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EFFECTS OF GRAPHITE FIBER STABILITY ON THE  
PROPERTIES OF PMR POLYIMIDE COMPOSITES

Peter Delvigs, William B. Alston,  
and Raymond D. Vannucci  
Lewis Research Center  
and

AVRADCOM Research and Technology Laboratories  
Cleveland, Ohio 44135

Abstract

Studies were performed to investigate the effect of the stability of graphite fibers on composite properties after exposure in air at 600°F. Composites were fabricated from PMR-15 and PMR-II monomer solutions, using HTS-2 and Celion 6000 graphite fibers as the reinforcement. The effect of long-term exposure in air at 600°F on composite weight loss and mechanical properties was determined. These composites exhibited a significantly increased lifetime at 600°F compared to composites fabricated from HTS fiber sold prior to 1975. The effect of the PMR-15 and PMR-II resin compositions on long-term composite performance at 600°F is also discussed.

1. INTRODUCTION

In response to the need for easily processable, high temperature matrix resins for fiber-reinforced composites, investigators at the NASA Lewis Research Center developed the so-called PMR polyimides.<sup>(1)</sup>

The advantages and versatility of the PMR approach have been reviewed.<sup>(2)</sup>

At the present time two versions of the PMR, differing in stoichiometry and chemical composition, have been identified. The earlier version has been designated

PMR-15, while the more recently developed second generation material has been designated as PMR-II.<sup>(3)</sup>

Graphite fiber-reinforced composites using the PMR-II material have shown a significant increase in composite lifetime on exposure in air at elevated temperatures.<sup>(3)</sup> A further improvement in PMR polyimide composite performance at elevated temperatures has been made possible by the recent development of new high strength, intermediate modulus graphite fibers such as Hercules

HTS-2 and Celanese Celion 6000. These fibers exhibit a significantly improved thermo-oxidative stability over the older versions of high strength fibers, such as HTS-1.

The purpose of this study was to investigate the effect of HTS-2 and Celion 6000 graphite fibers on the mechanical properties and thermo-oxidative stability of PMR-15 and PMR-II polyimide composites. Composite weight loss and mechanical property retention characteristics were determined as a function of exposure time in air at 600°F. This paper also compares the effect of the PMR-15 and PMR-II resin compositions on long-term composite performance at 600°F.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 MONOMERS AND PMR SOLUTIONS

The monomers used in this study are shown in Table I. The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), para-phenylenediamine (PPDA), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were obtained from commercial sources. The 4,4'-(hexafluoroisopropylidene)-bis(phthalic anhydride) (HFDA) was prepared according to Vannucci and Alston.<sup>(4)</sup> The dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) and the dimethyl ester of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid) (HFDE) were prepared as 50 weight percent

solutions by refluxing a suspension of the corresponding dianhydrides in anhydrous methanol until the solids dissolved and then for an additional two hours.

The PMR monomer stoichiometry for PMR-15 solutions was 2 NE/3.087 MDA/2.087 BTDE. The solutions were prepared at room temperature by dissolving the monomers in a calculated amount of anhydrous methanol to give 50 weight percent solutions. The PMR-II solutions were prepared in a similar manner, using a monomer stoichiometry of 2 NE/2.67 PPDA/1.67 HFDE.

### 2.2 GRAPHITE FIBERS

The following graphite fibers were used for composite fabrication and fiber weight loss studies: HTS-2 from lot 66-7 and Celion 6000 (without finish) from lot HTA-7-6Y11. The HTS-1 fiber used for weight loss studies was taken from lot 34-2. The HTS-1 composite property data are taken from the literature.<sup>(3,5)</sup> Forced air convection ovens were used for long-term isothermal exposure of bare fibers at 600°F. The air change rate was 100 cm<sup>3</sup>/min.

### 2.3 COMPOSITE FABRICATION

Prepreg tapes were made by drum-winding and impregnating graphite fiber with PMR monomer solutions calculated to yield prepregs containing 45 percent monomers and 55 percent fiber by weight. The prepreg tapes were dried on the rotating drum for 1 hour at room

temperature and then for another hour at about 122°F to reduce the solvent content to a level that gave flexible tapes without excessive tack. The tapes were removed from the drum, cut into 3-inch by 8-inch plies, and stacked unidirectionally. Twelve plies per stack were used for prepreg prepared from HTS fiber, and 18 plies were used for prepreg made from Celion 6000 fiber. The prepreg stack was placed in a preforming mold and staged at 400°F for 1 hour under a pressure of approximately 0.1 psi. Composites were molded by placing the staged prepreg stack into a matched metal die preheated to 450°F. Following a dwell time of 2-5 minutes, a pressure of 500 psi was applied, and the temperature was increased to 600°F at a rate of 10°F per minute. Pressure and temperature were maintained for 1 hour. After removal from the mold, all composites were post-cured in air at 600°F for 16 hours.

