

High-Performance Composites from Polyimide Matrix Resins that Utilize a Cross Linking Reaction of Biphenylene End-Caps with Acetylene Units in the Main Chain

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Synopsis

Graphite-reinforced composites were prepared with oligomeric polyimides having biphenylene end-caps and acetylene linkages in the polymer chain. The oligomers were crosslinked by the reaction of the biphenylenes with the diphenyl acetylenes to form 9,10-diphenylphenanthrene units. The resulting composites had good mechanical properties. Thermal oxidative aging studies show that the unidirectional graphite fiber composites maintained good mechanical properties up to 1200 h at 316°C.

INTRODUCTION

Polyimides are some of the most important thermally stable polymers and matrix resins for use in high-temperature fiber-reinforced composites.¹ The insolubility of most polyimides and imide oligomers in common organic solvents, however, presents processing difficulties. A number of approaches have been utilized to circumvent these processing difficulties.

The polymerization of monomer reactants (PMR) approach² uses an alcohol solution of monomers to impregnate the fiber. By delaying the formation of the oligomers until after the casting and fabrication steps, the PMR technology offers excellent resin processibility. However, uneven cure rates or incomplete polymerization can leave voids in the fabricated composite. By contrast, the use of soluble polyamic acids introduces problems because polyamic acids are hydrolytically unstable,¹ and solution processing of the polyamic acids requires the use of *N*-methylpyrrolidone, *N,N*-dimethylacetamide, dimethyl sulfoxide, or similar high-boiling solvents. Isoimide oligomers, which are more soluble than the imide analogs, can be converted thermally at a later stage in processing to the corresponding imides.³

The solubility of imide oligomers may be improved by the incorporation of flexible segments such as methylene, isopropylidene, or hexafluoroisopropylidene,⁴ but the introduction of the first two of these units lowers the thermal stability of the resin since these units are more susceptible to thermooxidative degradation. In addition, glass transition temperature (T_g) of the resin is

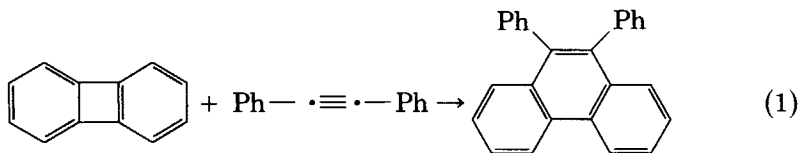
lowered and the mechanical properties of the resin above T_g are decreased even when the resin is crosslinked.

A number of different reactions have been utilized to crosslink these oligomers, by incorporating reactive groups, usually as end caps.⁵ Acetylene⁶ and nadic (bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride)^{2a,7} end caps are currently being used in commercially available prepolymers. While these prepolymers give crosslinked resins that show impressive performance at high temperatures, the retention of mechanical properties for extended times at high temperatures is less than for the corresponding high molecular weight polyimides.⁸ The efficiency of the cyclotrimerization of acetylenic end caps to yield benzene links⁹ is low (< 30%),¹⁰ and instead vinyl and other thermally unstable crosslinks are generated. Cured nadic end-capped polyimide, PMR-15, contains aliphatic units resulting from the norbornene imide end groups¹¹ (in addition to the methylene units in the main chain) and as a result, the thermooxidative stability could be expected to be lower than that exhibited by high-molecular-weight polyimides void of aliphatic units.⁸

Modified PMR polyimide resins containing hexafluoroisopropylidene units in the main chain have better thermooxidative stability and comparable high-temperature mechanical properties as compared with PMR 15,¹² but still have the potential to undergo degradation at the crosslinking site. In fact, polyimide resins containing a higher content of nadic cross-linking units have improved processibility but exhibit lower thermal stability.^{7a, d, 13}

In an attempt to avoid the generation of thermally unstable units in the crosslinking reaction we had utilized biphenylene end caps, which were expected to generate tetrabenzocyclooctatetraene units.¹⁴ Unfortunately, carbon fiber-reinforced composites prepared from quinoline and imide oligomers having biphenylene end caps did not exhibit good thermooxidative stability, since the tetrabenzocyclooctatetraene unit was not as thermally stable as had been anticipated.¹⁵ In addition, this curing reaction takes place primarily by a chain extension reaction, thus producing a resin that exhibited thermoplasticity above the T_g .

Biphenylene is known to react thermally with diphenylacetylene to yield 9,10-diphenylphenanthrene [Eq. (1)],¹⁶ and this reaction has been utilized as a



curing reaction for quinoline¹⁷ and imide oligomers.¹⁸ Graphite-cloth-reinforced composites prepared by utilizing a matrix resin composed of biphenylene end-capped quinoline oligomers containing acetylene linkages in the main chain showed excellent mechanical properties that were maintained after 400 h of isothermal aging at 316°C.¹⁷ This was a dramatic improvement over the 50–100 h lifetime of polyquinolines and polyimides cured utilizing biphenylene end caps only. The best properties were realized when an exact stoichiometric balance of acetylenic and biphenylene units were present, suggesting that

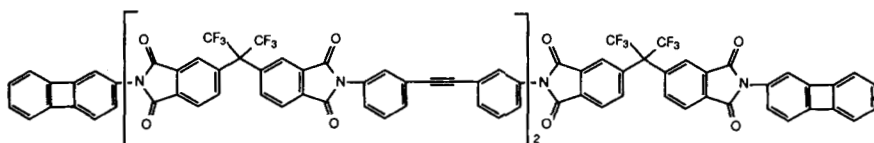
residual acetylenic and biphenylene units were thermooxidatively unstable centers.

Accordingly, a series of imide oligomers were prepared for possible use as matrix resin components.¹⁸ Oligomers containing either acetylene or biphenylene end caps were synthesized. The mechanical properties (above T_g) of melt-processed films containing acetylene end groups were best, with a film obtained from a stoichiometric blend of oligomers containing the acetylene end caps and biphenylene end caps showing better mechanical properties than film prepared from the biphenylene end-capped oligomer alone. Cured imide oligomers containing both biphenylene end caps and internal acetylenic units exhibited superior thermal properties. The most readily processable imide oligomers were obtained from those containing hexafluoroisopropylidene units, particularly from the monomers, 2,2-bis(3,4-phenyldicarboxylic)hexafluoropropane dianhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane.

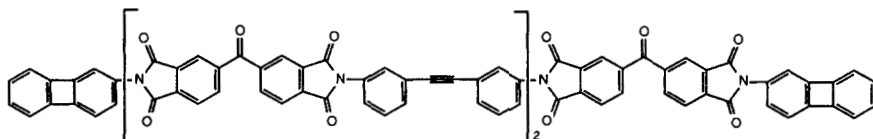
EXPERIMENTAL

Thermal analyses were performed with a DuPont 942 and 943 Thermo-mechanical Analyzer interfaced with an Omnitherm data reduction system. Isothermal aging of the composites was done in circulating air ovens at 316°C.

