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PROCESSABLE HIGH TEMPERATURE RESISTANT POLYMER MATRIX MATERIALS

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PROCESSABLE HIGH TEMPERATURE RESISTANT POLYMER MATRIX MATERIALS

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Introduction

Advanced fiber reinforced polymer matrix composites are becoming accepted as engineering materials for aeronautical and aerospace structural applications. Currently, the most widely used polymer matrix materials are the epoxy resins. The main reason for their wide usage as matrix resins is that epoxy resin/fiber materials can readily be processed into a variety of hardware items. In fact, the processing characteristics of epoxy resins have been adopted as practical standards for measuring the processability of other potential matrix resins. A disadvantage of epoxy resins is that their relatively low thermal stability restricts the application of polymer matrix composites to temperatures below 175°C (347°F). The use of high temperature polymers, such as the polyimides and polyphenylquinoxalines, as matrix resins could increase the upper use temperature of polymer matrix composites to as much as 315°C (600°F). However, because of the intractable nature of high temperature polymers, severe processing problems have been encountered and the full potential of high temperature polymers as matrix resins has not been realized.

In 1968 investigators at the Systems Group of TRW, Inc., working under NASA sponsorship, developed an approach to prepare polyimides by means of an addition reaction (ref. 1). Low molecular weight amide-acid prepolymers end-capped with norbornene rings were cured without the evolution of volatile material.

Subsequent studies at the NASA-Lewis Research Center led to the development of an improved method for preparing addition-cured polyimides (ref. 2 and 3). In this approach in situ Polymerization of Monomer Reactants (PMR) occurs on the surface of the reinforcing fibers.

The purpose of this report is to review the studies conducted with addition-type polyimides. Particular emphasis is given to the studies concerned with the development of the PMR approach.

Discussion

Condensation type aryl polyimide resins are generally synthesized by the reaction of aryl diamines with aromatic dianhydrides or dialkyl esters of aromatic tetracarboxylic acids. The diamine/dianhydride reaction is preferred for preparing polyimide films whereas the reaction of diamines with dialkylesters of aromatic tetracarboxylic acid is generally preferred for preparing polyimide matrix resins. A polyimide varnish (precursor) solution is prepared by dissolving the reactants in aprotic high boiling solvents such as dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP). This precursor solution which consists of a mixture of unreacted monomers and low molecular weight oligomers is used to prepare prepreg materials. Mild heating of the prepreg to effect chain extension and solvent removal also causes appreciable imidization (dehydrocyclization) converting the polymer to an almost intractable state. Limited resin flow together with volatilization of residual solvent and reaction by-products results in composites with high void contents having inferior mechanical properties and thermo-oxidative stability.

Studies performed by TRW, Inc., under NASA sponsorship to develop improved ablative resins led to the development of a novel class of polyimides which cure by an addition reaction (ref. 1). This approach utilizes low molecular weight amide-acid prepolymers end-capped with reactive norbornene groups that polymerize at temperatures in the range of 271° to 350°C (520° to 662°F) into thermo-oxidatively stable polyimides without the evolution of by-products. The molecular structures of amide-acid and imidized prepolymers prepared from 5-norbornene-2, 3-dicarboxylic anhydride (NA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-methylenedianiline (MDA) are shown in figure 1. A solution of amide-acid prepolymer having a formulated molecular weight (FMW) of 1300 (n=1.67) in DMF known as P13N is commercially available.

Subsequent studies were performed to develop addition-type polyimides having improved thermo-oxidative stability at 315°C (600°F) for use as laminating resins. Figure 2 shows the results from isothermal-gravimetric analysis in air at 315°C (600°F) for several addition-type polyimides (ref. 4). The label given on each curve identifies the reactants used to synthesize the prepolymers, which were subsequently cured to cross-linked polyimides. The stoichiometry of the reactants was selected to prepare prepolymers having an average FMW of 1300. The most significant finding was that the polymer made from the NA/MDA/PMDA prepolymer exhibited higher thermo-oxidative stability than any of the other polymers including P13N (curve labeled NA/MDA/BTDA in figure 2). Composite fabrication studies with NA/MDA/PMDA prepolymers showed that in order to obtain adequate resin flow it was necessary to adjust the stoichiometry of the reactants to yield prepolymers having an FMW of 1000. This prepolymer became known as P10P. A major shortcoming of P10P amide-acid prepolymer solutions is their limited and variable shelf life characteristics. Changes in solution viscosity, gelation and precipitation occurred during storage at room temperature.

