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371° C (700° F) Properties of Celion 6000/N-Phenylnadimide Modified PMR Polyimide Composites

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INTRODUCTION

High performance graphite/polyimide composites are being evaluated for use in aircraft engine components, which operate at temperatures up to 371° C. Though the properties of these composite materials at 316° C and below have been extensively documented, their performance at higher temperatures, particularly at 371° C, has not been extensively investigated(1). Because of this lack of the 371° C property data, a realistic assessment on the use of the composite materials in extremely hostile environments is not possible at the present time.

Recently, we reported a new series of N-phenylnadimide (PN) modified PMR-15 polyimides(2) designated as PN-PMR-P1, -P2, -P3, etc., where P-1, -2, -3 etc. refers to a formulation containing a given quantity of PN. These polyimides are formed from in-situ thermopolymerization of four monomer reactants. A possible reaction scheme is shown in Figure 1. A variety of PN-PMR resin compositions can be easily formulated by adding various quantities of PN to the standard PMR-15 composition. Table 1 lists the resin compositions studied. Our initial study revealed that composites prepared from these matrices and Celion 6000 graphite fibers exhibited excellent processability and thermo-oxidative stability at 316° C for 1500 hours.

The purpose of this investigation was to determine the useful life of graphite fiber reinforced PN-PMR composites at 371° C. Celion 6000/PN-PMR composites were subjected to isothermal aging at 371° C in air. The glass transition temperatures, weight loss characteristics, and dimensional stability were determined for isothermally exposed composites. Composite interlaminar shear and flexural properties were measured at room temperature, 316° C, and 371° C. In addition, composite interfacial degradation process as a function of exposure time at 371° C was followed by scanning electron microscopy.

MATERIALS AND METHODS

The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4-4'-methylenedianiline (MDA), and 3,3'4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and Celion 6000 graphite fibers were obtained commercially. PN and a 50 weight percent methanol solution of the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) were prepared in-house. The synthetic procedures for these compounds have been reported[2]. The prepreg materials were first staged at 204° C for 1 hour and then compression molded at 316° C under 3.45 MPa pressure for 2 hours following a procedure described in the previous report(2). The fiber contents of the composite systems ranged between 59 to 61 volume percent, as determined by the H_2SO_4/H_2O_2 digestion method. All composites were then subjected to a free standing postcure at 371° C in air for time periods of up to 300 hours. Composite specimens having a size of 2.54 cm by 6.86 cm and 0.2 cm were isothermally aged at 371° C in flowing air at a rate of approximately 100 cc/minute. At various time intervals for up to 300 hours, isothermally aged composite specimens were removed from the air-circulating oven and their physical and mechanical properties were then determined. Flexural tests were performed in accordance with ASTM D790. All values of the flexural properties were normalized to 60 volume percent fiber. Interlaminar shear strengths were measured following ASTM D2344 specifications. Glass transition temperatures were determined by thermomechanical analysis with a heating rate of 10° C/minute. For comparison purposes, a control sample (PMR-15) was also studied along with the PN-PMR composite specimens.

RESULTS AND DISCUSSION

Composite Processing

As indicated by ultrasonic examination, optical microscopy, and acid-digestion determination, high quality and void-free composites were obtained from all PN-PMR formulations and the control PMR-15 (Table 1). These "as fabricated" composite specimens were postcured at 371° C in air. Table 2 shows the effects of the postcuring on the weight losses and dimensional shrinkages of the composite specimens. All composites underwent approximately two percent weight loss during the first 30 hours of the postcure. During the first 16 hours of the postcure, all composites invariably exhibited approximately one percent shrinkage in the direction transverse to fibers. However, as expected, there were no detectable dimensional changes in longitudinal direction during the same time period. No additional dimensional changes were observed between the 16 to 30 hour postcure. The transverse shrinkage is undoubtedly governed by the matrices, whereas the longitudinal shrinkage is fiber controlled.

