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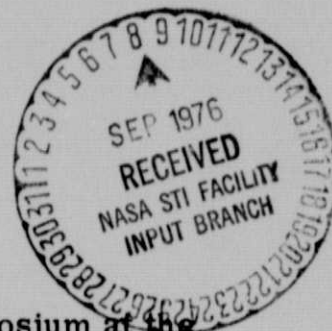
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**EFFECTS OF TETRAAMINE CROSSLINKING AGENTS ON THE
THERMOMECHANICAL PROPERTIES OF PMR
POLYIMIDE COMPOSITES**

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EFFECTS OF TETRAAMINE CROSSLINKING AGENTS ON THE
THERMOMECHANICAL PROPERTIES OF PMR POLYIMIDE COMPOSITES

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NASA-LEWIS RESEARCH CENTER

Studies were performed to investigate the effects of partial substitution of tetraamine crosslinking agents for diamine reactants on the thermomechanical properties of PMR polyimide resins and graphite fiber-reinforced composites. The effect of tetraamine content on isothermal weight loss, glass transition, and softening temperatures of neat resin samples is discussed. Composites were fabricated using PMR methodology. Monomeric solution of various stoichiometric ratios were used to impregnate Hercules HTS graphite fiber. The mechanical property retention characteristics of the composites at 316° C (600° F) are described.

I. INTRODUCTION

One of the potential applications of high temperature resistant polymers is their use as matrix resins in fiber-reinforced composites for turbofan engine components. Prior studies in our laboratory (1-3) have demonstrated the effectiveness of the PMR (in situ polymerization of monomer reactants on the surface of the reinforcing fibers) approach for preparing high temperature resistant fiber-reinforced polyimide matrix composites. The PMR polyimide resins are beginning to achieve acceptance by fabricators because of their facile processability characteristics. Currently available PMR polyimide resins are based on the monomers 5-norbornene-2,3-dicarboxylic acid monomethyl ester (NE), 3,3',4,4'-benzophenonetetracarboxylic acid dimethyl ester (BTDE), and 4,4'-methylenedianiline (MDA). The final cure of these resins proceeds by a complex set of reactions involving chain extension and some degree of crosslinking by the norbornene end-caps. However, these PMR resins must be subjected to a postcure at 316° C (600° F) to eliminate thermoplastic yielding under load at elevated temperatures. Recent studies (4) have shown that substitution of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid) dimethyl

ester (HFDE) for BTDE significantly increases the thermooxidative stability of the PMR polyimide composites. However, because of their lower glass transition temperatures (T_g), the HFDE/MDA/NE resin composites exhibit considerably lower mechanical properties at 316° C (600° F) than the BTDE/MDA/NE composites.

The purpose of this investigation was to reduce thermoplastic behavior of graphite fiber-reinforced PMR polyimide composites by partial substitution of the diamine monomer MDA with tetraamine crosslinking agents. Recent studies with condensation type polyimide films (5) have shown that partial substitution of tri- and tetrafunctional amines for the diamine component significantly increases the polymer T_g and softening temperature (T_s).

This paper describes the effect of tetraamine content on isothermal weight loss, T_g , and softening temperatures of molded neat PMR polyimide samples prepared from NE, MDA, BTDE, and NE, MDA, HFDE. Composites were fabricated from HTS graphite fiber using PMR methodology. The effect of crosslink density on the mechanical properties of composites at room temperature and 316° C (600° F) is discussed.