#### 2.4 COMPOSITE TESTING

Prior to specimen preparation all laminates were inspected for acceptance using an ultrasonic C-scan technique. Flexural strength tests were performed using a three-point loading fixture with a fixed span of 2 inches. The rate of center loading was 0.05 in/min. The thickness of the HTS composite specimens ranged from 0.082 inches to 0.091 inches, resulting in a span/depth ratio of 24.5 to 22. The thickness

of the Celion composites ranged from 0.104 inches to 0.123 inches, resulting in a span/depth ratio of 19 to 16. Elevated temperature tests were conducted in an environmental heating chamber following a 15 minute soak at the test temperature. The mechanical property values reported are averages of three tests at each condition.

Forced air convection ovens were used for long-term isothermal exposure of composites at 600°F. The air change rate was 100 cm<sup>3</sup>/min. Composite weight loss measurements were made throughout the exposure period.

The fiber content of composites fabricated from HTS fiber was determined by H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> digestion. The fiber content of Celion 6000 laminates was determined by a hydrazine digestion technique.<sup>(6)</sup>

#### 3. RESULTS AND DISCUSSION

Prior to composite fabrication, the thermo-oxidative stability (TOS) of the various graphite fibers was investigated. Figure 1 shows the weight loss characteristics of the fibers after isothermal exposure in air at 600°F. It can be seen that the Celion 6000 and HTS-2 fibers exhibited higher TOS than HTS-1. However, considerable variability in TOS was observed among HTS-2 samples taken from different spools of the same lot. The weight loss variability within each spool was not as pronounced. Figure 1 shows

the two extremes in weight loss characteristics for the HTS-2 fibers observed in this study, where each data point represents an average of 3 tests.

Table II shows the initial mechanical properties of unidirectional composites fabricated from HTS-2 and unsized Celion 6000 fibers, using PMR-15 polyimide as the resin matrix. The interlaminar shear strength (ILSS) values of the two composites are closely comparable. However, the flexural strength and modulus values of the Celion composite are significantly lower than the corresponding properties of the HTS-2 composite. The low values could be the result of using a span-to-depth ratio of 16.3 in testing the Celion composite flexural specimens, compared to a span-to-depth ratio of 22.5 for the HTS-2 composites. Inspection of the tested Celion composite specimens indicated a compressive failure mode.

Figures 2-5 compare the weight loss characteristics and mechanical property retention of PMR-15 composites fabricated from HTS-1, HTS-2 and Celion 6000 fibers after isothermal exposure in air at 600°F. The HTS-1/PMR-15 composite data are taken from the literature,<sup>(5)</sup> since the fiber was no longer commercially available at the time of this study. Similarly, the HTS-1/PMR-II composite properties shown in Table III and Figures 6-9 are also taken from the literature.<sup>(3)</sup>

Figure 2 shows the weight loss characteristics of PMR-15 composites using HTS-1, HTS-2 and Celion 6000 as the graphite fiber reinforcement. The isothermal exposure at 600°F was terminated when significant surface degradation became apparent, as evidenced by the presence of copious loose fibers. The first appearance of loose fibers in the HTS-2 and Celion 6000 composites occurred between 1200 and 1500 hours of exposure at 600°F. It is apparent that both HTS-2 and Celion 6000 composites exhibited a significantly improved TOS compared with the HTS-1 composite. This can be attributed to the superior TOS of the bare HTS-2 and Celion 6000 fibers.

Figure 3 compares the interlaminar shear strength (ILSS) retention of the three composites after exposure in air at 600°F. It can be seen that both the HTS-2 and Celion composites exhibit 100% retention of their initial ILSS values during the first 1000 hours of exposure. There is a gradual decrease of the ILSS values during further exposure. The HTS-1 composites exhibited a consistently lower ILSS throughout the 600 hour exposure time.

The effect of isothermal exposure at 600°F on the flexural strength of the PMR-15 composites is shown in Figure 4. The HTS-2 composite shows excellent flexural strength retention during 800 hours of

exposure, followed by a gradual decrease. As noted before, the Celion composite exhibited a significantly lower initial flexural strength, probably due to the low span-to-depth ratio for the test specimens. However, the important point to note is that the composite exhibited excellent flexural strength retention throughout the exposure period.