Another approach was developed in our laboratories for preparing fiber reinforced addition-type polyimides (ref. 2 and 3). Our approach eliminates the need for prepolymer synthesis and circumvents many of the shortcomings associated with the use of addition-type amide-acid prepolymers. The method involves the use of ester-acids rather than anhydrides, thereby preventing the formation of prepolymers at room temperature. A diamine and the ester-acids are dissolved in anhydrous methanol and the monomeric solution is used to impregnate the reinforcing fibers. In situ polymerization of the monomer reactants (PMR) occurs upon heating the impregnated fibers. Complete details concerning the fabrication of composites are given in references 2 and 5. Table I shows the structures of the various ester-acids used in the study reported in reference 2. Figure 3 shows the variation of solution viscosity with time for monomer and prepolymer solutions. The monomer solution was formulated to approximate the composition of the P10P amide-acid prepolymer. Figure 3 shows the following: (1) monomer solutions exhibit considerably less viscosity variation with time than prepolymer solutions, and (2) monomer solutions have a much lower viscosity. Their lower viscosity enhances fiber wetting and also permits the use of a solution having a higher solids content. It needs to be emphasized that the use of DMF and the relatively low solids content of 20 weight percent was governed by the solubility characteristics of the amide-acid prepolymer. Low viscosity monomer solutions in methanol with solids contents up to 60 weight percent and which are stable for two weeks can be prepared.

The physical and mechanical properties of HTS graphite fiber composites (fiber volume (V_f) of approximately 55 percent) made from P10P amide-acid prepolymer and the corresponding monomer solution were compared over an extended period of time at 315°C (600°F). The effect of isothermal aging on composite weight loss is shown in figure 4. The composite weight loss data for both composites is essentially identical, which indicates that the use of monomer solutions does not have an adverse effect on composite thermo-oxidative stability. The effect of thermal aging on interlaminar shear strength for the same two composite systems is illustrated in figure 5. It can be seen that the interlaminar shear strength retention of the PMR/HTS fiber composites was nearly identical to the interlaminar shear strength retention characteristics for the composites made from the amide-acid prepolymer P10P. Comparisons of other properties established the utility of the PMR approach (ref. 2). In fact, a composite made from a NE/MDA/BTDE solution, in which the stoichiometry had been adjusted for an FMW of 1500, exhibited a 9.5 percent weight loss after 600 hours in air at 315°C (600°F). Under identical conditions the P10P/HTS composite weight loss was approximately 18 percent.

Studies conducted to establish the validity of the aforesaid finding and to improve the thermo-oxidative stability of PMR polyimides are reported in reference 5. In the earlier work using the PMR approach, the diamines used in preparing the monomer solutions were either MDA or 4,4'-thiodianiline. The results from a screening study conducted with diamines other than MDA did not result in composites with improved properties (ref. 5). Results from the screening study also showed that simply varying the stoichiometric ratio of the reactants in the NE/MDA/BTDE or NE/MDA/PMDE/BTDE systems was a more promising approach.

The chemical composition and some properties of eleven different composites are summarized in Table II. The fiber volume for all composites was approximately equal to 55 percent. The data given in Table II were taken from Table II of reference 5. The stoichiometry of the reactants was governed by the desired number of imide rings or by the desired percent of alicylic content. The formulated molecular weight is considered to be the molecular weight of the polymer prepared in situ on the fiber. For any given monomer combination the molar ratio of NE/MDA/tetracarboxylic acid dimethyl ester was $2/(n+1)/n$.

Samples 1 to 5 are chemically similar to the commercially available P13N resin. All of them, however, have a lower alicylic content than P13N. Samples 1 to 3 possessed a combination of unusually high thermo-oxidative stability and high initial interlaminar shear strength at room temperature. The results from a more detailed study of their mechanical properties after exposure at 315°C (600°F) will be described in a subsequent section of this paper. Samples 4 and 5 were excluded from further study because of considerably inferior interlaminar shear strength values at room temperature.

The weight loss data for samples 6 and 8 together with their comparatively inferior processing characteristics showed that the use of NE/MDA/PMDE compositions was not a promising approach.

The monomers used in samples 9 to 11 were selected to investigate the effect of increasing the number of imide linkages for a given FMW or alicylic content. For example, sample 9 has the same alicylic content as sample 1, but a higher number of imide linkages. The higher number of imide rings is achieved by partial substitution of BTDE with PMDE. Theoretically this should provide a correspondingly higher thermo-oxidative stability. The data presented in Table II show that the thermo-oxidative stability of samples 1 to 3 and samples 9 to 11 are approximately equivalent. Sample 9 was selected for further evaluation as a representative of the NE/MDA/(1 PMDE:1 BTDE) monomer combination.