Figure 2 shows the effects of the postcure on the glass transition temperatures (Tg's) of the composites. Three important results are revealed in Figure 2: (1) The rate of increasing composite glass transition temperature (Tg) follows a stepwise process. (2) All composites exhibited a linear dependence of Tg on the postcure time. And (3) considerably long postcure time at 371° C is required for attaining a Tg of 371° C. Two stages were seen in increasing the Tg for all composite systems. The first stage occurred from 0 to 30 hours of the postcure during which the glass transition temperature increased rapidly. The rate constant for this step (k_1) varied from 2.0° C/hour for the control (PMR-15) to 1.5° C/hour for the PMR-P4 specimen. Increasing PN concentration in the matrices appears to slow down the rate of increase in the Tg. The second stage was observed from 30 to 160 hours or longer depending on the resin formulation used. The rate constant for the second step (k_2) was found to be approximately 0.11° C/hour for all composite specimens. It is clear that rate constant k_2 is considerably lower than rate constant k_1 by a factor of about 14. After 160 hours for the control sample or longer for the PN-PMR specimens, a plateau was reached in which all composites exhibited a common maximum Tg at 382° C. It appears that the concept of vitrification(3) holds for the present resin systems. The fact that two distinct stages were seen in the rate of increase in Tg suggests that two different mechanisms may be operating in postcuring of the resin. The elucidation of the cure mechanisms is beyond the scope of this study. The dependence of Tg on the postcure time can be expressed in the following equation:

$$Tg = ki \ln t + C$$

where ki is the rate constant for either stage-one or stage-two, t is the postcure time, and C is a constant. Further, a minimum of 50, 75, 90, 105, and 110 hours of postcuring at 371° C in air are required for the PMR-15, PMR-P1, PMR-P2, PMR-P3, and PMR-P4 composite materials, respectively, to obtain a 371° C glass transition temperature for 371° C structural applications.

Figures 3 and 4 show composite mechanical properties measured at 316° C and at room temperature, respectively, as a function of the postcure time. Figure 3 shows that all composite systems exhibited a marked increase in the elevated temperature mechanical properties during the first 16 hours of the postcure. This property increase for the PN modified composites appeared to level off between 16 to 30 hours of the postcure. Contrary to the elevated temperature properties, the room temperature shear strength decreased with increasing postcure time (Figure 4) while the flexural modulus and strength were unaffected. Our previous study showed that PN-PMR composites exhibited flexural and interlaminar shear properties equivalent to PMR-15 control sample, after postcure for 16 hours at 316° C in air(2). This is also observed in the present study as indicated by the data listed in Figures 3 and 4 for the composites after the postcure for 30 hours. Based on the composite Tg's and mechanical property data presented above, a postcure time of 30 hours at 371° C in air was selected for composite thermo-oxidative stability study described in the following paragraphs.

Figure 5 shows the 371° C mechanical properties of the composites as a function of 371° C exposure time. During 0 to 100 hours of the exposure, composites exhibited an average flexural strength of 310 MPa (45.0 ksi), an average flexural modulus of 43 GPa (6.2 x 10^6 psi), and an average interlaminar shear strength of 24 MPa (3.5 ksi). In view of that the testing temperature (371° C) was above or close to the glass transition temperatures, most of the composite materials exhibited reasonably good performance at 371° C throughout the first 100 hours of the aging. The 30 hour postcure time appears to be adequate for attaining a useful level of performance at 371° C. Kimmel, Bilow, and Landis reported a value of 132 MPa (19.1 ksi) for the flexural strength of HR 600 polyimide/A-S graphite composite after being aged for 62 hours at 371° C in air(4). Initially, PN-PMR composites exhibited lower flexural strengths, but somewhat higher interlaminar shear strengths, compared to the control. After 100 hour exposure at 371° C, all PN-PMR composites exhibited higher flexural and interlaminar shear strengths than the control specimen PMR-15, particularly the PMR-P1 and PMR-P2 composite systems.

In addition to the mechanical properties presented above, the trend for higher thermo-oxidative stability of PMR-P1 and PMR-P2 composite systems at 371° C is further supported by the weight loss data in Figure 6, and the fiber retention comparison illustrated in Figure 7. Thus, the results of the present study are consistent with those of the previous work that thermo-oxidative stability of the PN-PMR composite systems follows the order:

PMR-P1 ~ PMR-P2 > PMR-P3 ~ PMR-15 > PMR-P4(2).