The flexural modulus values of the PMR-15 composites during extended exposure at 600°F are shown in Figure 5. It is apparent that the HTS-2 and Celion 6000 composites exhibit excellent retention of the flexural modulus during the first 600 hours of exposure, compared to the HTS-1 composite.

Table III shows the initial mechanical properties of composites using the second generation PMR-II polyimide as the resin matrix. The properties of the HTS-1 composite are taken from the literature.<sup>(3)</sup> It can be seen that the mechanical properties of the HTS-1 and HTS-2 composites are closely comparable. The flexural properties of the Celion 6000 composite are lower, probably because the use of a lower span-to-depth ratio resulted in a compressive failure mode.

The weight loss characteristics of the PMR-II composites during extended exposure in air at 600°F are shown in Figure 6. The difference in fiber stability between HTS-1 fibers and the more thermo-oxidatively

stable HTS-2 and Celion 6000 fibers is reflected in the superior TOS of the HTS-2 and Celion composites. No surface degradation was observed in the HTS-2 composite specimens after 2000 hours of exposure, at which time the test was terminated. A very small amount of loose fibers appeared in the Celion composite specimens after 2400 hours. The surface degradation was still minimal after 3000 hours, when the exposure was terminated.

The effect of isothermal exposure at 600°F on the ILSS properties of the PMR-II composites is shown in Figure 7. There is no great difference in the ILSS retention characteristics of the composites during the first 1000 hours of exposure; both HTS-2 and Celion 6000 composites retained over 80% of their initial 600°F ILSS after 2000 hours of exposure.

Figure 8 shows the flexural strength retention of the PMR-II composites after exposure at 600°F. The HTS-2 composite exhibited excellent retention of the flexural strength throughout its exposure time. The Celion 6000 composite exhibited a gradual decrease of flexural strength. Nevertheless, the composite retained 78% of its initial flexural strength after 1800 hours of exposure.

Most of the comments made about the flexural strength retention of PMR-II composites apply also to

the flexural modulus retention after exposure at 600°F, shown in Figure 9. It may be noted that the HTS-1 composite exhibited lower flexural modulus values throughout its exposure period than the HTS-2 or Celion composites.

Figures 10-17 compare the effect of the PMR-15 and PMR-II resin compositions on long-term composite performance at 600°F. Figure 10 shows the weight loss characteristics of PMR-15 and PMR-II composites fabricated from HTS-2 fiber, and Figure 11 shows the weight loss of composites fabricated from Celion 6000 fiber after long-term exposure in air at 600°F. The superior weight retention of the PMR-II composites, compared to the corresponding PMR-15 composites, is evident. It was noted earlier that the PMR-15/HTS-2 and PMR-15/Celion 6000 composites began to exhibit surface degradation after 1200-1500 hours of exposure. In contrast, there was no evidence of loose surface fibers for the PMR-II/HTS-2 composite after 2000 hours, and only a minimal amount for the PMR-II/Celion 6000 composite after 2400 hours of exposure.

Comparison of the PMR-15 and PMR-II composite ILSS retention characteristics after isothermal exposure at 600°F is shown in Figure 12 for the HTS-2 composites and Figure 13 for the Celion 6000 composites. It can be seen that the ILSS of the PMR-15 composites remains at a consistently higher level during their

entire exposure time than the ILSS of the corresponding PMR-II composites.

The comments made about the ILSS retention apply also to the flexural strength comparison of the PMR-15 and PMR-II composites, shown in Figures 14 and 15. It may be noted that both the ILSS and flexural strength of the PMR-15/HTS-2 composite have decreased to the same level as the corresponding PMR-II/HTS-2 composite properties after 1500 hours of exposure at 600°F (Figures 12 and 14).

The flexural modulus characteristics of the PMR-15 and PMR-II composites are compared in Figure 16 (HTS-2 composites) and Figure 17 (Celion 6000 composites). The flexural modulus of the PMR-15 composites (in contrast to the flexural strength values) remained consistently lower than the modulus of the corresponding PMR-II composites. It is interesting to note the outstanding modulus retention characteristics of the PMR-II/HTS-2 composite, which exhibited a 90% retention of its original 600°F modulus after 2000 hours of exposure at 600°F.