Figure 6 shows the variation of interlaminar shear strength for samples 1 to 3 and 6 after exposure at 315°C (600°F) as a function of exposure time. Also presented in the figure are the room temperature values. The range of the room temperature values is 95×10^6 to 123×10^6 newtons per square meter (13,800 to 17,800 psi). It can be seen (figure 6) that the short-time elevated temperature interlaminar shear strength values are considerably lower. The large difference between room temperature and short-time 315°C (600°F) interlaminar shear strength values appears to be a peculiar phenomenon associated with intermediate modulus graphite fibers derived from polyacrylonitrile fibers (ref. 6). Because the interlaminar shear strength of samples 1 to 3 increased during exposure at 315°C (600°F), it appears that these samples underwent a post cure, whereas the decrease in interlaminar shear strength for sample 6 can be attributed to oxidative degradation. The important fact to note is that the interlaminar shear strength of samples 1 to 3 remained nearly constant from 100 to 600 hours. The data represent the best interlaminar shear strength retention at 315°C (600°F) for polyimide/HTS graphite fiber composites to date.

Photomicrographs of a cross section of composite sample 1, before and after exposure, are shown in figure 7. There is no evidence of voids in the composite as a result of fabrication. After exposure at 315°C (600°F) for 600 hours, the composite shows an extremely small number of voids. This indicates that the original void-free composite was very resistant to oxidative degradation that might occur by a diffusion mechanism. Any degradation that did occur, took place on the surface of the composite. The absence of internal voids after exposure also indicates that the composite is very resistant to thermal decomposition.

Figure 8 compares the effects of long-term exposure at 315°C (600°F) on the interlaminar shear strengths of samples 1, 6, and 9. It can be seen that the interlaminar shear strength retention of sample 9 was inferior to that of sample 1.

Based on the results of the screening study and detailed investigation of samples 1, 2, 3, 6, and 9, the monomer system that displayed the best overall balance of processability and thermomechanical properties was NE/MDA/BTDE with an FMW of 1500 (n=2.087). The polyimide matrix prepared by using this monomer system with n=2.087 is known as PMR-15. It is common practice to denote the resin obtained from the monomers NE/MDA/BTDE as $\mathrm{PMR}_{\frac{\mathrm{FMW}}{100}}$. The equation for FMW is:

$$\mathrm{FMW} = n\,\mathrm{MW}_{\mathrm{BTDE}} + (n+1)\,\mathrm{MW}_{\mathrm{MDA}} + 2\,\mathrm{MW}_{\mathrm{NE}} - 2(n+1)\left[\mathrm{MW}_{\mathrm{H_2O}} + \mathrm{MW}_{\mathrm{CH_3OH}}\right] \qquad (1)$$

where $\mathrm{MW}_{\mathrm{BTDE}}$, $\mathrm{MW}_{\mathrm{MDA}}$ etc. are the molecular weights of the indicated reactants and by-products. Additional composites studies conducted with PMR-15 are reported in reference 7.

In the earlier studies (ref. 2 and 5) to develop PMR polyimides with improved thermo-oxidative stability it was noted that the PMR approach provided a facile means to obtain a range of processing characteristics and properties. Studies reported in reference 8 demonstrated the feasibility of using the PMR approach to "tailor make" polyimide matrix resins.

The effect of FMW on percent resin flow is shown in figure 9. It can be seen that the resin flow increased significantly (from 3 to 20 percent) as the FMW was decreased from 1500 to 1000. The fiber volume ranged from 55 percent (for FMW=1500) to 63 percent (for FMW=1000). The monomer stoichiometries are given in Table III. These results clearly show that the resin flow characteristics of PMR polyimides can be varied over a wide range or "tailor made" to meet specific requirements. It needs to be emphasized that ultrasonic C scan examination of all the laminates revealed them to be void free. The resin flow results also show the sensitivity of resin flow to imide ring content. As the imide ring content decreased by approximately 30 percent in going from PMR 15 to PMR 10, the resin flow increased by nearly 600 percent.

Figure 10 shows the variation of percent resin weight loss as a function of matrix FMW for PMR/HTS graphite fiber composites after exposure in air for 600 hours at 232°C (450°F) and 288°C (550°F). It can be seen that all of the PMR composites exhibited excellent thermo-oxidative stability at 232°C (450°F). At 288°C (550°F) the resin weight loss of the PMR compositions in the FMW range of 1000 to 1400 was appreciably higher than for PMR 15. The greater thermo-oxidative stability of PMR 15 can be attributed to the lower alicylic content of PMR 15 compared to the other compositions (see Table III).

