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PMR POLYIMIDE PREPREG WITH IMPROVED TACK CHARACTERISTICS

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Abstract

Current PMR Polyimide prepreg technology utilizes methanol or ethanol solvents for preparation of the PMR prepreg solutions. The volatility of these solvents limits the tack and drape retention characteristics of unprotected prepreg exposed to ambient conditions. Studies conducted to achieve PMR 15 Polyimide prepreg with improved tack and drape characteristics are described. Improved tack and drape retention were obtained by incorporation of an additional monomer. The effects of various levels of the added monomer on the thermo-oxidative stability and mechanical properties of graphite fiber reinforced PMR 15 composites exposed and tested at 316° C (600° F) are discussed.

Introduction

Ever since their introduction in the early to mid-fifties the inherent intractibility of high temperature polymers has limited their usefulness as matrix resins for fiber reinforced composites. State-of-the-art high temperature polymer matrix composites, that is, composites having void contents in the range of 5 to 10 percent, can be achieved only by employing complicated processing cycles.

In response to the need for high temperature polymers with improved processability investigators at the NASA Lewis Research Center developed the so-called PMR Polyimides (Ref. 1). In the approach used to prepare these highly processable polyimides in situ Polymerization of Monomer Reactants (PMR) occurs on the surface of the reinforcing fibers. The advantages and versatility of the PMR approach has been reviewed (Ref. 2). At the present time two general types of PMR Polyimides each differing in the stoichiometry and chemical composition have been identified. Both versions, the earlier PMR 15 (first generation) as well as the more recently developed second generation material (PMR II) (Ref. 3) employ low boiling point alcoholic solvents. The volatility of these solvents, which is highly desirable for obtaining void-free composites, limits the tack and drape retention characteristics of unprotected prepreg exposed to the ambient.

STAR Category 24

The purpose of this investigation was to identify PMR Polyimide compositions which provide prepreg materials with improved tack and drape retention characteristics. This report describes studies in which various amounts of reactive diluents containing an olefinic double bond were added to the PMR monomer reactant solutions. The tack and drape retention characteristics of graphite fiber prepreg exposed at ambient conditions were qualitatively measured. Composites were fabricated and their mechanical properties were determined at room temperature and 316° C (600° F). Composites weight loss and mechanical properties retention characteristics as a function of exposure time in air at 316° C (600° F) were also determined.

Experimental Procedures

Monomers

The monomers used in this study are shown in Table I. The monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) and 4,4'-methylenedianiline (MDA) were purchased from commercial sources. The dimethyl and diethyl esters of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE and BTDET) were synthesized by refluxing a suspension of the calculated amount of 3,3',4,4'-benzophenonetetracarboxylic dianhydride in the calculated amount of either methanol or ethanol until the solid had dissolved and then for an additional 2 hours to give a 50 weight percent solution of BTDE or BTDET.

The reactive diluents used in this study are shown in Table II. These monomers were purchased from commercial sources.

Preparation of PMR Solutions

PMR reactant solutions were prepared at room temperature by dissolving the monomers and calculated amounts of the reactive diluent in either anhydrous methanol or ethanol to form 50 weight percent solutions. The monomer stoichiometry for PMR 15 solutions using methanol (designated PMR 15M) was 2 NE/3.087 MDA/2.087 BTDE. The stoichiometry for PMR solutions using ethanol (designated PMR 15E) was NE/3.087 MDA/2.087 BTDET. The amount of added reactive diluent is expressed as percent of total monomer weight.

Composite Fabrication

Prepreg tapes were made by drum-winding and impregnating Hercules HTS graphite fiber with the PMR monomer solutions to yield prepregs containing 45 percent monomers and 55 percent fiber by weight. The prepreg tapes were dried on the drum at about 50° C (122° F) for 1 hour. The tapes were removed from the drum, cut into 7.62 cm by 20.32 cm (3 in. by 8 in.) plies and stacked unidirectionally, 11 plies thick. The prepreg stack was placed in a preforming mold and staged at 120° C (248° F) for 3 hours under a pressure of 6.9×10^2 N/m^2 (0.1 psi). Composites were molded by placing the staged prepreg into a matched metal die preheated to 232° C (450° F). Following a dwell time of 10 minutes, a pressure of 3.45×10^6 N/m^2 (500 psi) was applied, and the temperature was increased to 316° C (600° F) at a rate of 5.5° C (10° F) per minute. Pressure and temperature were maintained for 1 hour. After curing, all composites were postcured for 16 hours at 316° C (600° F).

