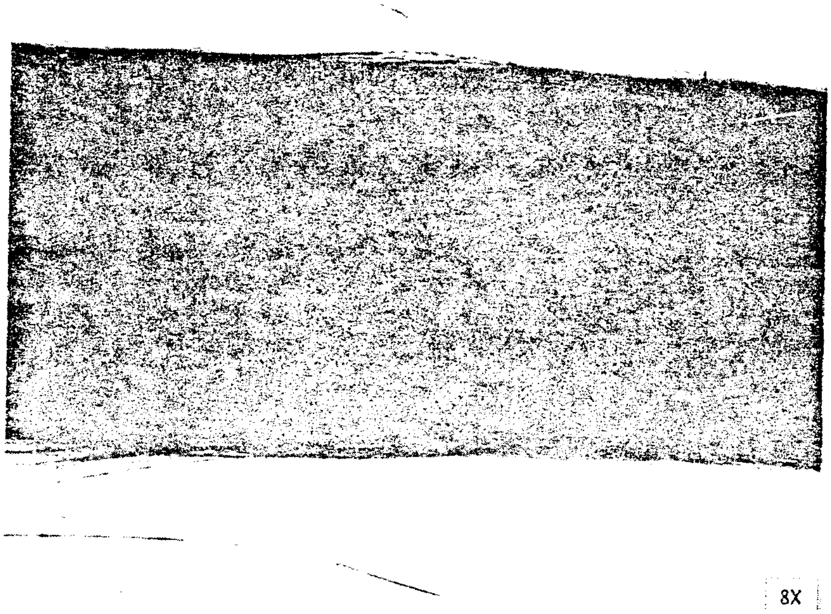
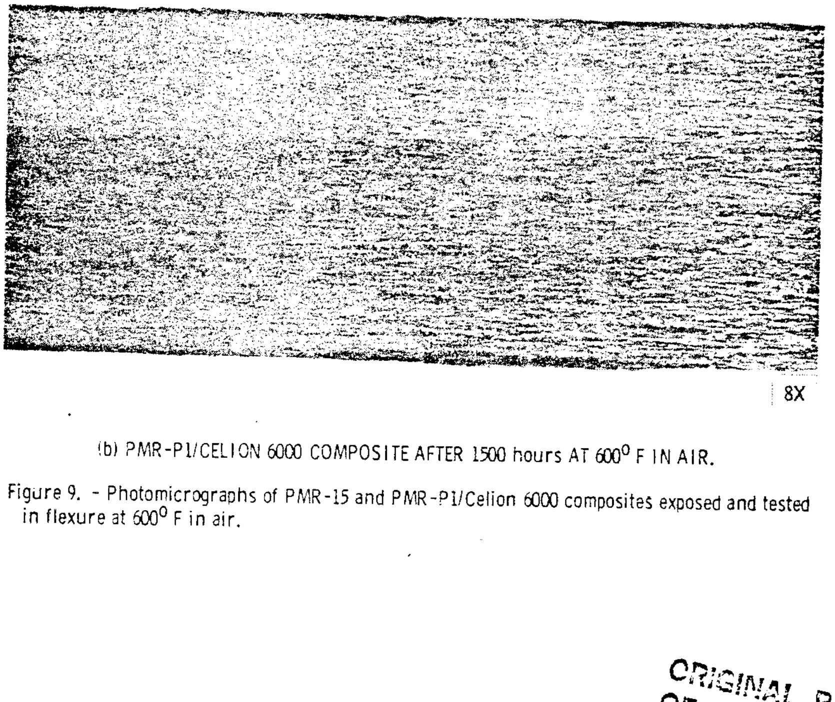


Figure 8 Weight loss characteristics of modified PMR polyimide/Celion 6000 composites exposed in air at 600° F up to 1500 hours



(a) CONTROL PMR-15/CELION 6000 COMPOSITE AFTER 1500 hours AT 600° F IN AIR.



(b) PMR-P1/CELION 6000 COMPOSITE AFTER 1500 hours AT 600° F IN AIR.

Figure 9. - Photomicrographs of PMR-15 and PMR-P1/Celion 6000 composites exposed and tested in flexure at 600° F in air.