The variation of flexural strength (normalized for V_f=55 percent) for the various PMR PI/HTS graphite fiber composites as a function of FMW is shown in figure 11. Results are shown for specimens tested at room temperature and at 232°C (450°F) and 288°C (550°F) after short-time exposure at the indicated test temperature. It is important to note that at 232°C (450°F) and 288°C (550°F) the composites exhibited excellent retention of room temperature flexural strength throughout the FMW range investigated. The retention levels at 232°C (450°F) ranged from 75 to 88 percent and at 288°C (550°F) from 70 to 78 percent. It can be seen that the room and elevated temperature properties decreased as FMW was increased. Because the cure of PMR polyimides involves a complex addition reaction of alicylic chain ends resulting in chain extension and crosslinking, resin matrices having decreased crosslink densities, and, therefore, decreased moduli result from increases in FMW. The room temperature results reflect the effect of matrix modulus. The elevated temperature results reflect the combined effect of matrix modulus and temperature.

Figure 12 shows the variation of room temperature, 232° and 288°C (450° and 550°F) short-time interlaminar shear strength with FMW. The data presented in figure 12 clearly show that the composites retained a high level of interlaminar shear strength at the elevated temperatures. The ranges for the retention levels at 232° and 288°C (450° and 550°F) were 66 to 75 percent and 57 to 61 percent, respectively.

In figure 13, short-time elevated temperature data are compared with the long-time elevated temperature properties. The data from tests conducted at 232°C (450°F) are shown in figures 13a and 13c for flexural strength and interlaminar shear strength, respectively. Figures 13b and 13d show the results from tests conducted at 288°C (550°F). The comparisons presented in the figure clearly illustrate the superior elevated temperature properties retention characteristics of the PMR polyimide compositions in the FMW range of 1000 to 1500.

Figure 14 is a flow chart of the PMR approach for the fabrication of high-performance-resin fiber composites. We have also successfully used the PMR approach to fabricate polyphenylquinoxaline/graphite fiber composites (ref. 9). The PMR approach as outlined in figure 14 is considerably less complex than conventional composites fabrication procedures. In addition to the advantages discussed previously, such as low viscosity, high solids content solutions, etc., the PMR approach eliminates the problems associated with packaging, shipping, and storage of prepreg. Other important advantages which the PMR approach provides are listed in Table IV.

We view the PMR approach as one that should permit the use of a number of polymers that have demonstrated outstanding high temperature thermo-oxidative stability but have not been used as matrix resins because of their inherent intractability.

Conclusions

The in situ polymerization of monomer reactants (PMR) approach is a powerful method for fabricating high performance polymer matrix composites. The PMR approach appears to be broadly applicable to a variety of high-temperature polymers. The PMR approach offers a number of significant advantages to the fabricators and users of polyimide/fiber composites. These are: superior high temperature properties, lower cost, greater safety, and processing versatility. The excellent processability and properties of PMR polyimide/fiber composites makes it possible to realize much of the potential of high temperature resin/fiber composites.

References

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9. Serafini, T. T.; Delvigs, P.; and Vannucci, R. D.: In Situ Polymerization of Monomers for High Performance Poly(phenylquinoxaline)/Graphite Fiber Composites. J. Appl. Polym. Sci., Vol. 17, 1973, pp. 3235-3238.

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14. Approach for preparation of resin/fiber composites using in situ polymerization of monomer reactants (PMR).

TABLE I. - STRUCTURES OF ESTER ACIDS

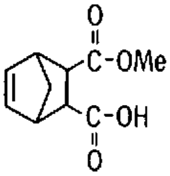
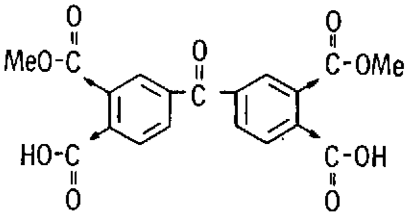
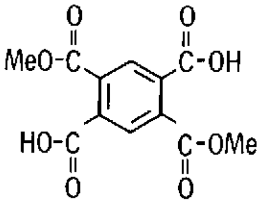
Structure	Name	Abbreviation
	Monomethyl ester of 5-norbornene-2, 3-dicarboxylic acid	NE
	Dimethyl ester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid	BTDE
	2, 5-dicarbomethoxyterephthalic acid	PMDE