Composite Testing

Prior to specimen preparation 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 5.08 cm (2 in.). The rate of center loading was 0.127 cm/min. (0.05 in./min.). The thickness of the laminates ranged from 0.1905 cm (0.075 in.) to 0.2159 cm (0.085 in.), resulting in a span/depth ratio of 24 to 27. Interlaminar shear strength tests were conducted at a constant span/depth ratio of 5. All mechanical property values are averages of 3 tests. The flexural property values were normalized to 55 volume percent fiber. The fiber content of the laminates was determined by digestion with H_2SO_4/H_2O_2. Glass transition temperatures were determined with a thermomechanical analysis (TMA) apparatus. The weight loss of the laminates was determined by isothermal exposure at 316° C (600° F) in a forced draft oven with an air change rate of 100 cm^3/min.

Prepreg Tack and Drape

Qualitative tack measurement was made by pressing together two prepreg sections, then pulling the sections apart. Loss of tack was indicated by lack of adhesion.

Qualitative drape measurement was made by bending the prepreg perpendicular to the fiber direction. Loss of drape was indicated by stiffening and cracking of the prepreg.

Results and Discussion

Prepreg Tack and Drape

The handing characteristics of prepreg materials are most frequently described using the following terms: (1) tack, (2) tack retention or tack out-life, and (3) drape. Tack describes the tendency of the prepreg to adhere to itself, or stated differently, to exhibit the behavior of a pressure sensitive adhesive. Tack retention, or tack out-life, refers to the time interval during which unprotected prepreg exposed to ambient conditions retains its tack. Drape denotes the ability of the prepreg to conform to contours without exhibiting cracking.

PMR Polyimide prepreg materials prepared from methanol or ethanol solutions of the monomer reactants exhibit adequate initial tack and drape. After exposure at ambient conditions for about 24 hours the prepreg prepared from methanol PMR solutions loses its tack and becomes somewhat boardy. Under similar exposure conditions the ethanol based prepreg retains its tack and drape characteristics for about 48 hours.

The volatility (low boiling point) of the alcohols employed as solvents in state-of-the-art PMR Polyimides is responsible for the limited tack and drape retention characteristics exhibited by PMR prepreg materials. An obvious approach to obtain improved tack and drape retention characteristics would be to replace all or at least a portion of the alcohol with a higher boiling point solvent. High boiling point aprotic solvents, such as N-methylpyrrolidone or dimethylformamide, were considered to be unsuitable. Composite processing difficulties encountered when using these solvents have been discussed previously (Ref. 2).

To improve the tack and drape retention characteristics of PMR prepreg, our approach in this study was to incorporate an additional, or fourth, monomer to the standard alcohol PMR solutions. Monomers which met the following criteria were selected for study: (1) The boiling point of the monomer needed to be greater than that of either methanol or ethanol, (2) The monomer needed to be compatible with the state-of-the-art PMR formulations, and (3) The molecular structure of the monomer needed to contain an olefinic double bond.

The reasons for criteria one and two are fairly straightforward. The third criterion was established to force the selection of monomers which could possibly enter into the final addition curing reaction and thus not be released as void causing volatile materials. To distinguish the fourth monomer from the other monomers used in formulating the PMR solutions we have chosen to refer to the added monomer as a "reactive diluent" (see Table II).

Table III summarizes the qualitative observations of the tack and drape retention characteristics of prepreg from PMR 15E (ethanol) and PMR 15M (methanol) solutions containing the various types and amounts of reactive diluents. The reactive diluent which provided the most marked improvement in prepreg tack and drape retention was styrene. The addition of 5 w/o styrene to a PMR 15E solution doubled the prepreg tack out-life. Although an improvement in drape retention was observed, the level of improvement was less than that observed for tack retention. As the solvent evaporates the prepreg surface assumes a skin-like quality. The lack of agreement between tack and drape retention may be due to the presence of the skin-like surface which restricts the flexibility of the prepreg, or more simply to inherent deficiencies in the qualitative tests used to assess tack and drape retention. Styrene additions of 1 and 2 w/o to the PMR 15E solutions resulted in only marginal improvements to the tack and drape retention.

Prepreg prepared from the more highly volatile PMR 15M solutions required an addition of 20 w/o styrene to effect a noticeable improvement in prepreg tack and drape retention. Styrene additions of 5 and 10 w/o had little or no beneficial effect on retention of tack and drape.