#### 4. CONCLUDING REMARKS

The results of this investigation show that the use of HTS-2 or Celion 6000 instead of HTS-1 graphite fibers as reinforcement in PMR polyimide composites significantly increased the composite

thermo-oxidative stability and retention of mechanical properties at 600°F. PMR-15 composites prepared from HTS-2 and Celion 6000 fibers exhibited a two-fold increase in useful lifetime at 600°F, compared to PMR-15/HTS-1 composites.

Similarly, a significant increase in the 600°F lifetime of PMR-II composites was obtained by using HTS-2 or Celion 6000 instead of HTS-1 as the graphite fiber reinforcement. The PMR-II composites fabricated from HTS-2 and Celion 6000 fibers exhibited a superior thermo-oxidative stability at 600°F and retention of their initial mechanical properties, compared to the corresponding PMR-15 composites.

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#### 6. BIOGRAPHIES

##### 6.1 PETER DELVIGS

Dr. Delvigs has been a staff member in the Polymer Matrix Composites Section of NASA-Lewis Research Center since 1967. He received a B.A. degree in chemistry from Case Western Reserve University and a Ph.D. in organic chemistry from the University of Minnesota. His current research involves the synthesis and characterization of processable polymer matrix systems for fiber-reinforced composites having improved moisture resistance and char characteristics, as well as improved long-term performance at elevated temperatures.

##### 6.2 RAYMOND D. VANNUCCI

Raymond Vannucci has been employed at NASA-Lewis Research Center since 1965. He received a B.S. degree in engineering from Cleveland State University. Presently he is working as a Materials Engineer in the Polymer Matrix Composites Section. His current research involves the fabrication and characterization of

polymer composites.

### 6.3 WILLIAM B. ALSTON

Dr. Alston is presently a Materials Engineer with the Propulsion Laboratory of the U.S. Army Aviation Research and Development Command, assigned to the Polymer Matrix Composites Section of NASA-Lewis Research Center since 1971. He received a B.S. in chemistry from the University of Wisconsin, M.S. and Ph.D. in chemistry from the University of Iowa. His current research is in the areas of polymer synthesis, crosslinking methods, and char formation.

TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

STRUCTURE	NAME	ABBREVIATION
	MONOMETHYLESTER OF 5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	4,4'-METHYLENEDIANILINE	MDA
	DIMETHYLESTER OF 3,3',4,4'-BENZOPHENONETETRACARBOXYLIC ACID	BTDE
	p-PHENYLENEDIAMINE	PPDA
	DIMETHYLESTER OF 4,4'-(HEXAFLUROISOPROPYLIDENE)-BIS (PHTHALIC ACID)	HFDE

TABLE II. - PHYSICAL AND MECHANICAL PROPERTIES OF PMR 15/GRAPHITE FIBER COMPOSITES

FIBER REINFORCEMENT	FIBER V/O	INTERLAMINAR SHEAR STRENGTH, KSI		FLEXURAL STRENGTH, KSI <sup>a</sup>		FLEXURAL MODULUS OF ELASTICITY, KSI <sup>a</sup>	
		75 <sup>o</sup> F	600 <sup>o</sup> F	75 <sup>o</sup> F	600 <sup>o</sup> F	75 <sup>o</sup> F	600 <sup>o</sup> F
HTS-2	56.9	14.1	7.6	233	146	16.3x10 <sup>3</sup>	16.0x10 <sup>3</sup>
Celion 6000	53.8	15.5	7.2	187	104	14.1	12.7

<sup>a</sup>Normalized to 55 v/o fiber

TABLE III. - PHYSICAL AND MECHANICAL PROPERTIES OF PMR 11/GRAPHITE FIBER COMPOSITES

FIBER REINFORCEMENT	FIBER V/O	INTERLAMINAR SHEAR STRENGTH, KSI		FLEXURAL STRENGTH, KSI <sup>a</sup>		FLEXURAL MODULUS OF ELASTICITY, KSI <sup>a</sup>	
		75 <sup>o</sup> F	600 <sup>o</sup> F	75 <sup>o</sup> F	600 <sup>o</sup> F	75 <sup>o</sup> F	600 <sup>o</sup> F
HTS-1 <sup>b</sup>	53.6	12.2	5.9	249	139	15.7x10 <sup>3</sup>	14.9x10 <sup>3</sup>
HTS-2	56.6	13.0	6.0	241	123	16.1	15.3
Celion 6000	59.4	15.3	6.8	191	105	15.5	13.7