TABLE II. - PROPERTIES OF POLYIMIDE/HTS GRAPHITE FIBER COMPOSITES

Sample number	Monomer solution composition	Moles of diester-diacid	Formulated molecular weight, FMW	Laminate properties				Composite weight loss, percent[a]
				Interlaminar shear at 24° C (75° F)		Interlaminar shear at 315° C (600° F)		
				N/m^2	ksi	N/m^2	ksi	
1	NE/MDA/BTDE	2.087	1500	105.5×10^6	15.3	41.4×10^6	6.0	9.5
2	↓	2.603	1750	99.3	14.4	37.9	5.5	9.8
3		2.913	1900	103.4	15.0	35.2	5.1	10.0
4		3.120	2000	67.6	9.8	31.7	4.6	11.4
5		5.186	3000	56.5	8.2	35.2	5.1	28.0
6	NE/MDA/PMDE	1.342	1000	74.5	10.8	42.7	6.2	17.6
7	NE/MDA/PMDE	1.868	1200	84.8	12.3	42.7	6.2	17.9
8	NE/MDA/PMDE	2.658	1500	42.1	6.1	20.0	2.9	20.8
9	NE/MDA/ (1BTDE:1PMDE)	2.338	1500	98.6	14.3	42.7	6.2	10.6
10	NE/MDA/ (1BTDE:1PMDE)	2.917	1750	93.8	13.6	37.9	5.5	8.6
11	NE/MDA/ (1BTDE:1PMDE)	3.264	1900	86.9	12.6	31.0	4.5	10.9

[a] After 600 hr in air at 315° C (600° F).

TABLE III. - MONOMER STOICHIOMETRY

Formulated molecular weight	Moles of BTDE,[a] (n)	Percent alicyclic content
1000	1.054	9.20
1100	1.260	8.37
1200	1.465	7.67
1300	1.672	7.08
1400	1.880	6.57
1500	2.087	6.13

[a] Molar ratio of NE/MDA/BTDE equals 2 : (n + 1) : n.

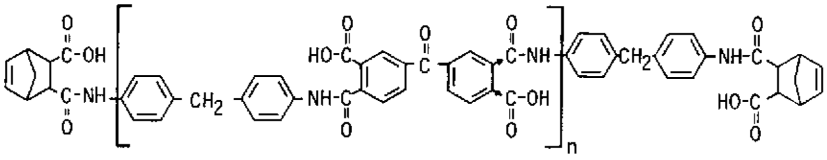
TABLE IV. - ADVANTAGES OF PMR POLYIMIDES

Improved composites performance

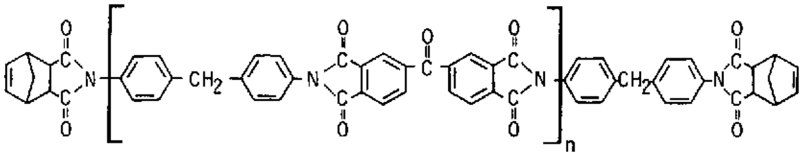
Greater safety

Lower cost

Processing versatility



(a) AMIDE-ACID PREPOLYMER



(b) IMIDIZED PREPOLYMER

CS-65005

Figure 1. - Addition-type prepolymers.

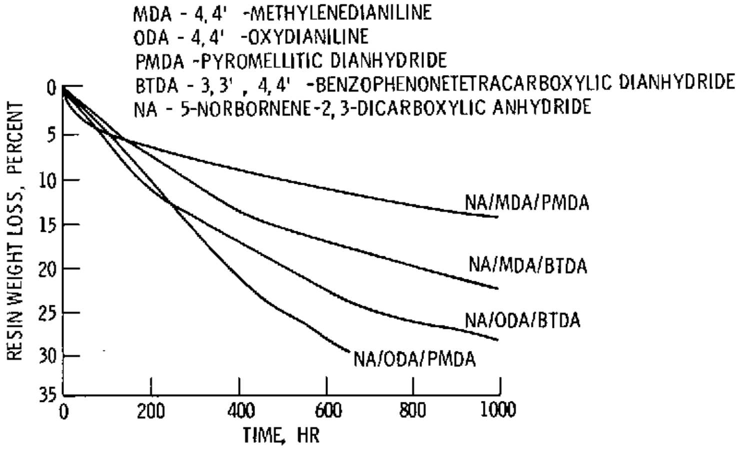


Figure 2. - Weight loss of A-type polyimides (ref. 4). Environment, air at 315° C (600° F); formulated molecular weight, 1300.

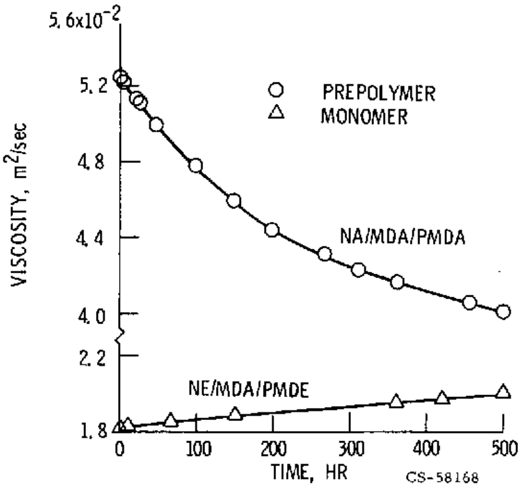


Figure 3. - Viscosity behavior of prepolymer and monomer solutions (ref. 2). FMW 1000. 20 weight percent solids in DMF at 25° C.