The addition of either BHD or NVP to PMR 15M solutions, even at levels of up to 20 w/o, provided only minimal improvements to tack and drape retention. Because of these results prepregs were not prepared from PMR 15E solutions containing BHD or NVP.

Attempts to provide a quantitative measure of tack and drape retention by monitoring the variation of prepreg volatile content with time and correlating these data with the qualitative observations proved to be unsuccessful.

Composite Properties

Improvements in prepreg tack and drape retention characteristics would be of no practical value if the composite thermal and mechanical properties were adversely affected. Composite data are summarized in Table IV. Composites prepared from prepreg derived from PMR 15E and PMR 15M solutions are designated PMR 15E and PMR 15M, respectively. Data are not presented in Table IV for the PMR 15M/NVP because the composites had a relatively high void content. The data given in Table IV show that the use of styrene and BHD as reactive diluents did not have an adverse effect on room temperature composite properties. These results indicate that the reactive diluent had either volatilized prior to final curing of the composites or had entered into the addition reaction which occurs during final curing. Studies to establish the exact nature of the interactions, if any, between the reactive diluents and the PMR Polyimides are in progress.

Figures 1 to 8 show the effects of isothermal exposure in air at 316° C (600° F) on the properties of PMR 15E/styrene and PMR 15M/styrene composites. Isothermal exposure data for PMR 15M/BHD composites are not shown. To aid the interpretation of data and because most of the data points are fairly well clustered together, curves have only been drawn through the data points for the control samples (composites prepared from prepreg without added styrene).

Weight loss data for PMR 15E composites exposed in air at 316° C (600° F) are presented in Figure 1. The figure shows that additions of styrene to the PMR solutions in the range of 1 to 5 w/o had no appreciable deleterious effect on the thermooxidative stability of the composites. The weight loss differences between the control samples and the samples prepared from PMR solutions with added styrene are not considered to be significant.

Figure 2 shows the retention of interlaminar shear strength (ILSS) for the PMR 15E composites after exposure in air at 316° C (600° F). It can be seen in the figure that the data for the samples prepared from prepreg containing styrene follow the same general trend as the data for the control samples. The same comment also applies to the retention of flexural strength and modulus for the PMR 15E composites (see Figs. 3 and 4).

The weight loss behavior of PMR 15M composites exposed in air at 316° C (600° F) is shown in Figure 5. The figure shows that the control samples experienced a greater weight loss than the PMR 15M/styrene samples. High temperature oxidative weight loss measurements undoubtedly reflect the net result of simultaneous thermal decomposition and oxidation reactions. Thermal decomposition, of course, causes a loss in sample weight. Depending on the nature of the oxidation reactions, either a weight gain or weight loss may result. If oxidation reactions which lead to the formation of relatively stable oxidation products (e.g., oxidatively crosslinked structures) predominate over oxidative degradation reactions (e.g., chain scission), a weight gain will be observed. Conversely, if oxidative degradation reactions predominate, a weight loss will be observed. The lower weight loss of the PMR 15M/styrene samples, compared to the controls, may be due to oxidative crosslinking of the complex polymer structures resulting from the addition polymerization of styrene and the PMR end-capping monomer (NE).

Figure 6 shows the retention of interlaminar shear strength (ILSS) for PMR 15M composites exposed in air at 316° C (600° F). it can be seen that the ILSS of the composites made from the prepreg containing styrene were lower than the controls throughout the exposure time. However, the difference is not considered to be significant. The important point to note is that the PMR 15M/styrene composites exhibited excellent retention of their ILSS during elevated temperature exposure.

The flexural strength and modulus of the PMR 15M exposed in air at 316° C (600° F) are shown in Figures 7 and 8, respectively. It can be seen in Figure 7 that the flexural strength of the PMR 15M/styrene composites was lower than that of the control samples throughout most of the exposure time. However, the flexural strength retention of the PMR 15M/styrene composites was excellent. It can be seen that the flexural modulus of the PMR 15M/styrene composites compares favorably to the flexural modulus of the controls except during the first 400 hours of exposure (Fig. 8).

In summary, from the data presented in Table IV and Figures 1 to 8 it can be seen that the properties of the PMR 15E and PMR 15M composites prepared from prepreg containing styrene compare favorably to the properties of the PMR 15E and PMR 15M control samples.