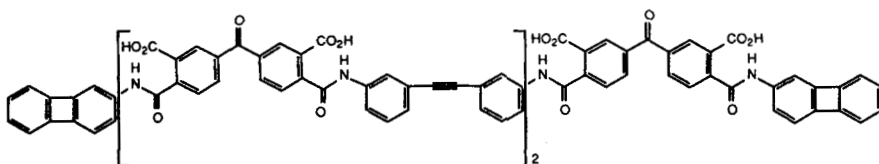
2,2-Bis(3,4-phenyldicarboxylic)hexafluoropropane dianhydride (American Hoechst) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (Alfa) were obtained commercially, and purified according to literature procedures.¹⁸ Bis(3-aminophenyl)acetylene, 2-aminobiphenylene, 1,3,5-tris(4-aminophenoxy)benzene, polymer 1 and polymer 3 were prepared by literature procedure.¹⁸



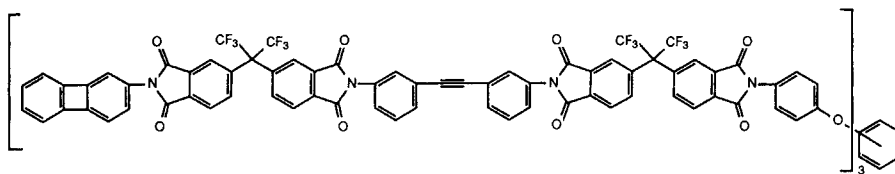
1



2



3



4

Prepreg Preparation

THF solutions of **1** and **3** were brushed onto enough drum-wound, unidirectional Celion-6000 fiber to achieve a 30 wt% resin content in the dried prepreg. The coated fiber was allowed to dry overnight, and then cut into pieces.

The following procedure was used for the preparation of prepreps by the PMR technique.

Prepreg of 1 (PMR)

To 8.8 mL of methanol were added 5.3435 g (12.030 mmol) of 2,2-*bis*(3,4-phenyldicarboxylic)hexafluoropropane dianhydride, and the reaction was heated to a gentle reflux for 2.75 h. The reaction was allowed to cool, and to the solution were added 1.6707 g (8.020 mmol) of *bis*(3-aminophenyl)acetylene and 1.3413 g (8.020 mmol) of 2-aminobiphenylene along with enough methanol to make a 40% solids solution. (If necessary, this mixture was heated up to help the materials dissolve.) The solution was then brushed onto enough Celion-6000 fiber to give 30 wt% resin content in the dried prepreg. The fiber was allowed to dry overnight and then was cut into pieces.

Composite Preparation

The cut pieces of prepreg were stacked into 12-ply lay-ups, and the lay-ups were placed in either a 1 in. × 2.7 in. or 3 in. × 8 in. steel die. The lay-ups were then placed in a 204°C oven for 1 h. (Lay-ups of **4** were staged in a 232°C oven for 1 h.) The resulting piece was then melt-pressed at 400°C under 1500 psi to yield the finished composite.

Postcure Treatment

The finished composites were postcured by placing them in a circulating-air oven for 12 h at 316°C.

Interlaminar Shear Strength (ILSS)

The interlaminar (or short beam) shear strength was determined as per ASTM D2344-76 by applying a load to a short (span/depth = 5/1) composite sample supported lengthwise in a variable-span vise. The ILSS fixture was mounted inside a variable temperature oven and testing was done after the specimen had equilibrated with the oven temperature for 15 min. The specimen was pushed against a pin until failure. The pressure at failure was measured by an Instron and used to calculate the ILSS. (Because the specimen is short, failure occurs between the plies. Thus, ILSS affords a measure of the resin's ability to transfer the load from one ply to the next in a composite.)

Flex Strength and Flex Modulus

An analysis similar to the above was performed except longer (2 in.) specimens were used and tested as per ASTM D790-1. (Because the specimen is considerably longer, failure occurs perpendicular to the longest axis and requires breakage of the fibers. As a result, flex strength and flex modulus are fiber-dependent properties and quantify the extent to which the composite retains the high strength imparted by the fiber reinforcement. Flex strength is an indication of the composites' ultimate strength while flex modulus is an indication of the composite's initial stiffness.)

RESULTS AND DISCUSSION

In order to assess the utility of such imide oligomers containing biphenylene end caps and internal acetylene units, fiber-reinforced composites were fabricated and their thermal and mechanical properties were evaluated.

Three resins were selected for testing, based on their ability to give good melt-pressed films (indicating that the polymers would flow) and the retention of mechanical properties of the film above T_g . The polymers had 5% weight loss at 490–500°C in air as measured by thermal gravimetric analysis (TGA).¹⁸

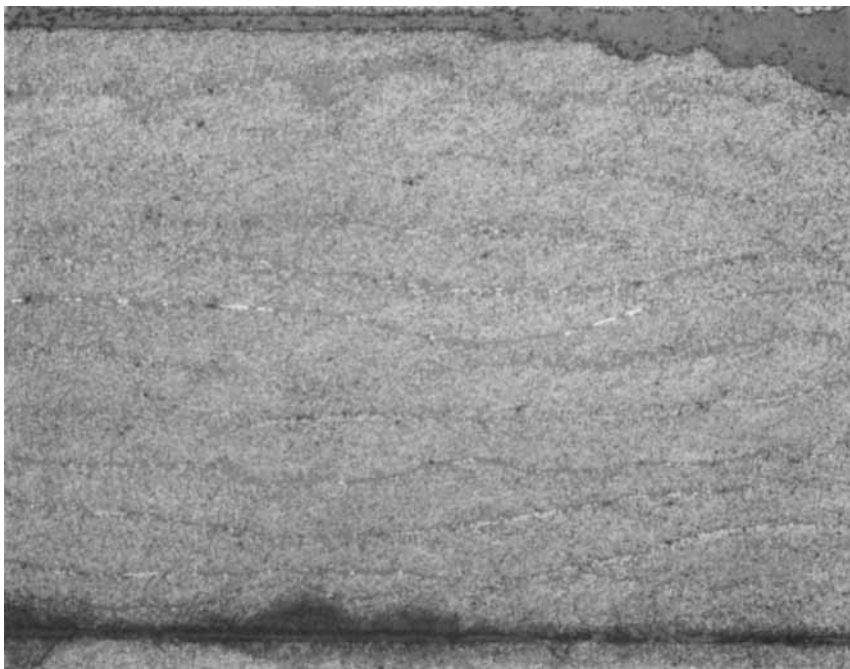
An oligomer prepared by reaction of 2,2-*bis*(3,4-phenyldicarboxylic)hexafluoropropane dianhydride with *bis*(3-aminophenyl)acetylene and end-capped with 2-aminobiphenylene, **1**, was soluble in common organic solvents such as tetrahydrofuran (THF). A melt-pressed film of this material had a T_g of 335°C.¹⁸ Alternatively, this oligomer was incorporated into the composites by using the PMR technique to give **1** (PMR). A resin containing a carbonyl linkage, **2** was prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride, *bis*(3-aminophenyl)acetylene, and 2-aminobiphenylene. Since **2** was insoluble, this resin was incorporated in the composite by utilizing the amic acid, **3**, which is soluble in THF. The amic acid can then be cyclized after casting to give **2**. In addition, the PMR technology also was utilized to provide **2** (PMR). A melt-pressed film of **2** had a T_g of 354°C.¹⁸ Finally, a star polyimide, **4**, was prepared from 1,3,5-*tris*(4-aminophenoxy)benzene (star point), 2,2'-(3,4-phenyldicarboxylic)hexafluoropropane dianhydride, *bis*(3-aminophenyl)acetylene, and the 2-aminobiphenylene end cap. This resin was insoluble, but **4** could be used to fabricate a composite *via* the PMR technique.

The composites were prepared using Celion-6000 graphite fiber. The soluble prepolymers, **1** and **3**, were applied to the fibers as 30% solutions in THF, while solutions of monomers (PMR solutions) leading to **1**, **2**, and **4** were applied as 40% solids in methanol. In every case, a 20 wt% resin content in the

TABLE I
Fiber Content of the Finished Composites^a

Polymer	1	2	2 (PMR)	1 (PMR)	12.5% 4/87.5% 1 (PMR)	25% 4/75% 1 (PMR)	50% 4/50% 1 (PMR)	4 (PMR)
Wt% fiber	74	81	80	84	81	80	70	77

^a Determined by digestion of finished composites with hydrazine hydrate.