<sup>a</sup>Normalized to 55 v/o fiber<sup>b</sup>Data from ref. 3ORIGINAL PAGE IS  
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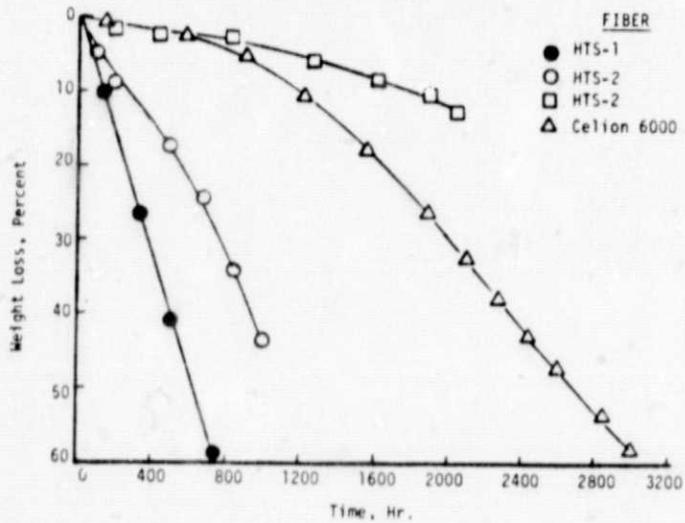


Figure 1.- Weight loss of graphite fibers exposed in air at 600°F.

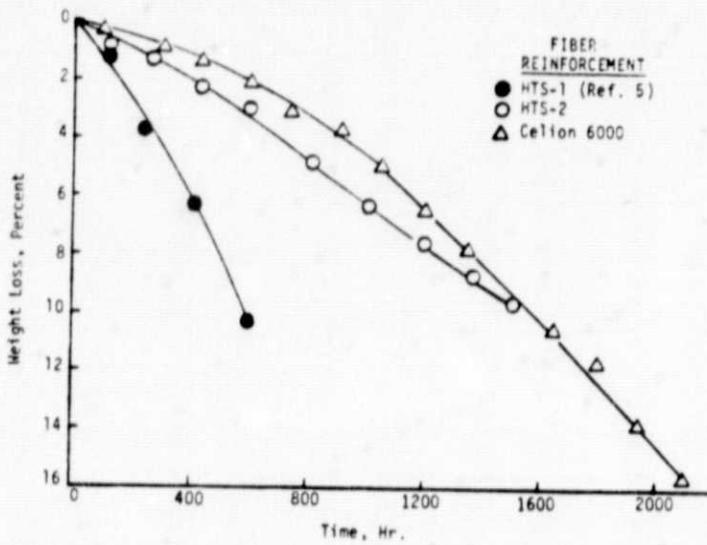


Figure 2.- Weight loss of PMR 15/graphite fiber composites exposed in air at 600°F.

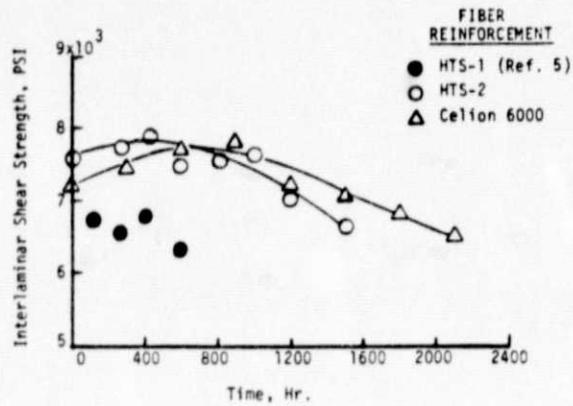


Figure 3.- Interlaminar shear strength of PMR 15/graphite fiber composites exposed and tested in air at 600°F.

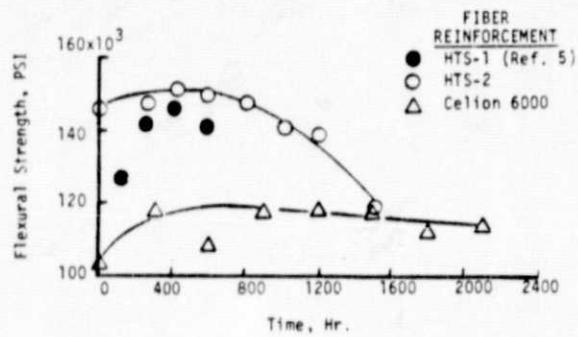


Figure 4.- Flexural strength of PMR 15/graphite fiber composites exposed and tested in air at 600°F.