Conclusions

The results of this investigation show that the tack and drape retention characteristics of PMR 15 Polyimide prepreg can be improved by the addition of a fourth monomer, or reactive diluent, containing an olefinic double bond. Styrene was found to be the most effective of the reactive diluents studied. Graphite fiber prepreg prepared from ethanol solutions of PMR 15 containing 5 w/o of added styrene exhibited good tack and drape characteristics after four days of unprotected exposure at ambient conditions. The use of styrene did not have an adverse effect on the room temperature and 316° C (600° F) properties of composites prepared from ethanol and methanol solutions of PMR 15.

References

1. T. T. Serafini, P. Delvigs, and G. R. Lightsey: J. Appl. Polym. Sci., 1972, vol. 16, pp. 905-915.

2. T. T. Serafini, International Conference on Composite Materials, Vol. 1, E. Scala, ed., pp. 202-220, AIME, New York, 1976. Also NASA TM X-71682, 1975.

3. T. T. Serafini, R. D. Vannucci, and W. B. Alston: NASA TM X-71894, 1976.

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Figure 5. - Weight loss of PMR 15M/HTS graphite fiber composites exposed in air at 316° C (600° F).

Figure 6. - Interlaminar shear strength of PMR 15M/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).

Figure 7. - Flexural strength of PMR 15M/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).

Figure 8. - Flexural modulus of elasticity of PMR 15M/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).

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TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

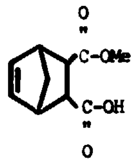
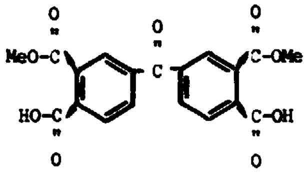
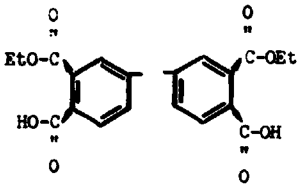
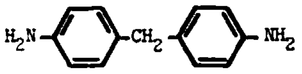
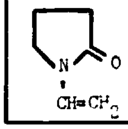
Structure	Name	Abbreviation
	Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid	NE
	Dimethyl ester of 3,3',4,4'-benzophenone-tetracarboxylic acid	BTDE
	Diethyl ester of 3,3',4,4'-benzophenone-tetracartoxylic acid	BTDET
	4,4'-Methylenedianiline	MDA

TABLE II. - REACTIVE DILUENTS

Structure	Name	Boiling point		Abbreviation
		°C	°F	
	Styrene	145	293	STY
	Bicyclo[2.2.1]hepta-2,5-diene	89	192	BHD
	1-Vinyl-2-pyrrolidinone	a		NVP

[a] Polymerizes above 135° C (275° F)

TABLE III. - SUMMARY OF QUALITATIVE OBSERVATIONS OF PREPREG TACK AND DRAPE RETENTION CHARACTERISTICS

Monomer system/Reactive diluent	Diluent level, w/o	Time to tack loss, days	Time to drape loss, days
PMR 15E/None	--	2	3-4
PMR 15E/Styrene	1	2	3-4
PMR 15E/Styrene	2	2-3	4-5
PMR 15E/Styrene	5	4	5-6
PMR 15M/None	--	1	1
PMR 15M/Styrene	5	1	1
PMR 15M/Styrene	10	1-2	1-2
PMR 15M/Styrene	20	2	2-3
PMR 15M/BHD	5	1	1
PMR 15M/BHD	10	1	1
PMR 15M/BHD	20	1-2	1-2
PMR 15M/NVP	5	1	1
PMR 15M/NVP	10	1	1
PMR 15M/NVP	20	1-2	2

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

Composite/Reactive diluent	Diluent level in PMR solution, w/o	Fiber v/o	Tg,		Mechanical properties at 24° C (75° F)					
					Interlaminar shear strength		Flexural strength		Flexural modulus of elasticity	
			°C	°F	N/m²	ksi	N/m²	ksi	N/m²	ksi
PMR 15E/None	--	60.0	346	655	106.2×10^6	15.4	144.1×10^7	209	106.9×10^9	15.5×10^3
PMR 15E/Styrene	1	57.9	336	637	100.7	14.6	146.2	212	108.9	15.8
PMR 15E/Styrene	2	59.1	344	651	99.3	14.4	143.4	208	108.9	15.8
PMR 15E/Styrene	5	58.3	357	675	100.0	14.5	155.8	226	113.8	16.5
PMR 15M/None	--	56.0	336	637	97.2	14.1	160.7	233	112.4	16.3
PMR 15M/Styrene	5	59.7	337	639	105.5	15.3	153.1	222	111.0	16.1
PMR 15M/Styrene	10	59.3	331	628	112.4	16.3	152.4	221	112.4	16.3
PMR 15M/Styrene	20	59.6	348	658	103.4	15.0	147.6	214	109.6	15.9
PMR 15M/BHD	5	55.6	340	644	95.8	13.9	149.6	217	108.9	15.8
PMR 15M/BHD	10	56.3	345	653	98.6	14.3	148.9	216	105.5	15.3
PMR 15M/BHD	20	58.1	342	648	88.9	12.9	155.1	225	113.1	16.4