(a)

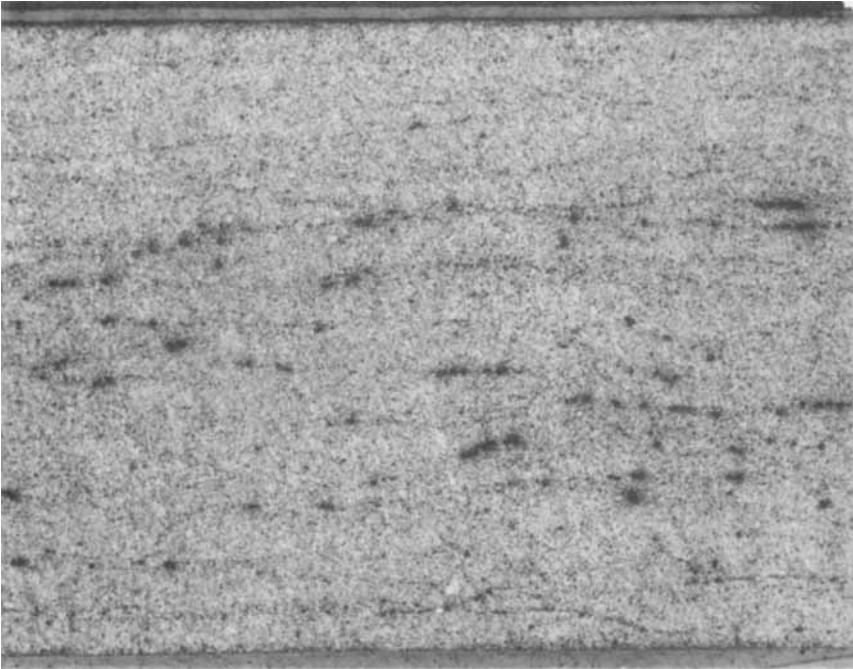
Fig. 1. Photomicrographs of the finished composites ($50\times$). (White areas are fiber ends, gray areas are resin, and black areas are voids.) (a) Composite made with 1. (b) Composite made with 1 (PMR). (c) Composite made with 2. (d) Composite made with 2 (PMR). (e) Composite made with 4 (PMR). (f) Composite of 2 after 1200 h at 316°C . (g) Composite of 2 (PMR) after 1200 h at 316°C .

finished composites was sought (Table I). The coated fibers, "prepregs," had good tack and drape, although 1 and 3 did not consistently penetrate the fibers (which left dry spots on the prepregs). The prepregs were cut to size and stacked into 12-ply lay-ups, which were then heated for 1 h in a 204°C oven to remove the volatiles. The staged lay-ups had weight losses of 2–3% for 1, 23% for 2, and 6% for all composites made by PMR.

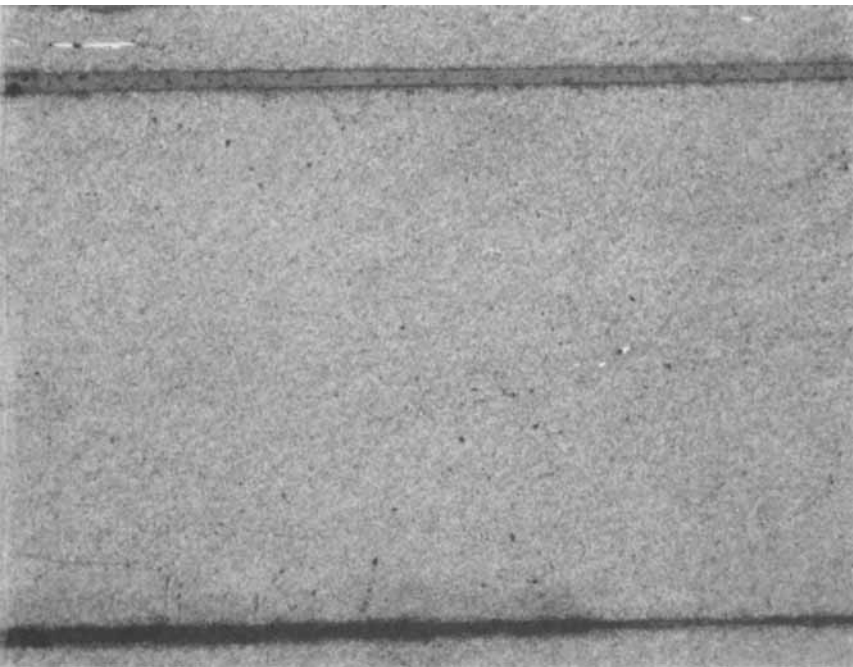
Initial Properties

All the polymers gave good composites, which produced a metallic ring when dropped on a hard surface, and had a smooth, lustrous appearance. A representative photomicrograph (Fig. 1) of the initial composites shows few voids as indicated by black areas in the photos.

The composites were tested for interlaminar shear strength (ILSS), flex strength (FS), and flex modulus (FM). Composites of 1 and 2 had good mechanical properties (Table II) even before the postcure cycle. The composites were postcured by placing them in a 316°C oven for 12 h. The result was an advancement in all the mechanical properties and the T_g of the composite matrices (Table II and III). Tables III and IV show the advancement of the T_g after the postcure.

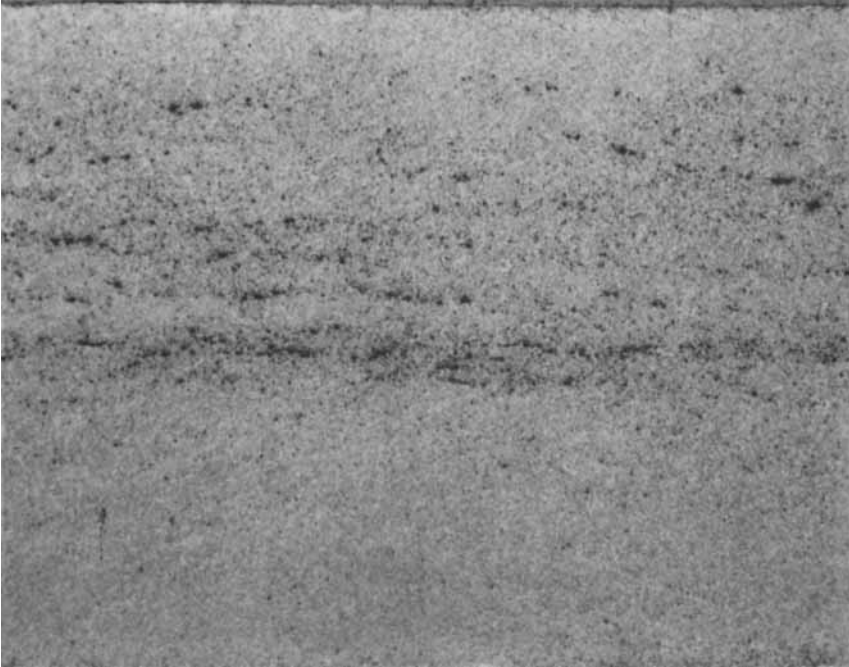


(b)