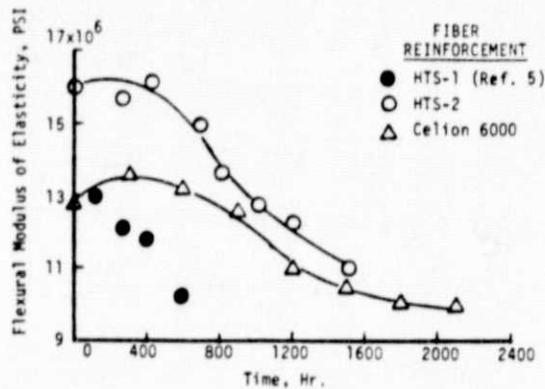


Figure 5.- Flexural modulus of elasticity of PMR 15/graphite fiber composites exposed and tested in air at 600°F.

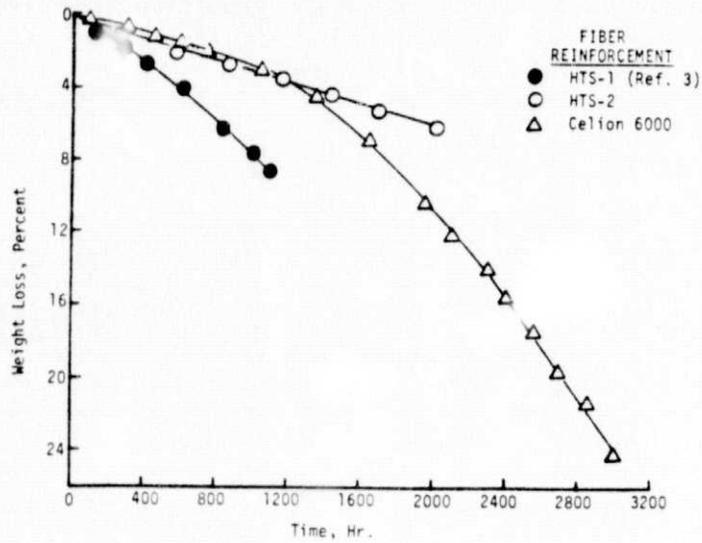


Figure 6.- Weight loss of PMR-II/graphite fiber composites exposed in air at 600°F.

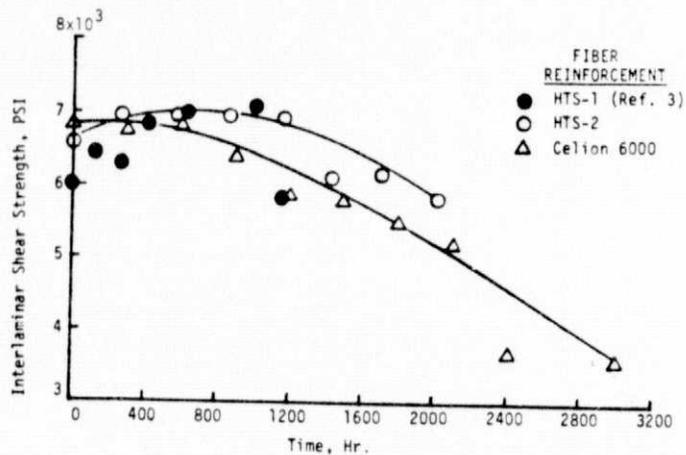


Figure 7.- Interlaminar shear strength of PMR-II/graphite fiber composites exposed and tested in air at 600°F.

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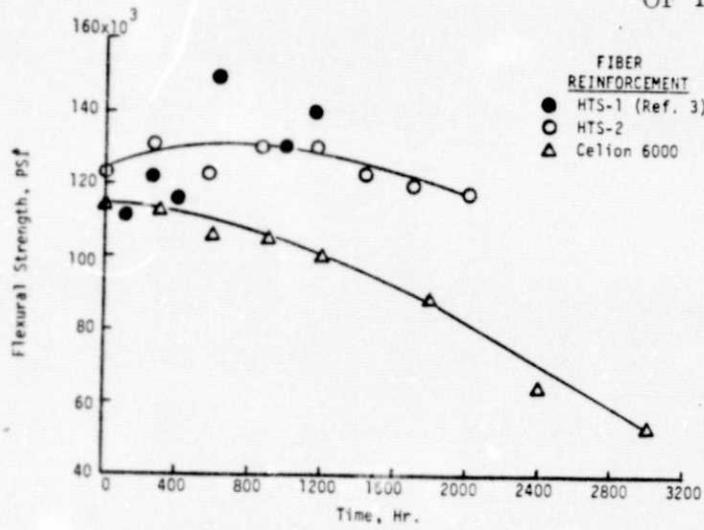


Figure 8.- Flexural strength of PMR-II/graphite fiber composites exposed and tested in air at 600°F.