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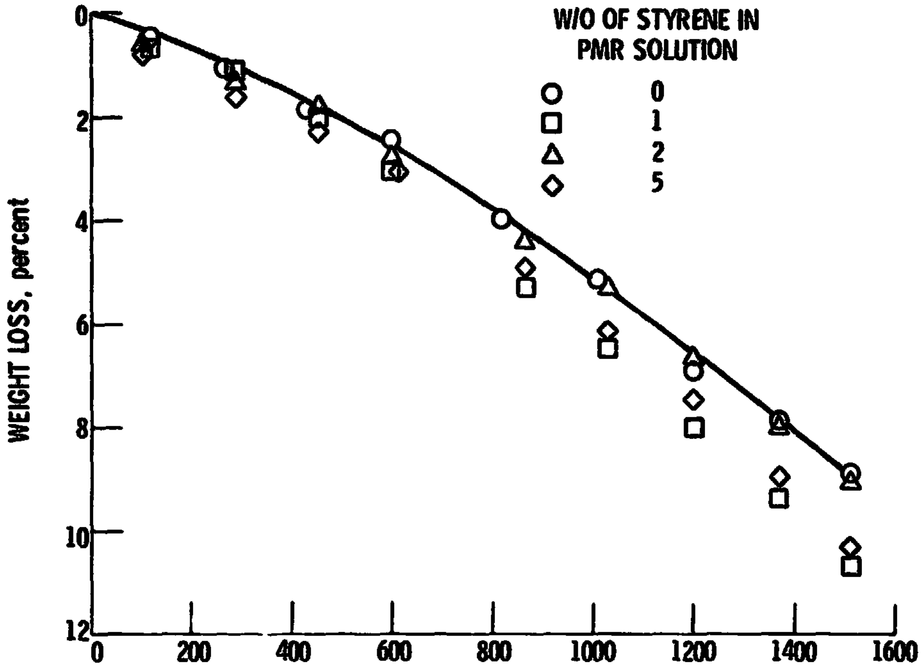

Figure 1. - Weight loss of PMR 15E/HTS graphite fiber composites exposed in air at 316° C (600° F).

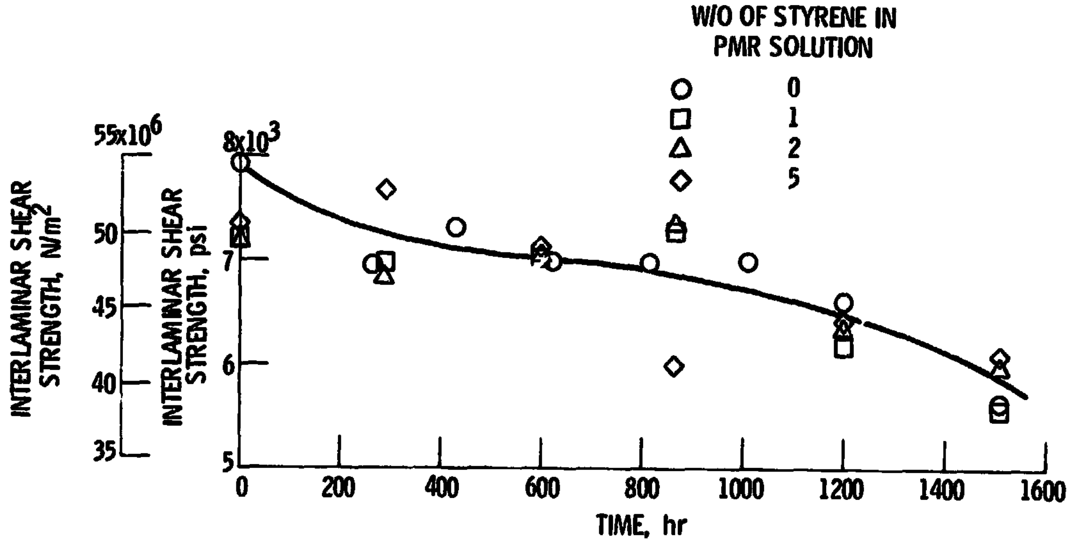

Figure 2. - Interlaminar shear strength of PMR 15E/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).