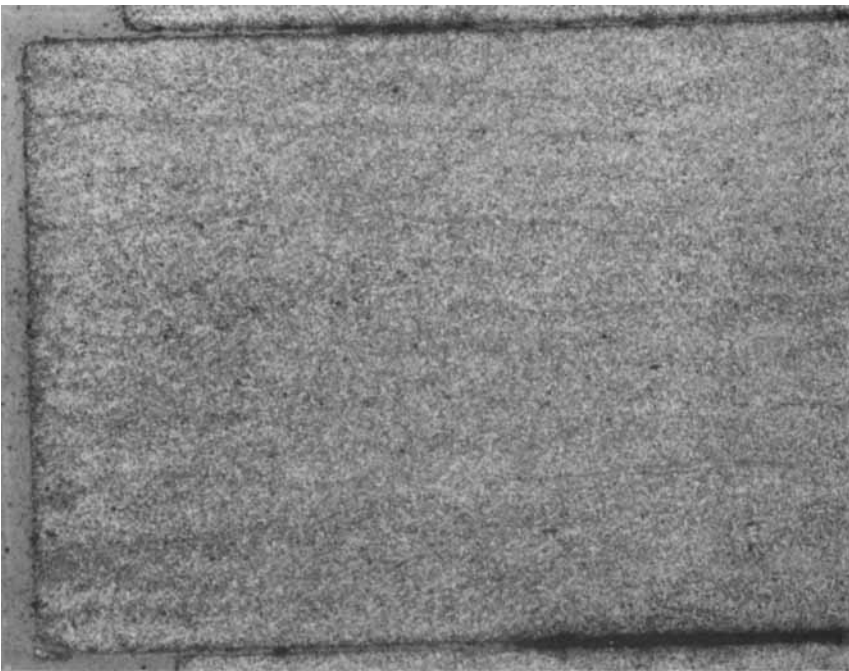


(c)

Fig. 1. (Continued from the previous page.)

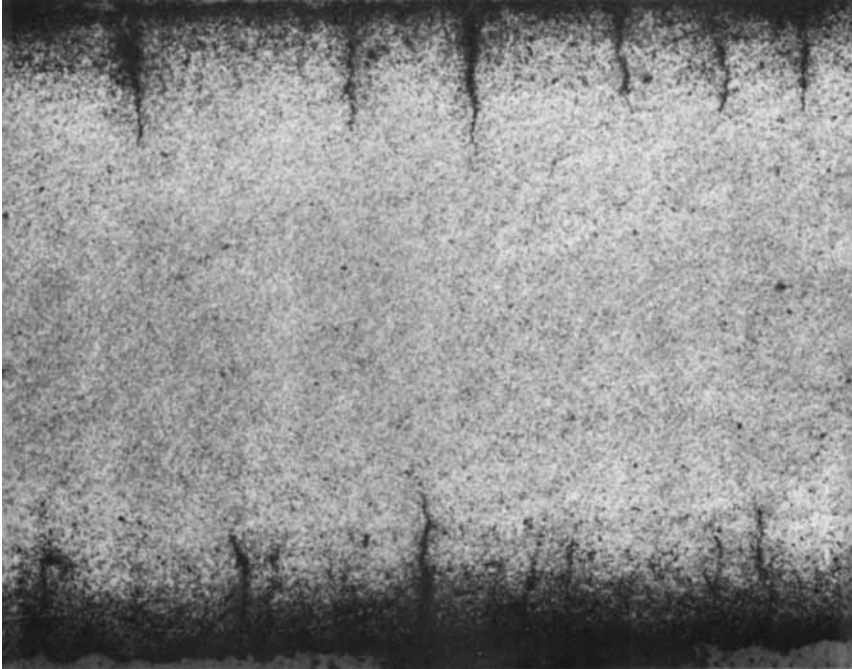


(d)

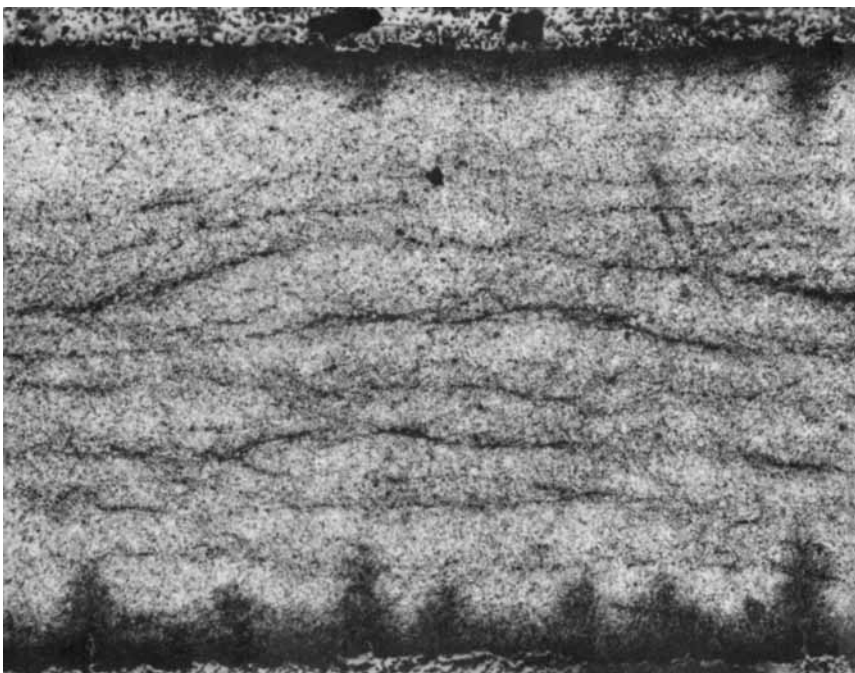


(e)

Fig. 1. (Continued from the previous page.)



(f)



(g)

Fig. 1. (Continued from the previous page.)

TABLE II
Initial Properties of Composites Prepared with 1 and 2

Test	Polymer	No postcure		Postcured ^a	
		RT	316°C	RT	316°C
ILSS (kpsi)	1	10.2	8.5	10.7	7.8
	2	16.5	9.7	17.1	10.3
FS (kpsi) ^b	1	174	103	174	109
	2	171	106	190	125
FM (Mpsi) ^b	1	11.7	9.7	12.1	10.6
	2	10.6	11.1	11.7	11.2

^aTreatment at 316°C for 12 h.

^bValues normalized to 80% fiber content.

TABLE III
Postcure Effects on T_g of Composites Prepared with 1 and 2 (°C)^a

Polymer	No postcure	Postcured ^b	Aged 400 h ^c	Aged 800 h
1	385	380	418	403
1 (PMR)	^d	342	359	385
2	370	375	399	395
2 (PMR)	^d	385	^d	^d

^aDetermined by thermomechanical analysis on the composites.

^b12 h at 316°C.

^cHours at 316°C after postcure treatment.

^dNot determined.

A comparison of 1 and 2 to 1 (PMR) and 2 (PMR) shows that the composites made with the preformed prepolymers 1 and 2 (processed from 3) developed slightly better initial properties than the composites made by PMR (Table V). A comparison of the photomicrographs of 1 and 2 to those of 1 (PMR) and 2 (PMR) (Fig. 1) shows the PMR composites to have more voids. This is the result of a processing problem. The outside of the PMR composites cured fast and formed a stiff frame of cured resin around the interior of the composite. This frame not only decreased the pressure on the uncured interior, but retarded further curing of the interior because of the poor thermal conductivity of the solidified exterior frame.¹⁹ This resulted in a spongy, mechanically weak zone through the center of the finished composite. This is

TABLE IV
 T_g 's of Polymers 1 and 4 (in °C)^a

Treatment	1 (PMR)	12.5% 4/87.5% 1 (PMR)	25% 4/75% 1 (PMR)	50% 4/50% 1 (PMR)	4 (PMR)
None	319	330	348	354	357
12 h at 316°C	341	340	354	360	369
12 h at 345°C	342	346	355	376	384

^aDetermined by thermomechanical analysis of the neat resin flash trimmed from the pressed composites.