II. EXPERIMENTAL

A. Monomers

The monomers and crosslinking agents used in this study are shown in figure 1. The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were obtained from commercial sources. The 4,4'-(hexafluoroisopropylidene)-bis(phthalic anhydride) (HFDA), the corresponding dimethyl ester (HFDE), and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) were prepared according to reference 4. The 6,6'-bis[2,3-di(p-aminophenyl) quinoxalyl] ketone (TABK) was synthesized according to reference 5. The 3,3',5,5'-tetraaminobenzophenone (TEAB) was synthesized by the following method: a solution of 3,3',5-trinitrobenzophenone (5) (9.51 g, 3.00×10^{-2} mole) in conc. H_2SO_4 (90 ml) and 90% fuming HNO_3 (45 ml) was stirred at 100° to 110° for 4 hours, cooled to room temperature and poured on crushed ice. The product was filtered, washed with H_2O until free of acid, and dried. The crude product (8.72 g) was crystallized from 1:1 EtOH/DMF to yield 6.29 g (58%) of 3,3',5,5'-tetranitrobenzophenone, m.p. 251° to 252° C (literature (6) m.p. 250°). The tetranitro compound (3.62 g, 1.00×10^{-2} mole) was added to a solution of $SnCl_2 \cdot 2H_2O$ (27.1 g, 1.20×10^{-1} mole)

in conc. HCl (36 ml). The mixture was stirred at room temperature for 0.5 hour, then at 100° C for 2 hours. After filtration, the solution was poured slowly into 40% aq. KOH (162 ml) while adding ice chips. The product was filtered, washed with H₂O and dried. Crystallization of the crude product from H₂O, then EtOH yielded 1.78 g (74%) of 3,3',5,5'-tetraaminobenzophenone, m.p. 210° to 211° C dec. Anal. - Calcd. for C₁₃H₁₄N₄O: C, 64.44%; H, 5.82%; N, 23.13%. Found: C, 65.01%; H, 5.84%; N, 23.00%.

B. Molding Powders and PMR Polyimide Plugs

Monomers in the desired stoichiometric ratios were dissolved in 1-methyl-2-pyrrolidinone (NMP) at a solids loading of 50 wt %, and the solution heated in vacuum at 150° C for 4 hours, then at 200° C for 2 hours. The dry solid was ground into a fine powder. The molding powder (approx. 5 g) was placed into a circular matched metal die (diameter 5.05 cm) preheated to 260° C (500° F). Following a dwell time of 5 to 30 minutes, 2000 psi pressure was applied, and the temperature raised to 321° C (610° F). Pressure and temperature were maintained for 1 hour.

The stoichiometry of the monomeric reactants used was $n/(1-m)(n+1)/\frac{m}{2}(n+1)/2$, where n = moles of BTDE or HFDE, $(1-m)(n+1)$ = moles of MDA, $\frac{m}{2}(n+1)$ = moles of TABK or TEAB, 2 = moles of NE, and where m = mole fraction of MDA replaced with TABK or TEAB.

The glass transition temperatures (T_g) and softening temperatures (T_s) of the polymers were determined with a thermomechanical analyzer (TMA) using a penetration probe at a heating rate of 10° C/min with a 5 g load. The weight loss of the polymers was determined by isothermal exposure at 316° C (600° F) in a forced draft oven with an air change rate of 100 cm³/min.

C. Composite Fabrication and Testing

Composites were fabricated essentially according to the method described in reference 4. Prepreg tapes were made by drum-winding and impregnating Hercules HTS graphite fiber with the PMR monomer solutions to yield prepregs containing 45.5 wt % monomers and 54.5 wt % fiber. The solutions were prepared by dissolving the monomers in the desired stoichiometric ratios in anhydrous methanol to give a solids content of 40 wt %. It should be noted that a 2:1 mixture of MeOH/NMP was employed for formulations containing the tetraamine TABK,

due to the extremely limited solubility of TABK in MeOH. The prepreg tapes were dried on the drum at room temperature for 1 hour, then at 50° C for 1 hour. The tapes were cut into 3 in by 8 in plies and stacked 8 plies thick unidirectionally. The prepreg stack was placed into a preforming mold and staged at 120° C for 3 hours under a pressure of 0.1 psi. Prepreg impregnated with solutions containing NMP was staged at 200° C for 3 hours. Composites were molded by placing the staged prepreg into a matched metal die preheated to 232° C (450° F). Following a dwell time of 5 to 10 minutes (depending on tetraamine content), 500 psi pressure was applied, and the temperature was increased to 316° C (600° F) at a rate of 5.5° C (10° F)/minute. Pressure and temperature were maintained for 1 hour. After curing, all composites were postcured for 16 hours at 316° C (600° F). All laminates were inspected 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 laminates ranged from 0.070 in to 0.085 in, resulting in a span/depth ratio of 24 to 29. Interlaminar shear strength tests were conducted at a constant span/depth ratio of 5. All mechanical property values are averages of 3 tests. Fiber content was determined for all laminates and ranged from 60.0 to 62.1 volume percent. For flexural tests all results were normalized to 60 volume percent fiber.