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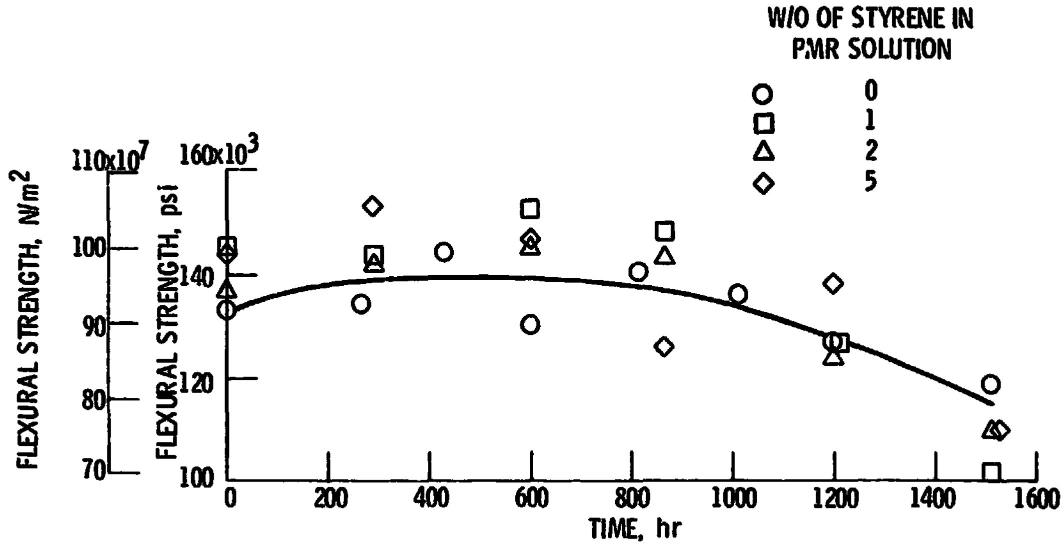

Figure 3. - Flexural strength of PMR 15E/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).

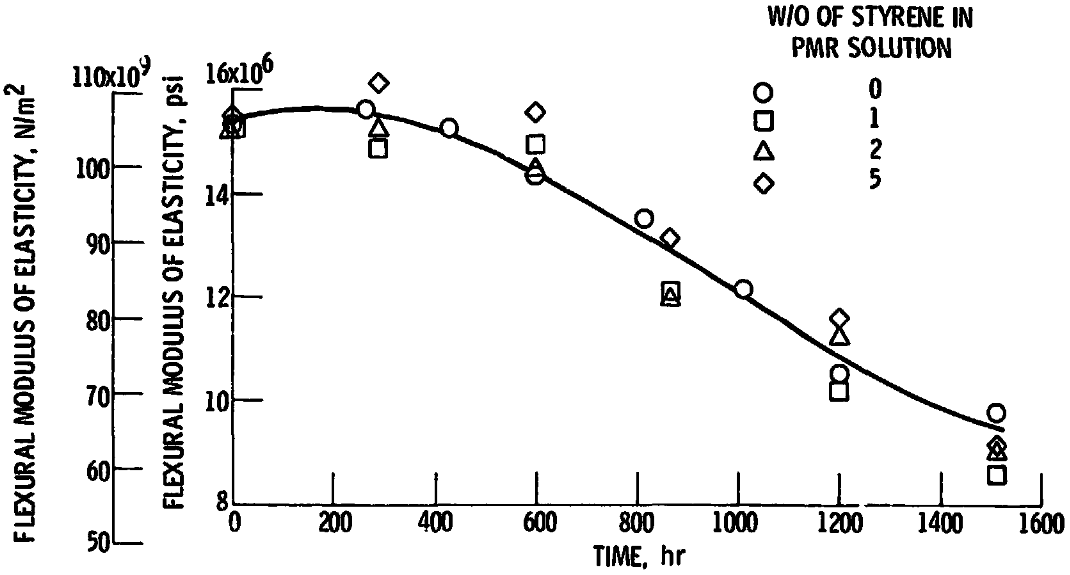

Figure 4 - Flexural modulus of elasticity of PMR 15E/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).