TABLE V
Effect of PMR on Initial Composite Properties^a

Test	Test temp. (°C)	Composite			
		1	1 (PMR)	2	2 (PMR)
ILSS (kpsi)	RT	10.7	10.0	11.4	9.4
	316	7.8	5.0	10.3	7.5
FS (kpsi) ^b	RT	174	144	191	95.0
	316	109	79.5	125	84.9
FM (Mpsi) ^b	RT	12.1	12.5	11.7	11.0
	316	10.6	10.9	10.6	10.5

^aAfter postcure of 12 h at 316°C.

^bValues normalized to 80% fiber content.

shown particularly well in Figure 1(b). Thus 1 and 2 flowed better, cured more evenly, and gave a more uniform composite than 1 (PMR) and 2 (PMR).

The addition of the star polymer 4 (PMR) had little effect on the initial composite properties (Table VI) except in the T_g (Table IV). All the composites with 4 (PMR) had properties comparable to 1 (PMR) and 2 (PMR).

Aging

After the postcure, all the composites were aged in air at 316°C in a circulating oven. This was done to determine the thermal stability of the supporting resins, and observe how well the composites could retain their mechanical properties in a harsh environment. Because we were interested in the composite's performance in the harsh environment, all the mechanical testing of the aged composites was done at 316°C.

The weight loss from the composites was followed for 1600 h at 316°C in air. The samples were aged in two ways. Some composites were aged just as they were fabricated (as a coupon), and then cut into test strips. Others, because of the scarcity of samples, had to be aged already cut into test strips in order to obtain a sufficient number of aged test points. Test specimens aged already cut had more resin exposed to air during the aging process than test specimens cut from an aged coupon. Consequently, composites aged as cut strips showed more weight loss and decomposition than samples aged in whole composites. Unless otherwise noted, all samples were aged as cut strips.

TABLE VI
Initial Properties of Composites of 1 (PMR) and 4^a

Test	1 (PMR)	12.5% 4/87.5%	25% 4/75%	50% 4/50%	4 (PMR)
		1 (PMR)	1 (PMR)	1 (PMR)	
ILSS (kpsi)	5.0	6.0	5.5	6.5	5.8
FS (kpsi) ^b	79.5	89.4	77.9	74.2	94.2
FM (Mpsi) ^b	11.1	10.9	10.6	7.5	10.1

^aAfter postcure of 12 h at 316°C, test temperature was 316°C.

^bValues normalized to 80% fiber content.

Weight Loss of 1 and 2 at 316°C.

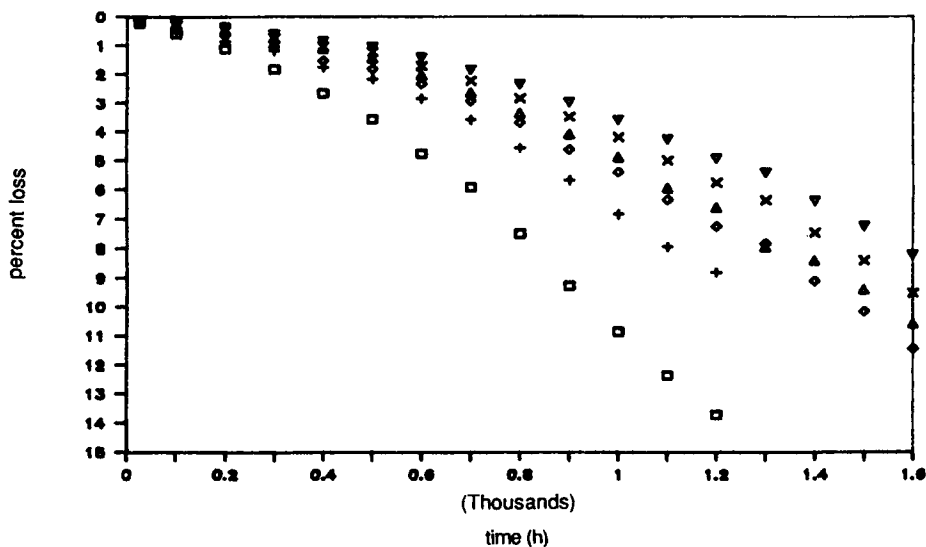


Fig. 2. Weight loss of 1 and 2 at 316°C. □ 2 (PMR); + 2, cut; ◇ 2, uncut; △ 1 (PMR); × 1, cut; ▽ 1, uncut.

Weight Loss of 4 at 316°C.

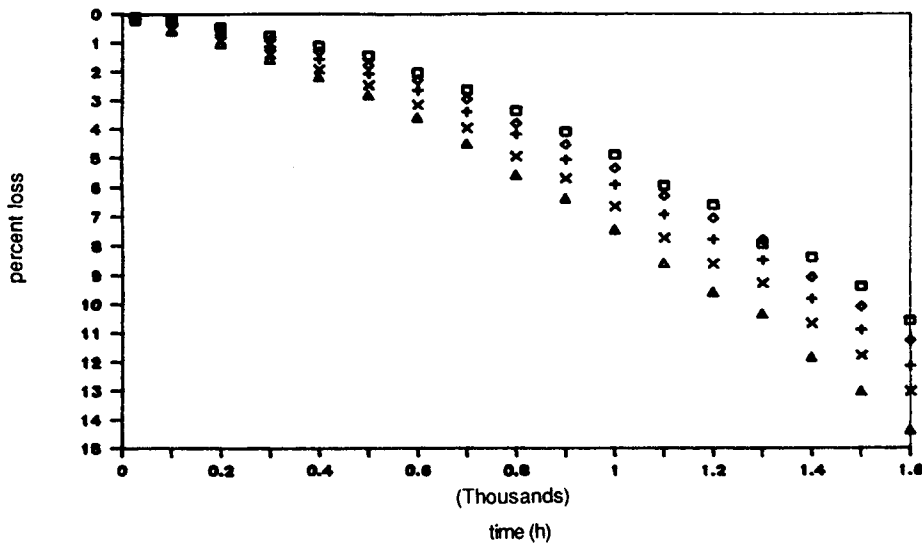


Fig. 3. Weight loss of 4 at 316°C. □ 1 (PMR); + 12.5% 4/87.5% 1 (PMR); ◇ 25% 4/75% 1 (PMR); △ 50% 4/50% 1 (PMR); × 100% 4 (PMR).

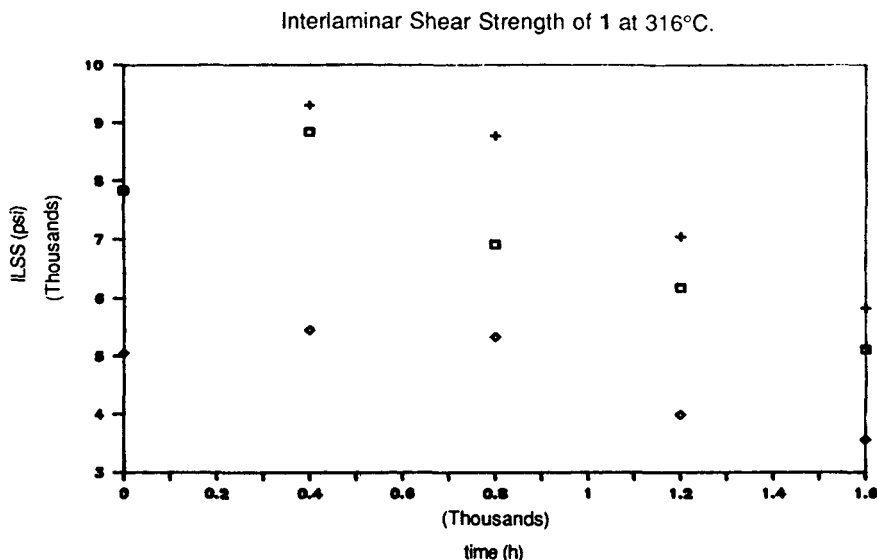


Fig. 4. Interlaminar shear strength of 1 at 316°C. □ 1, cut; + 1, uncut; ◇ 1 (PMR).