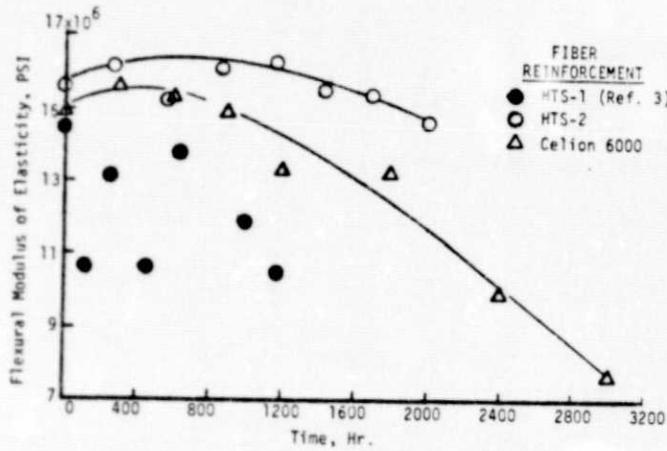


Figure 9.- Flexural modulus of elasticity of PMR-II/graphite fiber composites exposed and tested in air at 600°F.

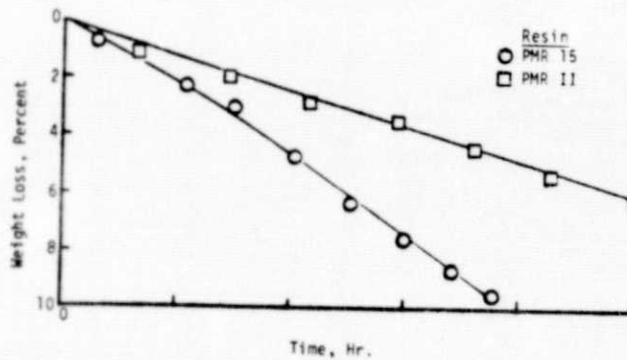


Figure 10.- Weight loss of PMR polyimide/HTS-2 graphite fiber composites exposed in air at 600°F.

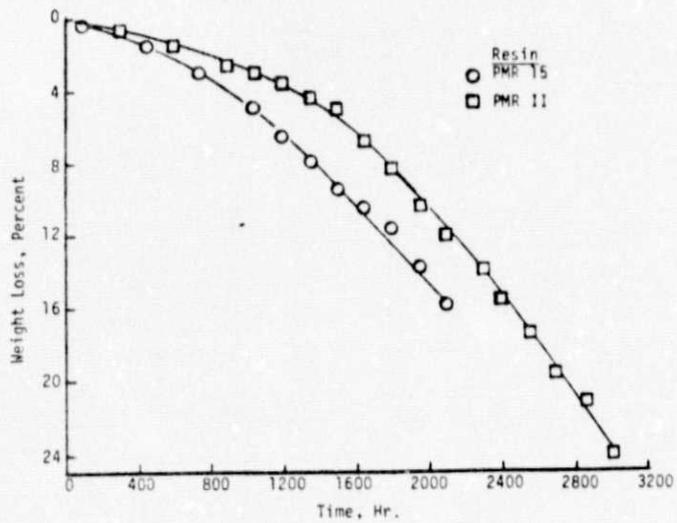


Figure 11.- Weight loss of PMR polyimide/Celion 6000 graphite fiber composites exposed in air at 600°F.

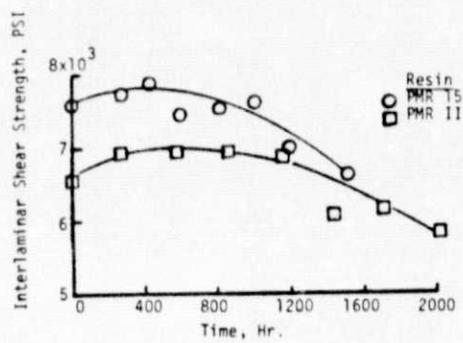


Figure 12.- Interlaminar shear strength of PMR polyimide/HTS-2 graphite fiber composites exposed and tested in air at 600°F.