III. RESULTS AND DISCUSSION

A. Properties of PMR Polyimide Plugs

Table 1 lists isothermal weight loss and glass transition temperature (T_g) of the BTDE-PMR control sample, as well as three other resin samples where the tetraamine crosslinking agent TABK is partially substituted for the diamine MDA. It can be seen that the T_g shows a significant increase as the tetraamine content is increased, from 352° C in control sample 1 to 390° C for sample 2. Samples 3 and 4 did not exhibit a T_g value below 400° C, at which temperature the polymers began to decompose.

While the isothermal weight loss of samples 1 and 2 on exposure in air at 316° C (600° F) for 1000 hours was not significantly different, there is nevertheless a trend toward a higher weight loss as the tetraamine content of the polymer is increased. This could be attributed to decreased thermooxidative stability of the bisquinoxaline nucleus of the tetraamine TABK, or to the possible higher concentration of unreacted amino groups.

Table 2 summarizes the T_g values and isothermal weight loss of PMR polyimide plugs prepared from the monomer HFDE. The weight loss of all three samples after exposure to 316°C (600°F) for 1000 hours shows no significant difference, indicating a comparable thermoxidative stability. The T_g values of the polymers again show a significant increase with increasing tetraamine content. However, due to the more flexible hexafluoroisopropylidene connecting group of HFDE compared to the more rigid carbonyl group of BTDE, the T_g of all three polymers was found to be below 316°C (600°F). In addition, samples 1 and 2 exhibited a softening temperature (T_s), which was not shown by the BTDE-PMR polyimides. After the polymer samples were subjected to a 16 hour postcure at 316°C (600°F), their T_g values were increased by approximately 40°C , and all polymers failed to exhibit softening behavior below 450°C , at which temperature significant decomposition began to occur. The TMA curves for control sample 1 before and after postcure are shown in figure 2.

The results obtained in this phase of the investigation indicate that incorporation of tetraamine crosslinking agents in the PMR polyimide matrix would significantly decrease the thermoplastic behavior of graphite fiber-reinforced PMR composites and increase their mechanical properties.

B. Composite Properties

Table 3 summarizes T_g values and mechanical properties of BTDE-PMR/HTS graphite fiber composites containing the tetraamine TABK. The T_g values of the composites correspond closely with those of the corresponding neat resin T_g values shown in table I. It can be seen that the 316°C interlaminar shear strength (ILSS) of control sample 1 is considerably lower than its room temperature value. This seems to be a phenomenon associated with intermediate modulus graphite fibers derived from polyacrylonitrile fibers (7). The control sample also exhibits a large difference between the room temperature and elevated temperature flexural strength and modulus. Comparison of control sample 1 with samples 2 and 3 shows no increase in the elevated temperature mechanical properties with increasing crosslink density. The control sample of course already contains a certain amount of crosslinks due to the nature of the PMR curing mechanism involving the norbornene end-caps. It appears that no increase in elevated temperature mechanical properties can be achieved by using additional inchain crosslinking agents in BTDE-PMR composites. The mechanical properties of composite sample 4 are significantly lower than those of samples 1 to 3. This can be explained by the presence of voids in sample 4, as determined by ultrasonic inspection. It

should be noted that the resin flow during cure decreased with increasing tetraamine content. Sample 4, having the highest TABK content, exhibited a very severely restricted resin flow, which apparently prevented the fabrication of a void-free composite.