The composite with the lowest weight loss was 1, which after 1600 h had lost approximately 8% of the initial weight. The poorest composite was 2 (PMR), which lost approximately 14% after 1200 h (Fig. 2). Composites prepared by PMR lost more weight than composites prepared with preformed prepolymers (Figs. 2 and 3). This is in contrast to studies²⁰ showing that the two polymerizations proceed by the same reaction mechanism, and differ only in the process step in which polyimide is formed. Thus it is difficult to rationalize the difference in weight loss to anything other than processing

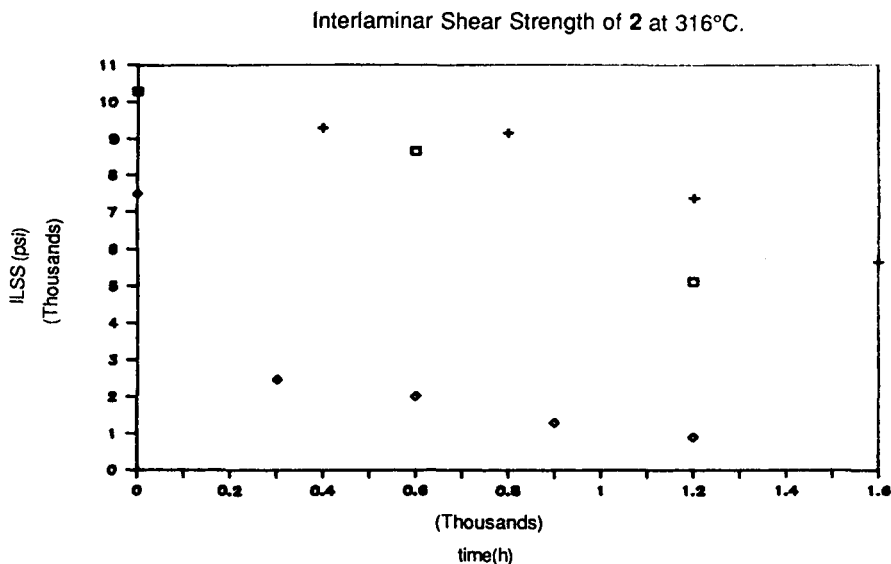


Fig. 5. Interlaminar shear strength of 2 at 316°C. □ 2, cut; + 2, uncut; ◇ 2 (PMR).

Interlaminar Shear Strength of 4 at 316°C.

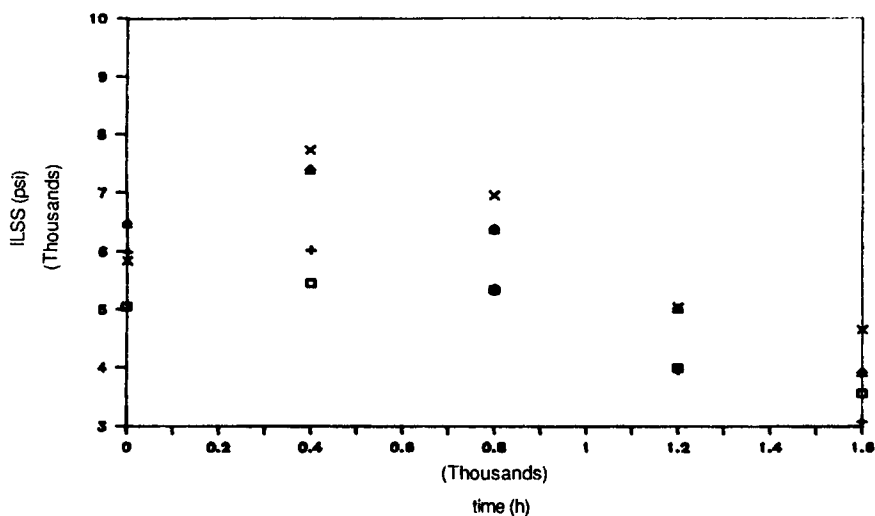


Fig. 6. Interlaminar shear strength of 4 at 316°C. □ 1 (PMR); + 12.5% 4/87.5% 1 (PMR); ◇ 25% 4/75% 1 (PMR); △ 50% 4/50% 1 (PMR); × 4 (PMR).

problems when the PMR technique is applied. The addition of the star point increased the weight loss in comparison with composites prepared with only linear polymers. It is possible that the added crosslink, along with the increased amount of biphenylene and acetylene, caused the resin to gel faster than the linear analog which trapped volatiles in the composite. Upon aging, loss of these volatiles occurred, and thus weight loss tended to increase with increasing star content (Fig. 3).

Normalized Flex Strength of 1 at 316°C.

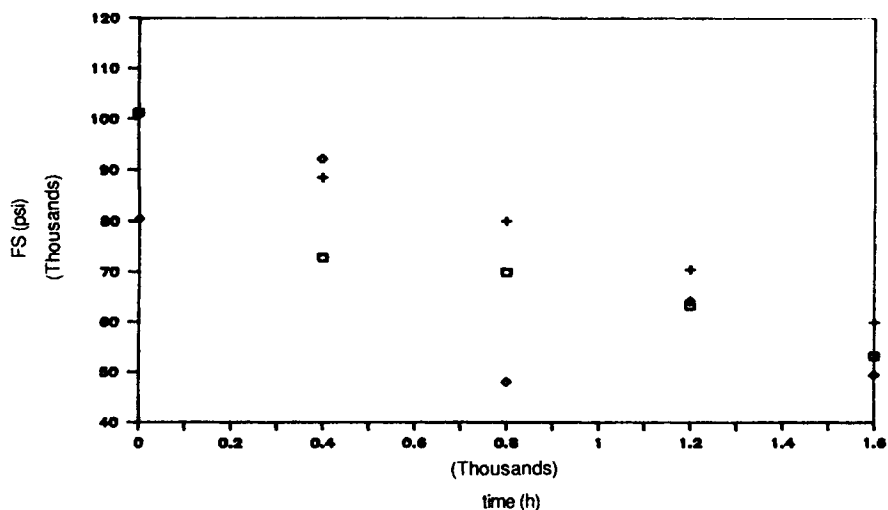


Fig. 7. Normalized flex strength of 1 at 316°C. □ 1, cut; + 1, uncut; ◇ 1 (PMR).

Normalized Flex Strength of 2 at 316°C.