Scola reported that the thermo-oxidative degradation of Celion 6000/PMR-15 at 335° C occurs only at exposed composite surfaces and that the thermo-oxidation and pyrolysis do not occur within the bulk of the composite system(5). Figure 8 shows the SEM micrographs of PMR-P1 composites aged at 371° C for time periods up to 200 hours. No matrix or interfacial degradation was observed as a result of 30 hour postcuring at 371° C in air (Figure 8A). However, some matrix degradation occurred between 0 and 120 hours at 371° C in air (Figure 8B). Continued exposure to 200 hours resulted in extensive matrix and interfacial degradation (Figure 8C and 8D). Other composite systems exhibited similar interfacial characteristics as that of PMR-P1 during the thermo-oxidative treatment.

The minimal degradation, as assessed by SEM analysis, and the levels of mechanical properties of the composites after 100 hours at 371° C in air suggest that the 371° C useful life of the PN-PMR composites is at least 100 hours.

CONCLUSIONS

On the basis of these results, it can be concluded : (1) The useful life of Celion 6000/PN-PMR composites under continuous exposure at 371° C in air is about 100 hours; (2) A free standing postcure in air at 371° C for 30 hours appears to be adequate for obtaining useful properties at 371° C; and (3) The addition of N-phenylnadimide (PN) appears to be a powerful approach for attaining PMR polyimide formulations with improved thermo-oxidative stability.

REFERENCES

1. R. A. Pike, and M. A. DeCrescente, in "The Wide World of Reinforced Plasitics," Society of the Plastics Industry, New York, 1974. p. 18-Fi.

2. R. H. Pater, in "Technology Transfer," p. 38, Society for the Advancement of Material and Process Engineering, Azusa, CA. 1981.

3. D. R. Hill, Polymer Prepr., Am. Chem. Soc., Div. Polym. Chem., 38, 590(1978).

4. B. G. Kimmel, N. Bilow, and A. L. Landis, AFML-TR-74-89, Hughes Aircraft Co., Culver City, CA., 1975.

5. D. A. Scola, in "Materials Overview for 1982," Society for the Advancements of Material and Process Engineering, Azusa, CA., 1982.

TABLE 1. COMPOSITIONS OF MODIFIED PMR POLYIMIDES

RESIN SYSTEM	PN MOLE PERCENT	MONOMER (MOLE) NE	MDA	BTDE	PN
PMR-15 (CONTROL)	0.0	2	3.087	2.087	0.0
PMR-P1	0.6	2	3.087	2.087	0.041
PMR-P2	1.4	2	3.087	2.087	0.099
PMR-P3	1.9	2	3.087	2.087	0.136
PMR-P4	2.4	2	3.087	2.087	0.177

TABLE 2. EFFECTS OF 371°C POSTCURE ON PHYSICAL PROPERTIES OF CELION 6000/MODIFIED PMR POLYIMIDE COMPOSITES

COMPOSITE PROPERTY	POSTCURE TIME, HOURS	RESIN SYSTEM				
		PMR-15 (CONTROL)	PMR-P1	PMR-P2	PMR-P3	PMR-P4
WEIGHT LOSS, PERCENT	16	1.6	1.6	1.6	1.6	1.7
	30	2.1	2.0	2.1	2.2	2.3
TRANSVERSE SHRINKAGE, PERCENT	16	0.9	0.9	1.0	1.0	1.0
	30	0.9	1.0	1.1	1.1	1.1