Table 4 shows the T_g values and mechanical properties of HEDE-PMR composites using the tetraamine crosslinking agent TEAB. Tetraamine TABK was not used in this composite series because of its extremely low solubility in methanol. The room temperature mechanical properties of all composites are closely comparable. The 316° C ILSS of control sample 1 exhibits a substantial dropoff from its room temperature value. This can be explained by the fact that the T_g of the composite (314° C) is slightly below the test temperature (316° C). Composite samples 2 to 4, using increasing amounts of tetraamine TEAB, show a gradual increase in 316° C ILSS. Composite sample 2 exhibits a 40% increase of 316° C flexural strength over that of the control sample 1, from 87 000 to 122 000 psi. Similarly, composite 2 exhibits a flexural modulus of 15.3×10^6 psi, compared to 9.4×10^6 psi for composite 1, an increase of 63%. It should also be noted that at 316° C, composite 2 retains 89% of its room temperature flexural modulus. However, the flexural strength and modulus values of composites 3 and 4, having progressively higher resin crosslink density, did not show an increase over the flexural strength and modulus of composite 2. It may be noted that composites 2, 3, and 4 exhibit almost identical T_g values (342° to 347° C). It is possible that the use of in-chain crosslinking agents above the level used in composite 2 would not lead to a further increase of flexural properties.

Figure 3 shows the weight loss characteristics of HFDE-PMR composites after exposure in air at 316° C (600° F). All of the composites exhibited excellent thermooxidative stability. Although the control sample had a slightly higher weight loss after 1000 hours than the composites prepared with tetraamine TEAB, the difference in weight loss was not pronounced.

The ILSS values of the HFDE-PMR composites during extended exposure at 316° C are compared in figure 4. It can be seen that composites 2 to 4 show excellent retention of their initial 316° C ILSS values throughout the exposure period, ranging from 87 to 89 percent after 1000 hours at 316° C. In contrast, the ILSS values of control sample 1 are consistently lower during the first 500 hours of exposure. On further exposure the ILSS shows a gradual increase, apparently due to a postcure effect. After 1000 hours of exposure the ILSS of composite 1 has increased to the same level as the ILSS of composites 2 to 4.

The effect of isothermal exposure at 316° C on the flexural strength of the HFDE-PMR composites is shown in figure 5.

Most of the comments made about the ILSS retention on isothermal exposure apply to the flexural strength retention as well. Composites 2 to 4 exhibited excellent flexural strength retention after 1000 hours exposure in air, ranging from 95 to 100 percent of their initial 316° C values. The flexural strength of the control sample again remained significantly lower during 600 hours of exposure, then showed a gradual increase during the next 400 hours.

Figure 6 shows the flexural modulus of the HFDE-PMR composites during extended exposure at 316° C. The flexural modulus values of composites 2 to 4 exhibited a decrease during the initial 400 hours of exposure at 316° C, but then remained at nearly the same levels during further exposure. After 1000 hours of exposure, composites 2 to 4 retained 67 to 75 percent of their initial 316° C modulus. The flexural modulus values of control sample 1 were significantly lower during the entire exposure period.

It can be seen in figures 4 to 6 that the 316° C mechanical properties of composite samples 2 to 4 are closely comparable at any given exposure time. There appears to be an overall trend toward higher mechanical properties with increasing tetraamine content. However, since only three measurements were taken to obtain each data point, no firm conclusion can be drawn about the relation of improved mechanical properties to the amount of the tetraamine crosslinking agent.

IV. CONCLUSIONS

The results of this investigation show that the use of tetraamines for introducing in-chain crosslinks into the PMR polyimide structure significantly increased the polymer glass transition temperature. The substitution of tetraamines had no significant effect on the thermooxidative stability of HFDE-PMR resins, but slightly decreased the thermooxidative stability of BTDE-PMR polyimides. The incorporation of tetraamine TABK into the polymer matrix of BTDE-PMR/HTS graphite fiber composites did not have a significant effect on composite mechanical properties. In contrast, substitution of tetraamine TEAB into the matrix of HFDE-PMR/HTS composites provided a substantial increase of elevated temperature flexural strength, flexural modulus, and interlaminar shear strength. The HFDE-PMR/HTS composites exhibited excellent thermooxidative stability and retention of elevated temperature mechanical properties after long-term isothermal exposure in air at 316° C (600° F).