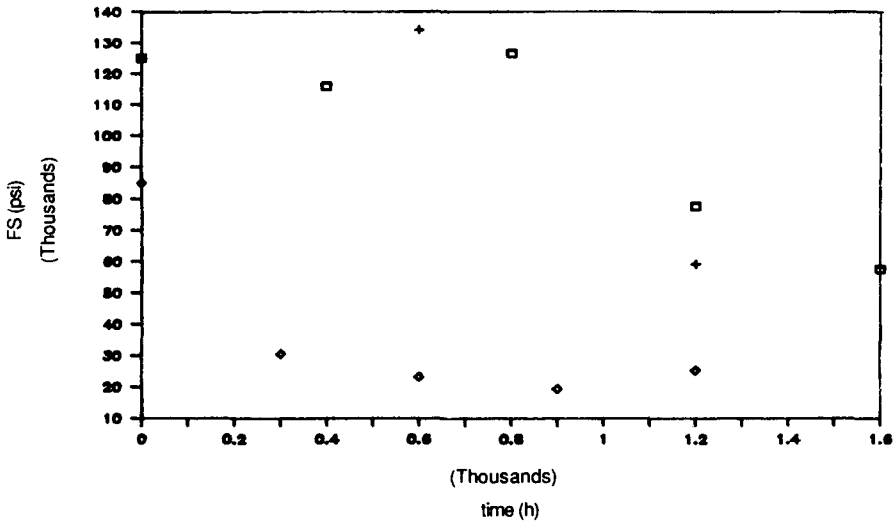


Fig. 8. Normalized flex strength of 2 at 316°C. □ 2, cut; + 2, uncut; ◇ 2 (PMR).

After 1200 h of aging at 316°C, all the composites had reasonable and useful mechanical properties with the exception of 2 (PMR) (Figs. 4-12).

The poor performance of the 2 (PMR) composite is probably due to a combination of the fact that the carbonyl link provides less thermal stability than the hexafluoroisopropylidene link and the uneven rate of curing (edge vs. center) of composites made by the PMR technique. That the carbonyl resin is thermally unstable can be seen from the sharp drop-off of mechanical proper-

Normalized Flex Strength of 4 at 316°C

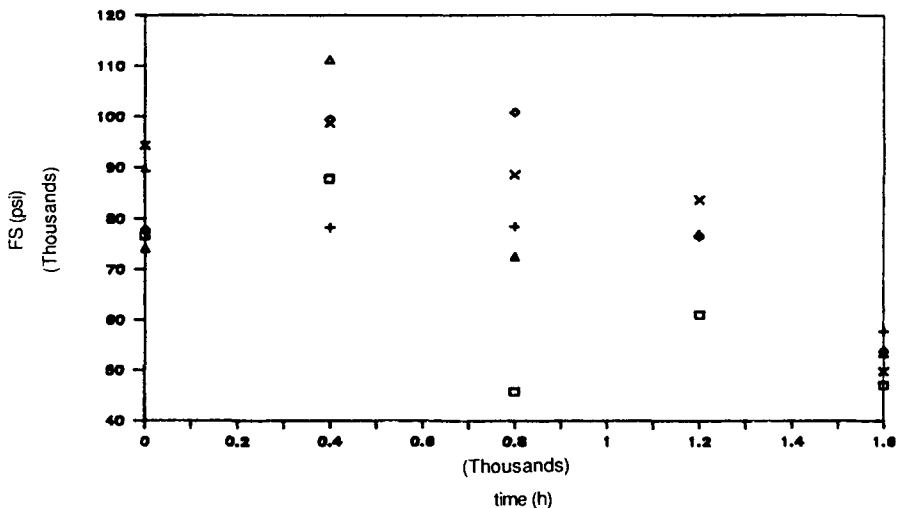


Fig. 9. Normalized flex strength of 4 at 316°C. □ 1 (PMR); + 12.5% 4/87.5% 1 (PMR); ◇ 25% 4/75% 1 (PMR); △ 50% 4/50% 1 (PMR); × 100% 4 (PMR).

Normalized Flex Modulus of 1 at 316°C.

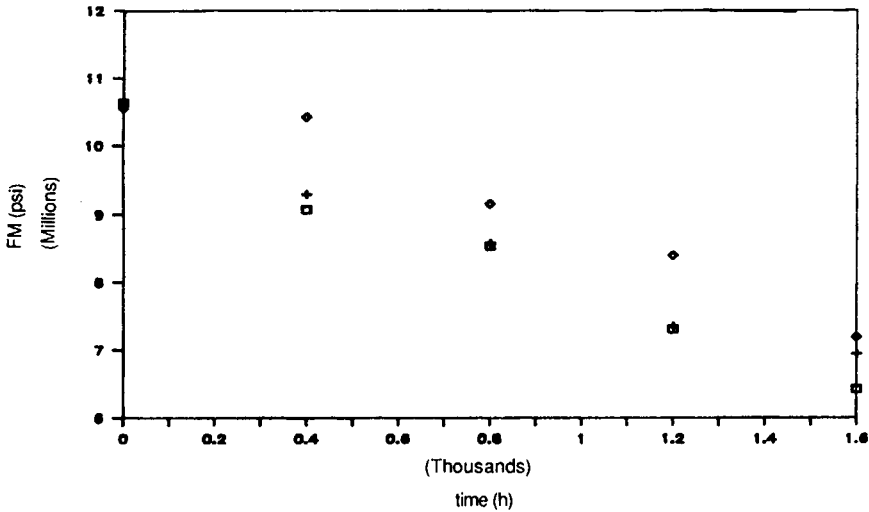


Fig. 10. Normalized flex modulus of 1 at 316°C. □ 1, cut; + 1, uncut; ◇ 1 (PMR).

ties with aging time of all composites made with 2 (Figs. 5, 8, and 11); however, 2 did not experience the total decrease in properties that 2 (PMR) did. When the composite was fabricated using the PMR technique, the problem of the external resin curing faster than the internal resin occurred. Photomicrographs 1f and 1g in Figure 1 show that after 1200 h at 316°C, the composites made from 2 show oxidation advancing from the edges, while composites of 2 (PMR) have large voids in the center as well as at the edges.

Normalized Flex Modulus of 2 at 316°C.

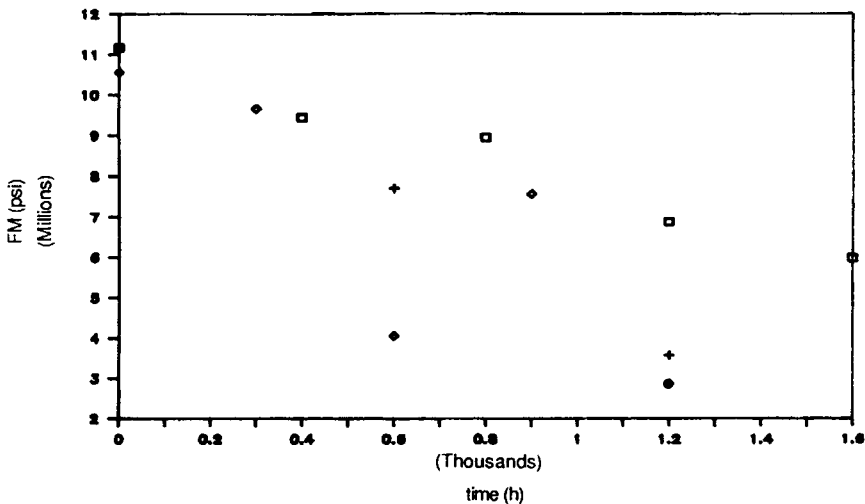


Fig. 11. Normalized flex modulus of 2 at 316°C. □ 2, cut; + 2, uncut; ◇ 2 (PMR).