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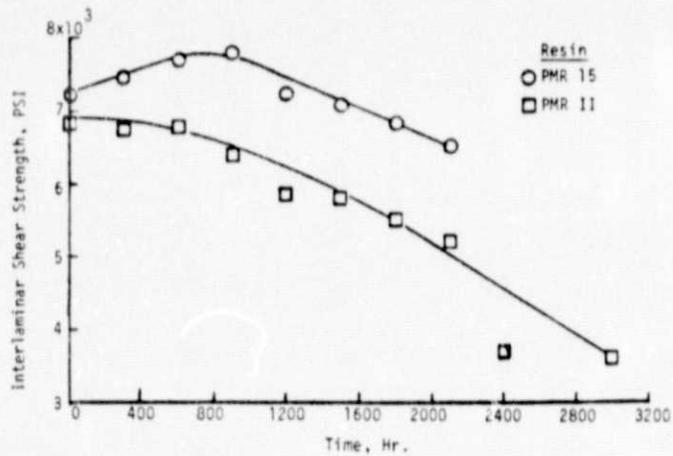


Figure 13.- Interlaminar shear strength of PMR polyimide/Celion 6000 graphite fiber composites exposed and tested in air at 600°F.

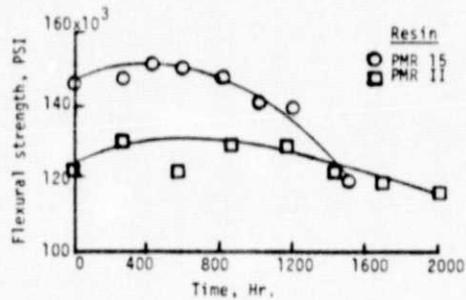


Figure 14.- Flexural strength of PMR polyimide/HTS-2 graphite fiber composites exposed and tested in air at 600°F.

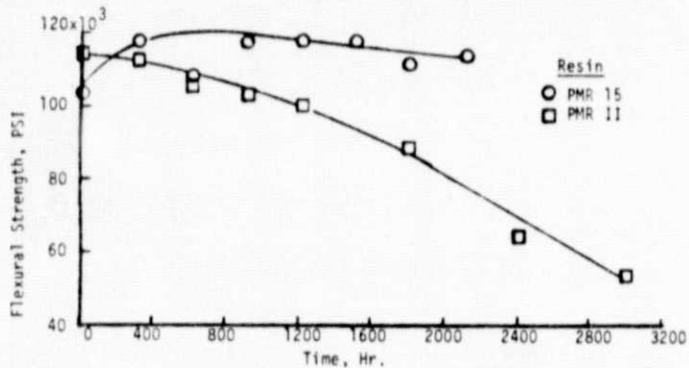


Figure 15.- Flexural strength of PMR polyimide/Celion 6000 graphite fiber composites exposed and tested in air at 600°F.

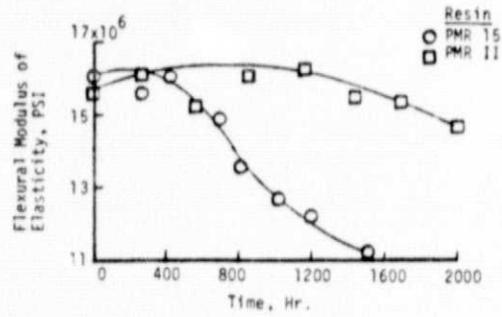


Figure 16.- Flexural modulus of elasticity of PMR polyimide/HTS-2 graphite fiber composites exposed and tested in air at 600°F.

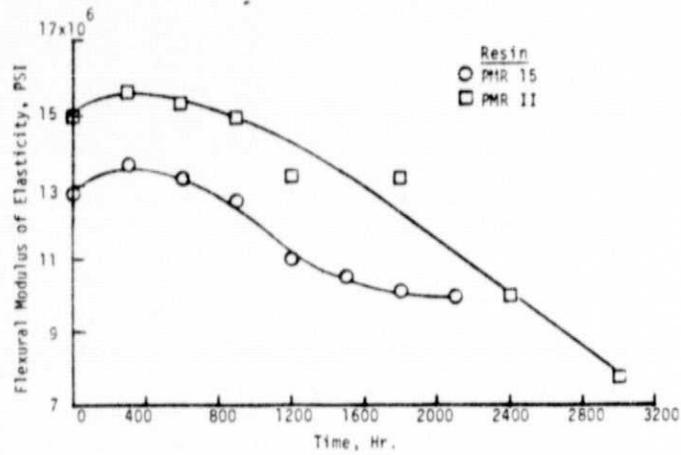


Figure 17.- Flexural modulus of elasticity of PMR polyimide/Celion 6000 graphite fiber composites exposed and tested in air at 600°F.