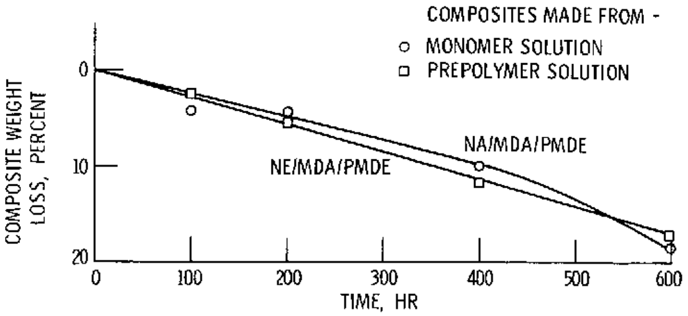


Figure 4. - Percent weight loss of polyimide - HTS-graphite-fiber composites aged in air at 315° C (600° F) (ref. 2). FMW = 1000.

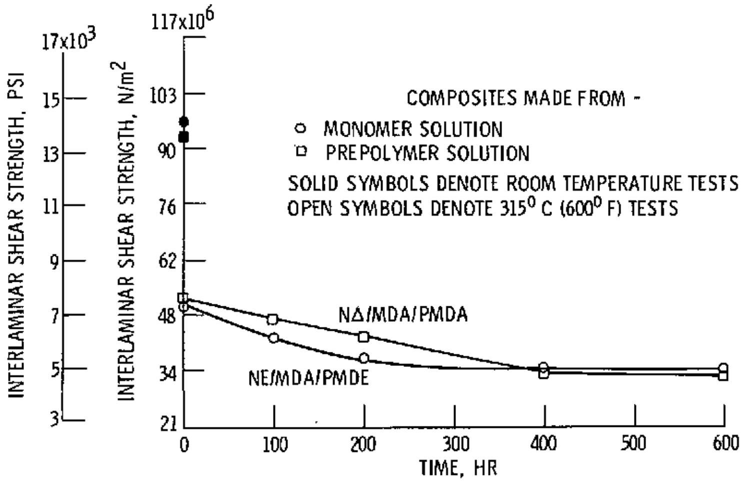


Figure 5. - Interlaminar shear strength of polyimide/HTS graphite-fiber composites (ref. 2). FMW = 1000.

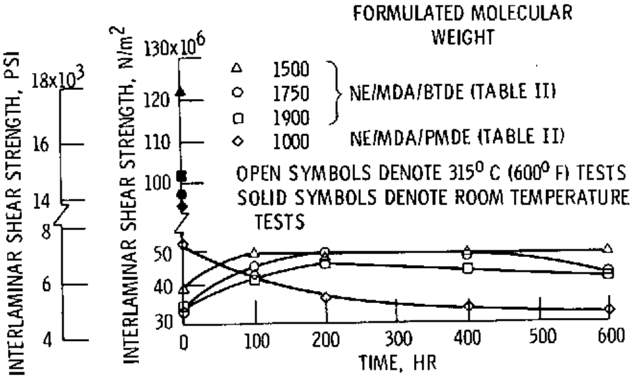
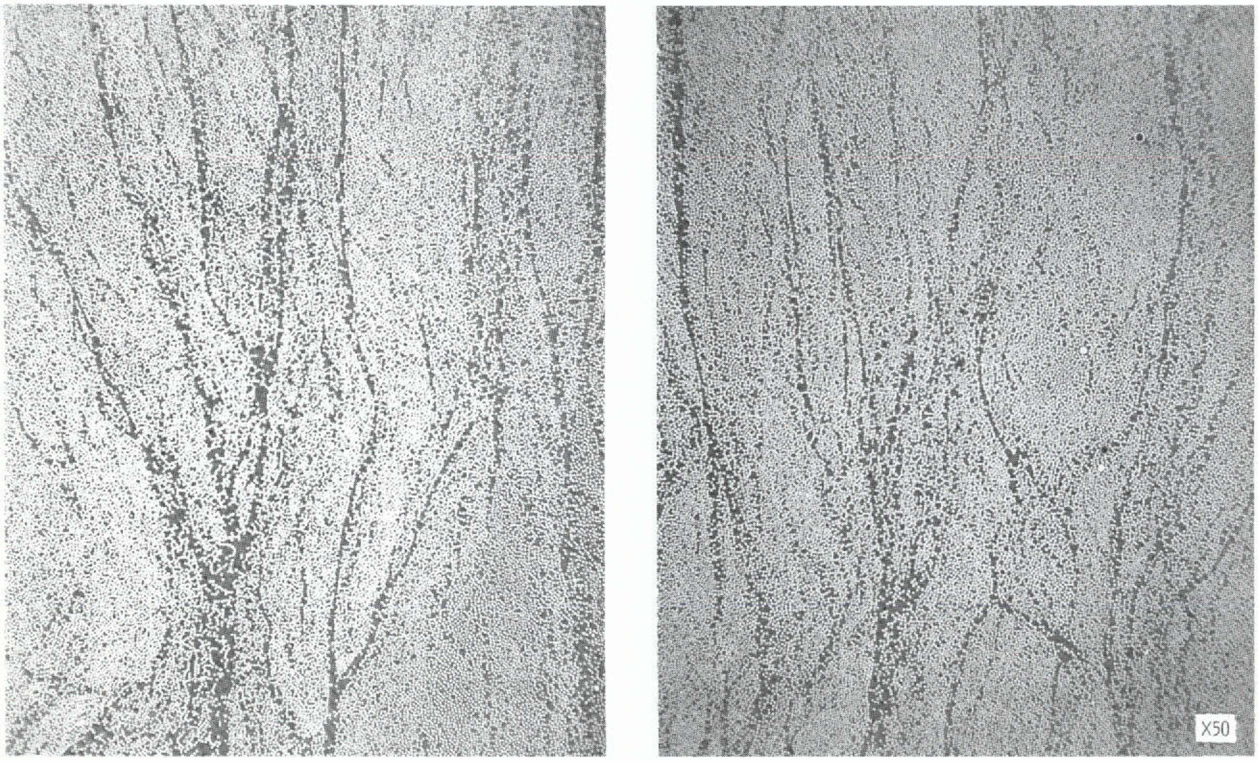