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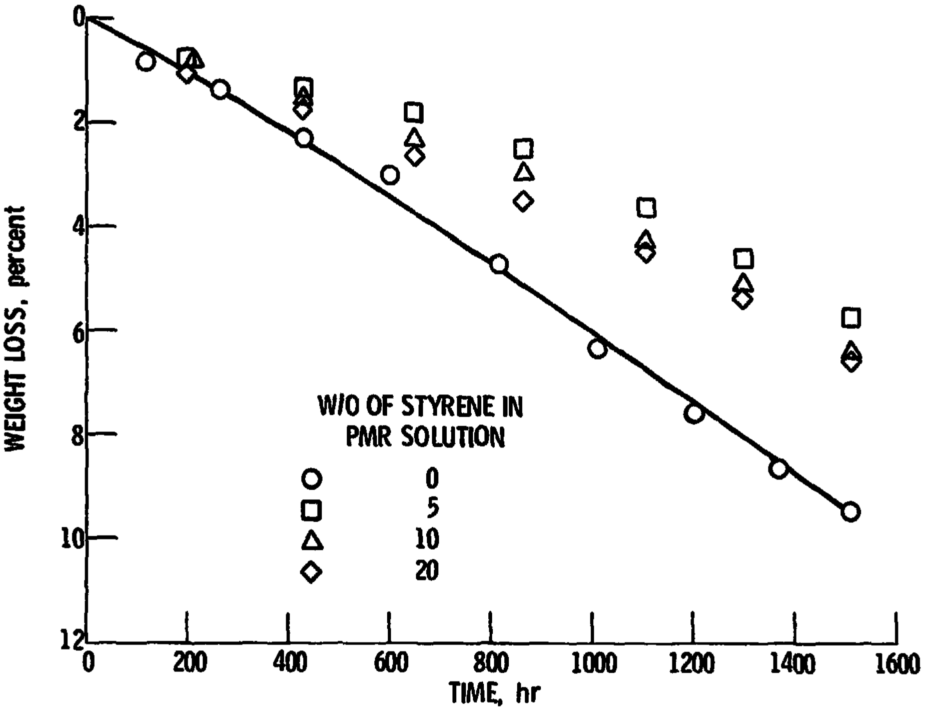

Figure 5. - Weight loss of PMR 15M/HTS graphite fiber composites exposed in air at 316° C (600° F).

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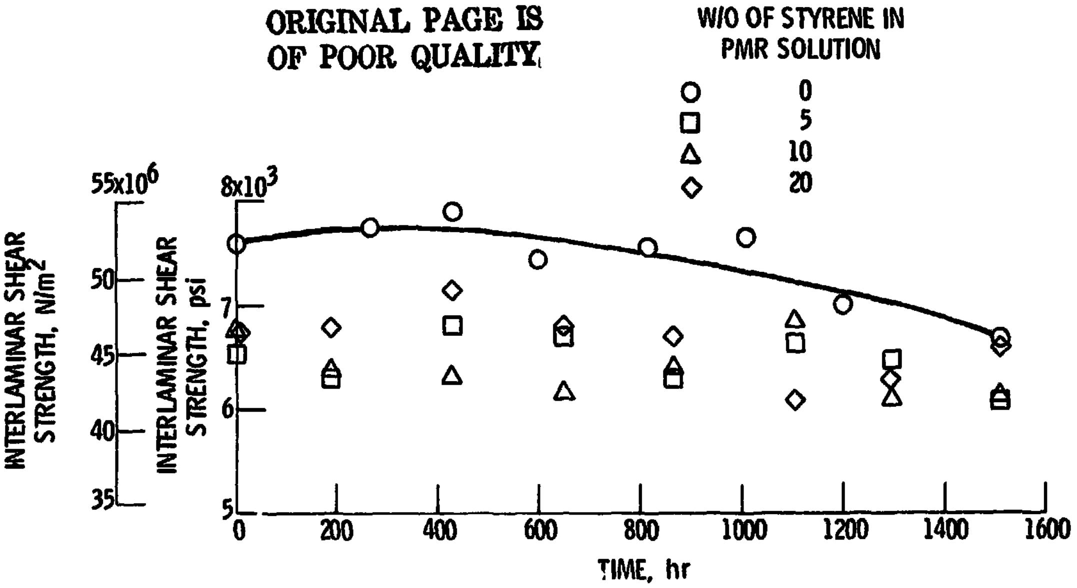

Figure 6. - Interlaminar shear strength of PMR 15M/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).