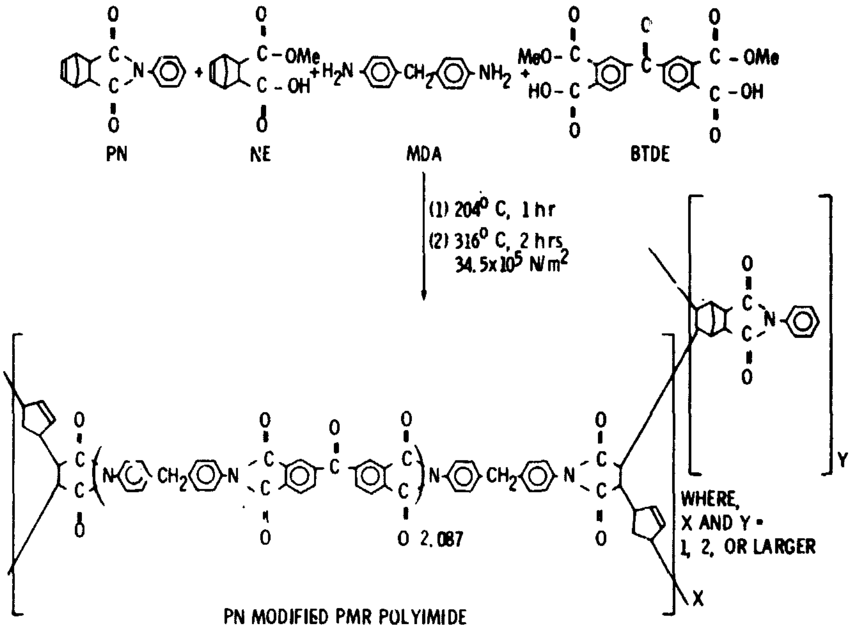

Figure 1. - Synthetic reaction for PN modified PMR polyimide.

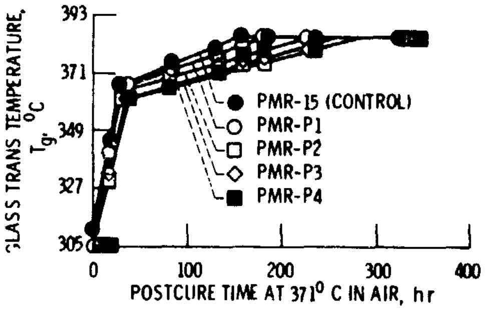

Figure 2. - Glass trans temperature, (T_g) vs postcure time for Celion 6000/PN modified PMR polyimide composites.

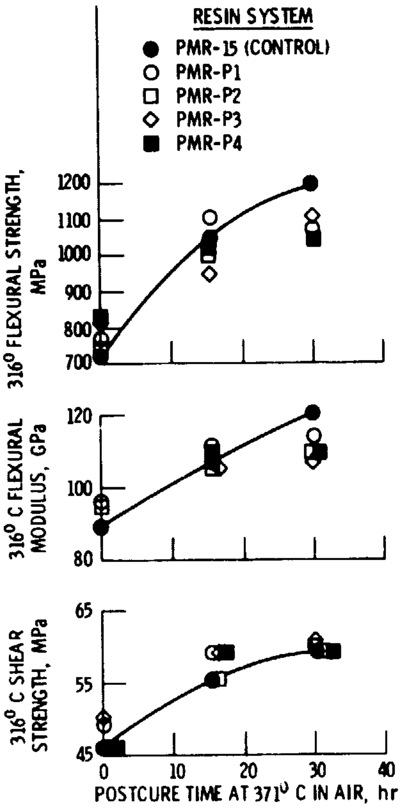

Figure 3. - Effects of 371° C postcure on elevated temperature (316° C) mechanical properties of Celion 6000/PN modified PMR polyimide composite.

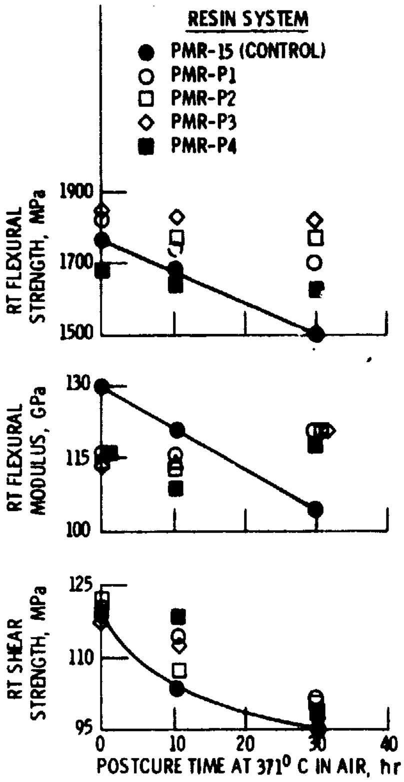

Figure 4. - Effects of 371° C postcure on room temperature mechanical properties of Celion 6000/PN modified PMR polyimide composites.