Figure 6. - Interlaminar shear strength of polyimide/HTS graphite fiber composites (ref. 5).



(a) UNEXPOSED.

(b) EXPOSED.

Figure 7. - Photomicrographs of PMR PI/HTS graphite fiber composites before and after 600 hour exposure in air at 315° C (600° F), FMW = 1500, (ref. 5). X50.

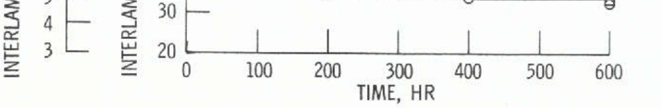


Figure 8. - Interlaminar shear strength of PMR polyimide/HTS graphite fiber composites exposed and tested in air at 315° C (600° F) (ref. 5).

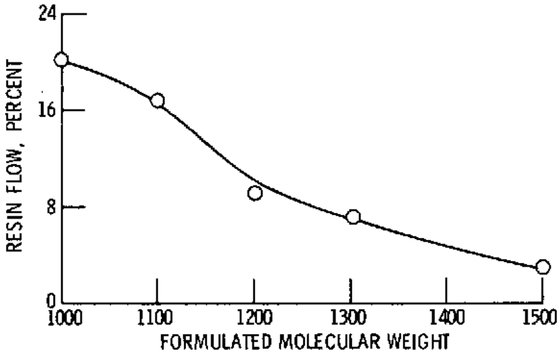


Figure 9. - Percent resin flow for PMR PI/HTS graphite fiber composites (ref. 8).

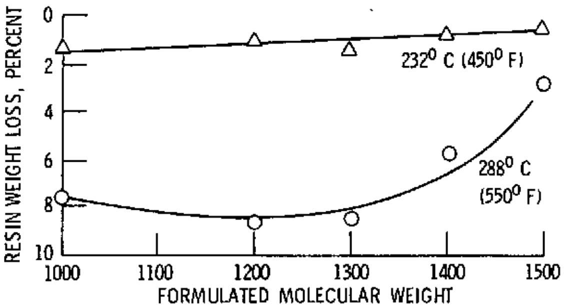


Figure 10. - Percent resin weight loss for PMR PI/HTS graphite fiber composites after 600-hour exposure in air at 232° C (450° F) and 288° C (550° F) (ref. 8).