V. REFERENCES

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TABLE 1. - THERMOMECHANICAL PROPERTIES OF

BTDE-PMR POLYIMIDES^a

Sample	m ^b	T _g , °C	Percent weight loss ^c
1	0	352	6.6
2	.08	390	7.7
3	.16	>400	10.2
4	.32	>400	14.2

^aPrepared from BTDE/MDA/TABK/NE, n = 1.672.^bMole fraction of MDA replaced by TABK.^cAfter 1000 hours in air at 316° C.TABLE 2. - THERMOMECHANICAL PROPERTIES OF HFDE-PMR POLYIMIDES^a

Sample	m ^b	T _g , °C		T _g , °C		Percent weight loss ^d
		Before postcure	After postcure ^c	Before postcure	After postcure	
1	0	269	309	420	>450	8.7
2	.08	297	335	440	>450	8.9
3	.16	306	346	>450	>450	9.5

^aPrepared from HFDE/MDA/TEAB/NE, n = 1.50.^bMole fraction of MDA replaced by TEAB.^c16 hours in air at 316° C.^dAfter 1000 hours in air at 316° C.

TABLE 3. - MECHANICAL PROPERTIES OF BTDE-PMR/HTS GRAPHITE FIBER COMPOSITES^a

Sample	m ^b	T _g , °C	Interlaminar shear strength, psix10 ⁻³		Flexural strength, psix10 ⁻³		Flexural modulus, psix10 ⁻⁶	
			25° C	316° C	25° C	316° C	25° C	316° C
1	0	358	16.3	6.6	251	111	15.6	11.0
2	.08	392	12.5	6.1	205	106	14.7	10.8
3	.16	>400	----	6.2	---	93	----	11.7
4	.32	>400	----	4.8	---	56	----	8.6

^aPrepared from BTDE/MDA/TABK/NE, n = 1.672.^bMole fraction of MDA replaced by TABK.TABLE 4. - MECHANICAL PROPERTIES OF HFDE-PMR/HTS GRAPHITE FIBER COMPOSITES^a

Sample	m ^b	T _g , °C	Interlaminar shear strength, psix10 ⁻³		Flexural strength, psix10 ⁻³		Flexural modulus, psix10 ⁻⁶	
			25° C	316° C	25° C	316° C	25° C	316° C
1	0	314	13.5	4.4	240	87	16.6	9.4
2	.02	342	15.0	5.9	230	122	16.8	15.3
3	.04	343	15.7	6.3	228	131	16.6	15.5
4	.08	347	16.1	6.7	233	124	17.1	15.2

^aPrepared from HFDE/MDA/TEAB/NE, n = 1.50.^bMole fraction of MDA replaced by TEAB.

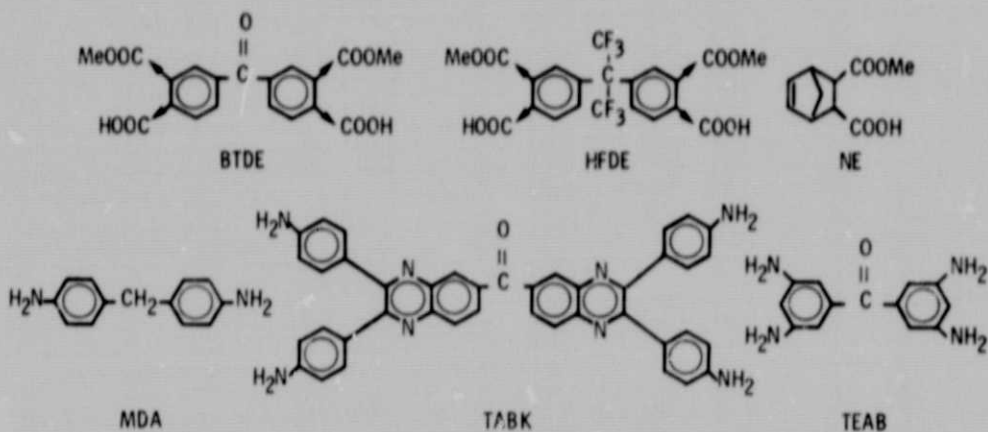


Fig. 1. Monomers used for PMR polyimide synthesis.