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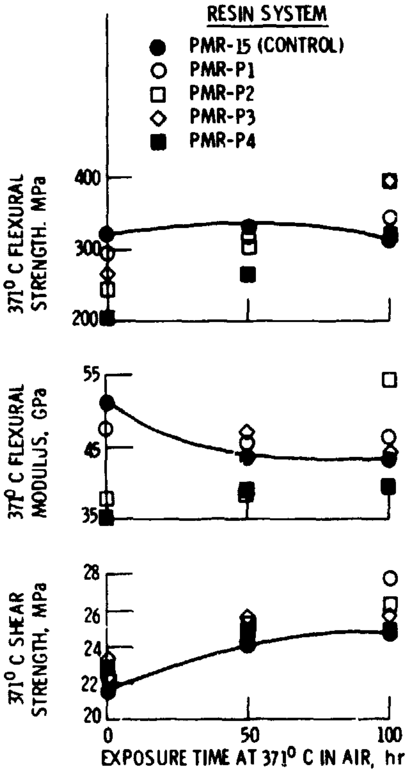


Figure 5. - Elevated temperature (371° C) mechanical properties vs exposure time for Celion 6000/PN modified PMR polyimide composites.

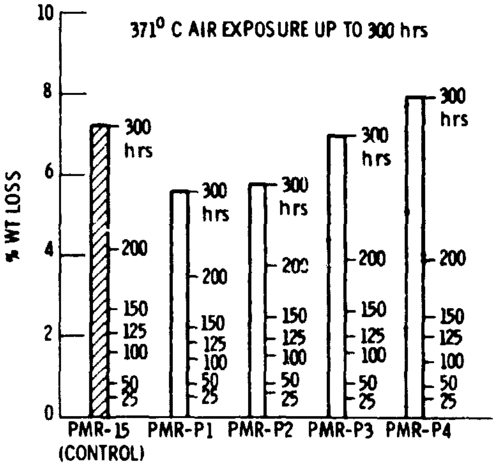
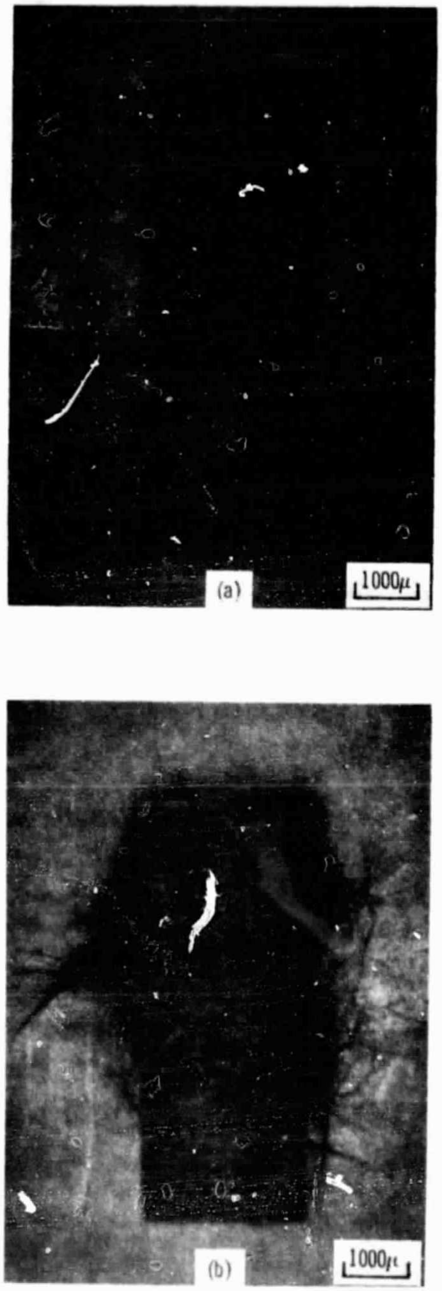