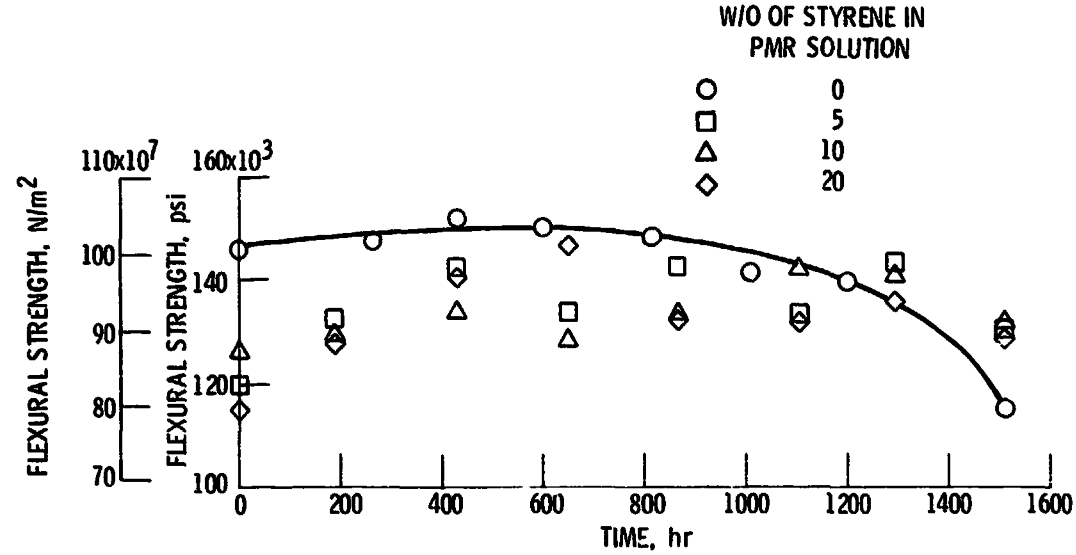

Figure 7. - Flexural strength of PMR 15M/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).

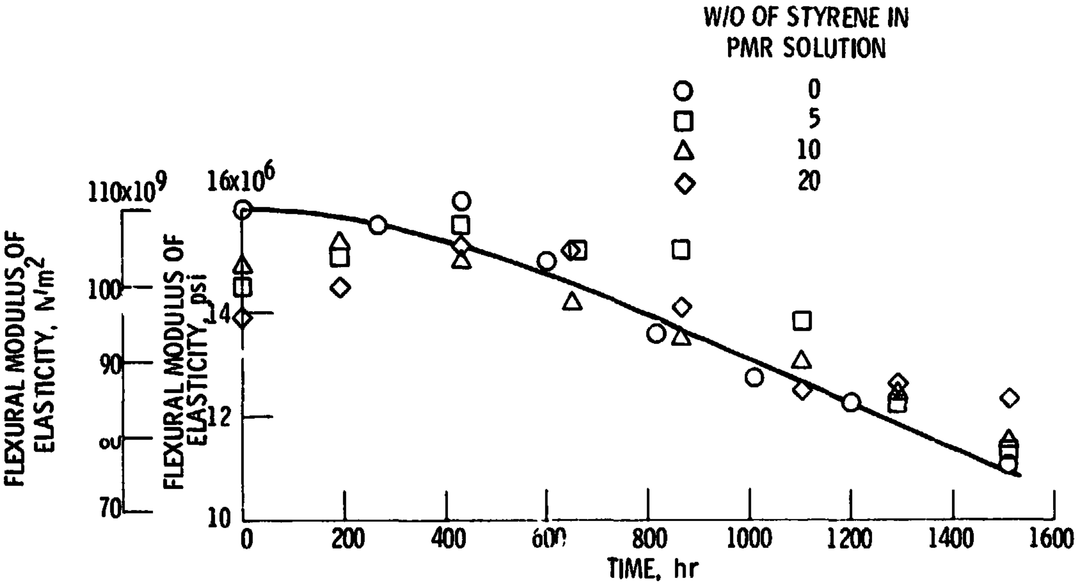

Figure 8. - Flexural modulus of elasticity of PMR 15M/HTS graphite fiber composites exposed and tested in air at 316° C (600° F).