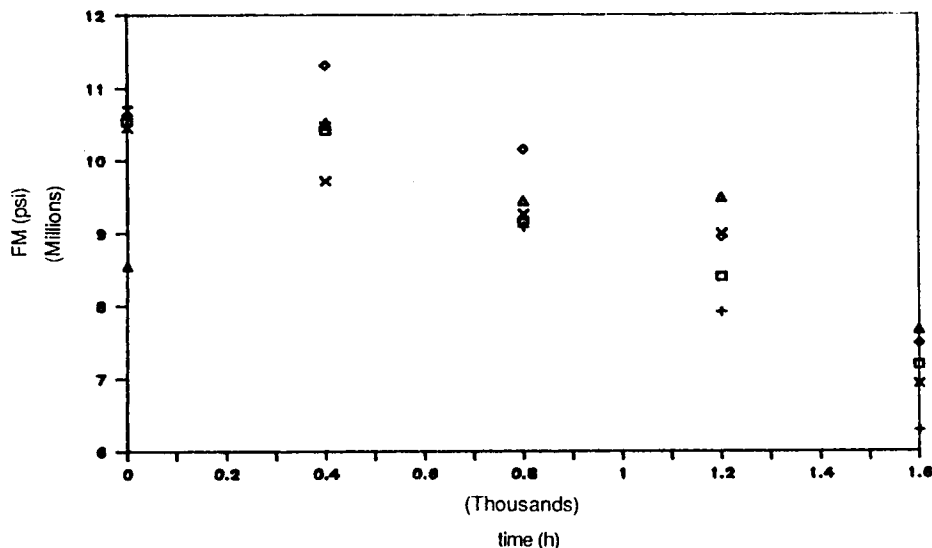


Fig. 12. Normalized flex modulus of 4 at 316°C. □ 1 (PMR); +12.5% 4/87.5% 1 (PMR); ◇ 25% 4/75% 1 (PMR); △ 50% 4/50% 1 (PMR); × 100% 4 (PMR).

The addition of star polymer 4 (PMR) to the composite neither harmed nor improved the composite's mechanical properties (Figs. 6, 9, and 12). This observation was surprising since the weight loss studies (Fig. 5) indicated that all the composites with 4 (PMR) in them lost more weight than composites prepared without the star point.

CONCLUSIONS

Oligomeric polyimides incorporating internal acetylenes and end-capped with biphenylene could be used to prepare good unidirectional composites with Celion-6000 graphite fiber. The composites had good initial mechanical properties, and they were able to maintain these properties after being aged at 316°C in air for 1200 h. For this crosslinking system, composites prepared by PMR technology were slightly inferior to those prepared with preformed prepolymers. The carbonyl composite (2) was not as thermally stable, and did not maintain its mechanical properties after aging as well as the hexafluoroisopropylidene composite (1). The use of star polymers to prepare composites of 4 (PMR), did not have any discernible effect on composite mechanical properties, but did tend to cause increased composite weight loss.

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References

1. P. M. Hergenrother and N. J. Johnson, *Resins for Aerospace*, American Chemical Society, Washington, DC, 1980, ACS Symp. Ser. No. 132.
2. (a) T. T. Serafini, P. Delvigs, and G. R. Lightsey, *J. Appl. Polym. Sci.*, **16**, 905 (1972), (b) T. T. Serafini, P. Delvigs, and G. R. Lightsey, U.S. Patent 2745149, July 1973. (c) T. T. Serafini, P. Delvigs, and W. B. Alston, "PMR Polyimides—Review and Update," NASA TM-82821, 1982, and Proceedings of the 27th National SAMPE Symposium and Exhibition, May, 1982.

3. A. L. Landis and A. B. Naselow, *High Temperature Polymer Matrix Composites*, NASA Conference, Publication 2385, 1985, p. 11.
4. (a) R. J. Jones, G. E. Chang, S. H. Powell, and H. E. Green, *High Temperature Polymer Matrix Composites*, NASA Conference, Publication 2385, 1983, p. 271. (b) F. E. Rogers, U.S. Patent 3356648, December 1967. (c) F. W. Harris, K. Sridhar, and S. Das, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **25**(1), 110 (1984).
5. P. M. Hergenrother, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **25**(1), 97 (1984).
6. P. M. Hergenrother, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C19**(1), 1 (1980).
7. (a) H. R. Lubowitz, U.S. Patent 3 528 950, 1970. (b) H. R. Lubowitz, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **12**(1), 329 (1971).
8. (a) H. H. Gibbs and C. V. Breder, *Copolymers, Polyblends, and Composites*, American Chemical Society, Washington, DC, 1975, *Adv. Chem. Ser. No. 142*, p. 442. (b) H. H. Gibbs, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **35**, 287 (1979).
9. (a) W. Reppe, N. Kutepow, and A. Magin, *Angew. Chem.*, **81**, 717 (1969). *Angew. Chem., Int. Ed., Engl.*, **8**, 727 (1969). (b) F. L. Bowden and A. P. B. Lever, *Organometal. Chem. Rev.*, **3**, 227 (1968). (c) F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969).
10. M. D. Sefcik, E. O. Stejskal, R. A. McKay, and J. Schaefer, *Macromolecules*, **12**, 423 (1979).
11. P. Delvigs, in *Chemistry and Properties of Crosslinked Polymers*, S. Labana, ed., Academic Press, London, 1977, p. 85.
12. (a) R. D. Vannucci and W. B. Alston, "PMR Polyimides with Improved High Temperature Performance" Proceedings of the 31st SPI Reinforced Plastics Composites Institute Conference, February 1976, and NASA TMX-71816. (b) T. T. Serafini, R. D. Vannucci, and W. B. Alston, *Second Generation PMR Polyimides*, NASA TMX-71894, 1976.
13. (a) T. T. Serafini and R. D. Vannucci, "Tailor-Making High Performance Graphite Fiber Reinforced PMR Polyimides," Proceedings of the 30th SPI Reinforced Composites Institute Conference, February 1975, and NASA TMX-71616. (b) W. B. Alston, "Characterization of PMR-15 Polyimide Resin Composition in Thermo-oxidatively Exposed Graphite Fiber Composites," Proceedings of the 12th National SAMPE Technical Conference, October 1980, and NASA TM-81565, 1981.
14. (a) J. Garapon and J. K. Stille, *Macromolecules*, **10**, 627 (1977). (b) A. Recca, J. Garapon, and J. K. Stille, *Macromolecules*, **10**, 1344 (1977). (c) A. Recca and J. K. Stille, *Macromolecules*, **11**, 479 (1978). (d) J. P. Droske and J. K. Stille, *Macromolecules*, **17**, 1 (1984). (e) J. P. Droske, U. M. Gaik, and J. K. Stille, *Macromolecules*, **17**, 10 (1984). (f) D. M. Sutherlin and J. K. Stille, *Macromolecules*, **19**, 12 (1986).
15. J. P. Droske, J. K. Stille, and W. B. Alston, *Macromolecules*, **17**, 14 (1984).
16. (a) L. Friedman and P. W. Rabideau, *J. Org. Chem.*, **33**, 451 (1968). (b) J. J. Eisch, A. M. Piotrowski, K. L. Han, C. Krüeger and Y. H. Tsay, *Organometallics*, **4**, 224 (1985).
17. D. M. Sutherlin, J. Stille, and W. B. Alston, *Macromolecules*, **19**, 257 (1986).
18. (a) T. Takeichi and J. K. Stille, *Macromolecules*, **19**, 2103 (1986). (b) T. Takeichi and J. K. Stille, *Macromolecules*, **19**, 2108 (1986). (c) T. Takeichi and J. K. Stille, *Macromolecules*, **19**, 2093 (1986).
19. J. P. Reardon, *Adv. Compos.*, **March**, 98 (1987).
20. J. C. Johnston, M. A. B. Meador, and W. B. Alston, *J. Polym. Sci. A-1*, **25**, 2175 (1987).

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