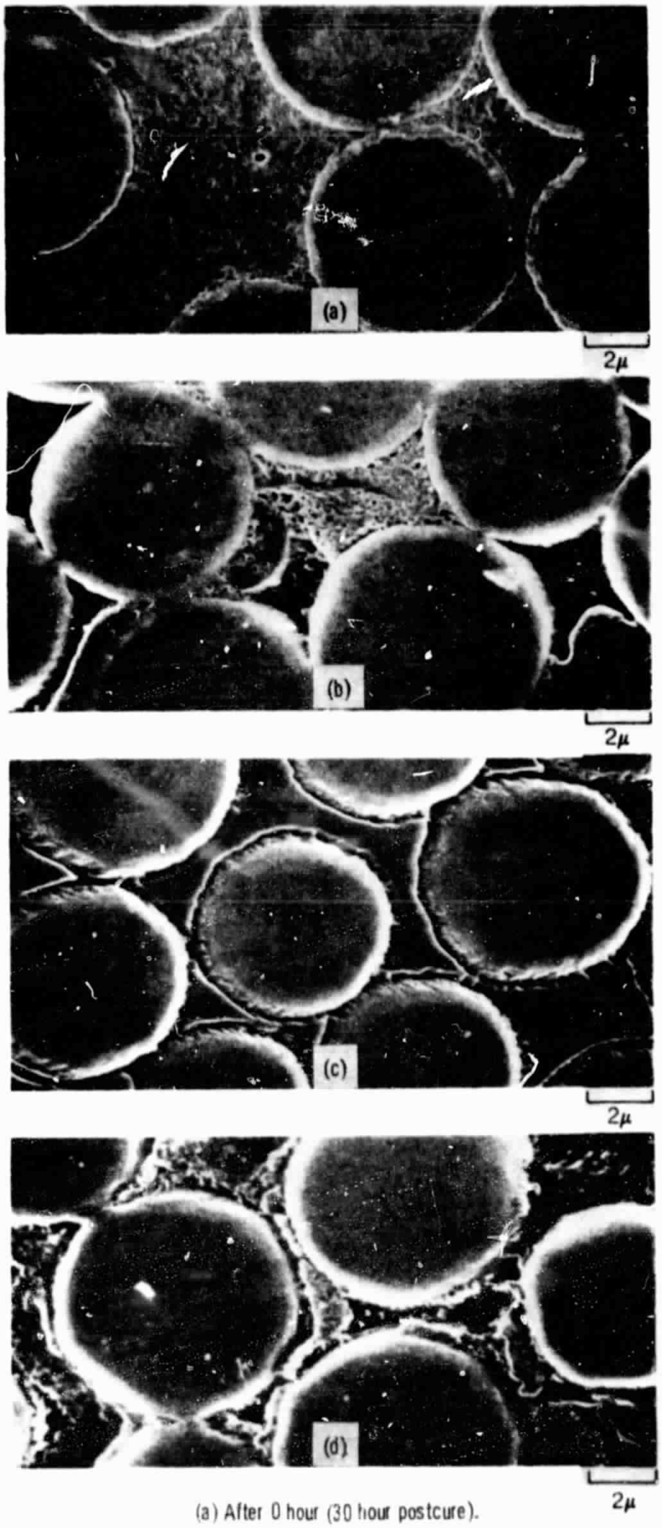
Figure 6. - Weight loss of Celion 6000/PN modified PMR polyimide composites.



(a) Celion 6000/PMR-P1.

(b) Control celion 6000/PMR-15.

Figure 7. - Comparison of Fiber Retention Characteristics for celion 6000/PMR-P1 and Control PMR-15 composites after 200 hours at 371° C in air.



(a) After 0 hour (30 hour postcure).

(b) After 120 hours.

(c) After 170 hours.

(d) After 200 hours.

Figure 8. - SEM photomicrographs of celion 6000/PMR-P1 composites exposed at 371° C in air.