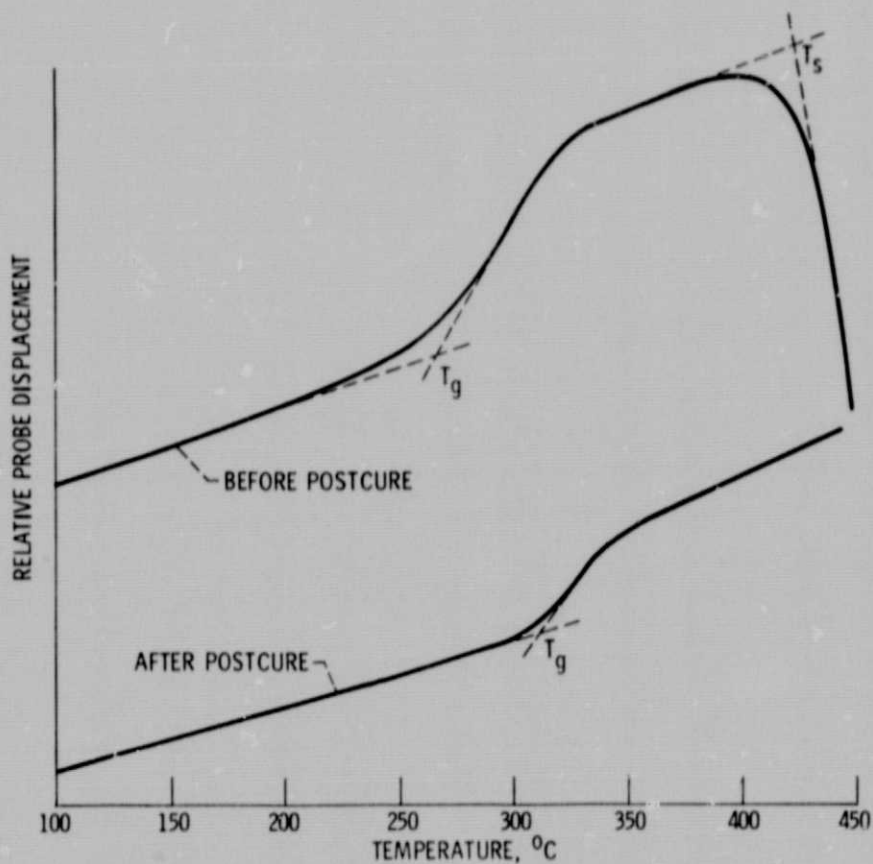


Fig. 2. TMA analysis of PMR polyimide from HFDE/MDA/NE, $n = 1.50$. Penetration probe; 5 g load, heating rate, $10^{\circ}\text{C}/\text{min}$.

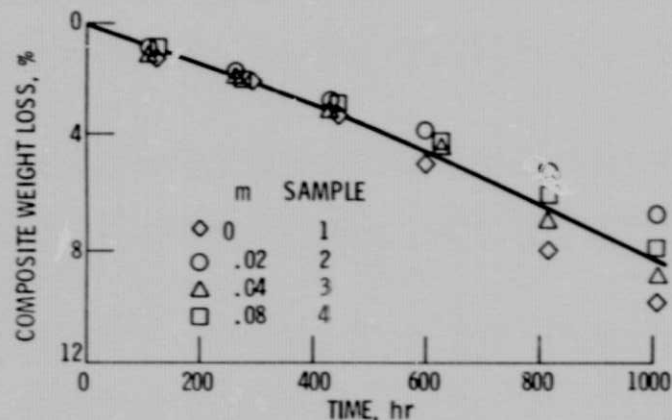


Fig. 3. Weight loss of PMR polyimide/HTS graphite fiber composites from HFDE/MDA/TEAB/NE, $n = 1.50$, exposed in air at 316°C