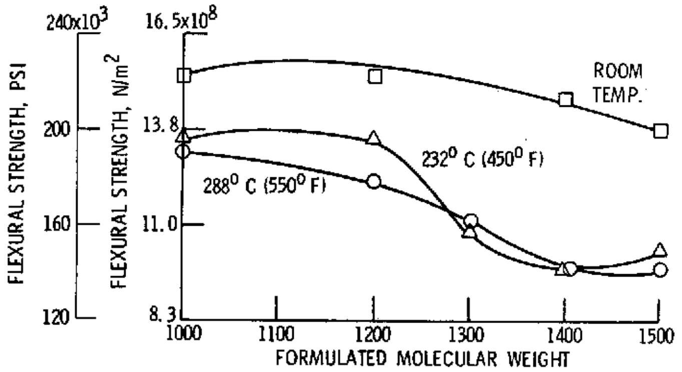


Figure 11. - Flexural strength of PMR PI/HTS graphite fiber composites. Tests conducted at room temperature and at 232° C (450° F) and 288° C (550° F) after short-time exposure at indicated test temperature (ref. 8).

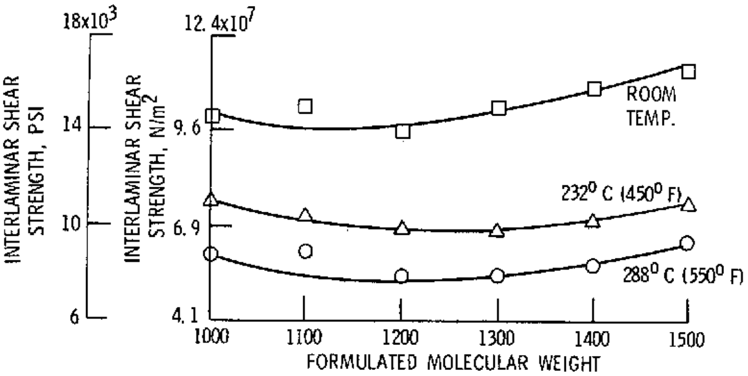
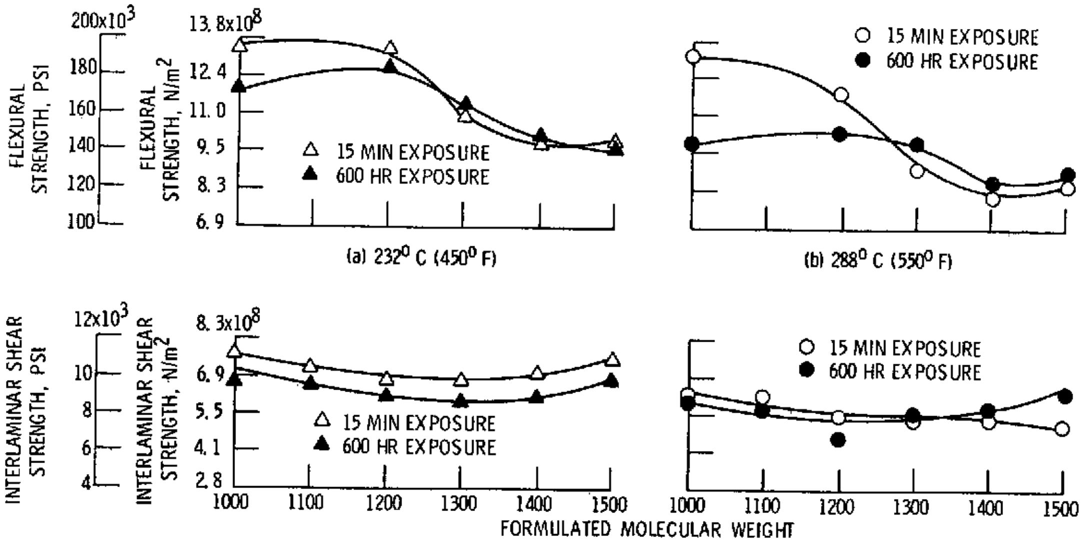


Figure 12. - Interlaminar shear strengths of PMR PI/HTS graphite fiber composites. Room temperature and short-time elevated temperature tests (ref. 8).



(a) 232° C (450° F)

(b) 288° C (550° F)

(c) 232° C (450° F)

(d) 288° C (550° F)

Figure 13. - Long-time and short-time elevated temperature properties of PMR PI/HTS fiber composites (ref. 8).

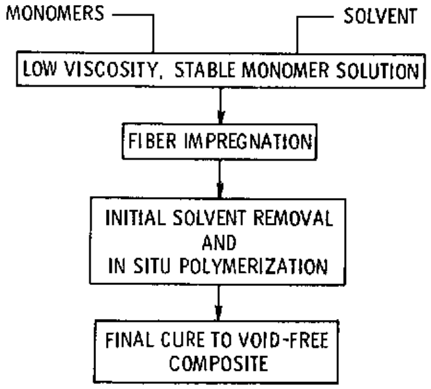


Figure 14. - Approach for preparation of resin/fiber composites using in situ polymerization of monomer reactants.