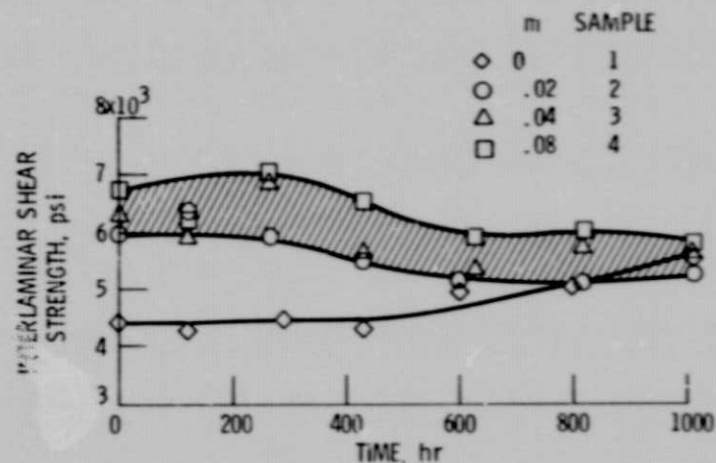


Fig. 4. Interlaminar shear strength of PMR polyimide/HTS graphite fiber composites from HFDE/MDA/TEAB/NE, $n = 1.50$, exposed and tested at 316°C .

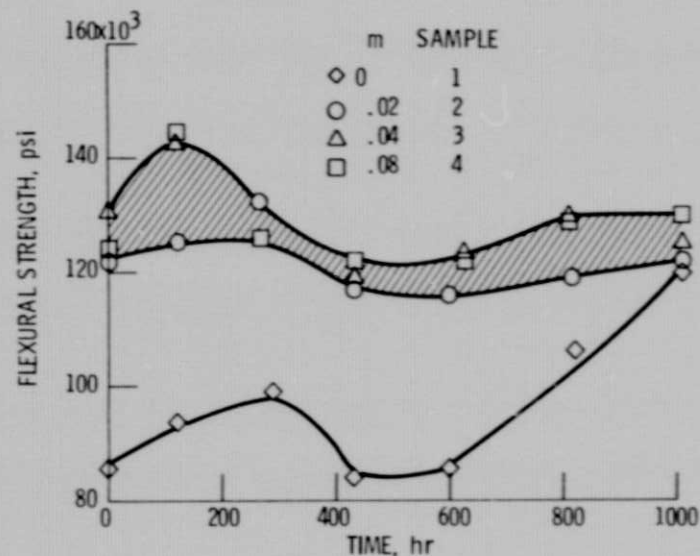


Fig. 5. Flexural strength of PMR polyimide/HTS graphite fiber composites from HFDE/MDA/TEAB/NE, $n = 1.50$, exposed and tested at 316°C .

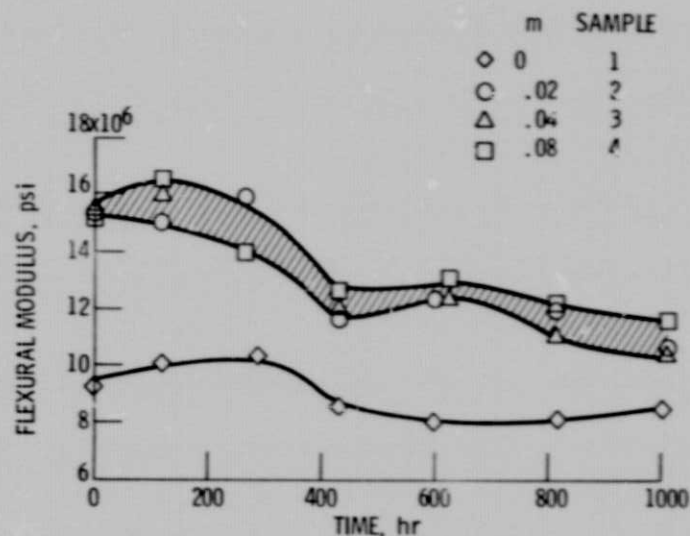


Fig. 6. Flexural modulus of PMR polyimide/HTS graphite fiber composites from HFDE/MDA/TEAB/NE, $n = 1.50$, exposed and tested at 316°C .