$[\eta]_{inh}$ = 0.44 dL/g (25.0 °C, 0.5% solution (w/w), sulfuric acid). Anal. Calcd: C, 83.50; H, 4.21; N, 9.64. Found: C, 83.69; H, 4.26; N, 9.31. The molecular weight of **6** is reported in Table II.

Resin Melt Processing. Catalyst was added to the prepolymers as follows. The appropriate amount of bis(triphenylphosphine)dicarbonylnickel(0) (Aldrich) was added to the prepolymer swelled in benzene. The mixture was stirred for 1 h, the solvent was removed under reduced pressure, and the resulting powder was dried at 75 °C (0.05 mmHg) for 18 h.

A modified Wabash hydraulic press (Model 12 10) fitted with Carver heated platens (no. 2102) was used for the neat resin processing. A 170-mg sample of the prepolymer powder was placed in a small pile between 2–6 in. × 6 in. pieces of copper foil (0.005-in. thick, Baker no. 1-1714) with a 0.005-in. copper foil spacer. The assembly was placed in the hydraulic press and melt processed at 300–371 °C (572–700 °F) under 500–1000 psi for various times. plunging of the assembly into cold water immediately after processing facilitated removal of the film from the copper foil. Any residual copper that adhered to the surface of the film was removed by placing the film in concentrated ammonium hydroxide for ~30 min, followed by thorough rinsing with water.

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Registry No. **2**, 87829-09-2; **4**, 87830-94-2; **6**, 87830-95-3; biphenylene-2-carbonyl chloride, 75292-39-6; 2-biphenylenyl benzyl ketone, 87830-92-0; 2-(phenylglyoxylyl)biphenylene, 87830-93-1; *N*-(2-biphenylene)acetamide, 86746-53-4; 2-biphenyleneamine, 55716-75-1; bis(triphenylphosphine)dicarbonylnickel, 13007-90-4.

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Biphenylene End-Capped Polyquinoline and Polyimide Prepolymers as Matrix Resins for High-Use-Temperature Composites

John P. Droske and John K. Stille*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

William B. Alston

NASA—Lewis Research Center, Propulsion Laboratory, U.S. Army, AVRADCOM Research and Technology Laboratories, Cleveland, Ohio 44135. *Received March 8, 1983*

ABSTRACT: Graphite-reinforced composites were prepared from biphenylene end-capped polyquinoline and polyimide prepolymers. The composites demonstrated excellent initial properties and low weight loss after oxidative aging at 316 °C. However, the mechanical properties were severely diminished after aging for 50–100 h at 316 °C in air, and photomicrographs of the composites after aging showed the presence of voids.

Introduction

In the preceding two papers, the synthesis of certain biphenylene end-capped, low molecular weight polymers in which the oligomeric main chain consisted of polyaromatic units that are known to possess good thermal stability was described. The high molecular weight analogues of these polymers containing those polyaromatic recurring units, but without the biphenylene end caps, are some of the most resistant polymers to thermooxidative degradation known. Of those prepolymers synthesized, the biphenylene end-capped polyquinolines had the best processing characteristics, in that they were readily soluble in common organic solvents and could be melt pressed into films.

The ultimate utility of such prepolymers is in the preparation of high-strength fiber-reinforced composities. In order to evaluate the biphenylene approach to fiber-reinforced composites, the preparation of laminates of biphenylene end-capped polyquinolines and polyimides was undertaken.

Polyquinolines were selected because of their excellent processing characteristics, and polyimides were included since 2-aminobiphenylene was compatible with the polyimide processing technology exhibited by the state-of-the-art nadic end-capped polyimide, PMR-15.[1] The polyimide resin PMR-15 contains not only a benzylic carbon (diphenylmethane-type unit) in the main chain but aliphatic units resulting from the norbornene imide end groups. Thus, the thermooxidative stability and long-term high-temperature properties of PMR-15[1,2] would be expected to be less than those of high molecular weight polyimide resins void of aliphatic groups.[3,4] Modified PMR polyimide resins containing aromatic perfluoroisopropylidene units in the main chain and phenyl groups in place of diphenylmethane units have better thermooxidative stability and comparable high-temperature me-

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Table I
Properties of Polyquinoline Composites Prepared in the Presence of Bis(triphenylphosphine)dicarbonylnickel(0) Unidirectional Celion-6000 Graphite Fiber[a]

postcure conditions[b] (h/temp)	T_g,[c] °C (TMA)	room-temp ILSS,[d] psi	flex strength,[d] psi		flex modulus,[d] psi	
			room temp	316 °C (600 °F)	room temp	316 °C (600 °F)
	222 (432 °F)	9000	228 000	36 000[e]	16 200 000	3 400 000
100 h/316 °C (600 °F)	261 (502 °F)	6800	182 000	59 000	14 800 000	7 900 000
51 h/343 °C (650 °F)		2200	145 000	52 000	15 200 000	4 500 000

[a] 36% resin content by weight. [b] In circulating air. [c] Thermal mechanical analysis. [d] Thermoplastic (nonbrittle) breaks observed in all cases. [e] Tested at 260 °C (500 °F) due to low T_g.

Table II
Properties of Polyquinoline Composites Prepared without Added Catalyst Celion-3000 Graphite Cloth[a]

postcure conditions[b] (h/temp)	T_g,[c] °C (TMA)	ILSS,[d] psi		room-temp flex strength,[d] psi	room-temp flex modulus,[d] psi
		room temp	316 °C (600 °F)		
	219 (426 °F)	5000		88 000	10 500 000
100 h/316 °C (600 °F)	242 (468 °F)[e]	3900	1300		

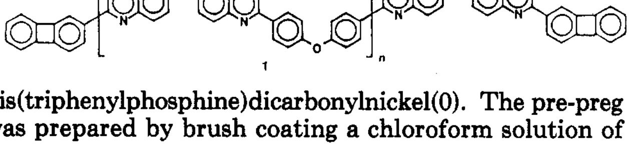
[a] 30% resin content by weight. [b] In circulating air. [c] Thermal mechanical analysis. [d] Thermoplastic (nonbrittle) breaks observed in all cases. [e] After 48 h at 316 °C (600 °F).

chanical properties as compared with PMR-15[5,6] but still have the potential to undergo degradation at the site of cross-linking due to the aliphatic cross-linker. Polyimide resins containing a higher content of nadic cross-linking groups have improved processability but, in fact, also exhibit lower thermooxidative stability.[7,8] The initial weight loss in the thermooxidative degradation of PMR-15 has been shown to be attributable to both the nadic and diphenylmethane units but ultimately the nadic cross-linking unit becomes the more significant contributor to overall resin weight loss.[9] Thus, biphenylene end-capped prepolymers—such as a polyquinoline or a polyimide containing no aliphatic in-chain units—held promise as a superior matrix resin, since the biphenylene end groups would undergo chain extension to yield the all-aromatic tetrabenzocyclooctatetraene unit or react with the polymer main chain to yield an aromatic cross-link.

Results and Discussion

In the preparation of laminates, large quantities (~500 g) of prepolymers usually are necessary for reasonable composite evaluation, due to the necessity of determining optimum processing and postcure cycles. Since there was a limited amount of biphenylene end-capped polyquinoline available, an alternative approach to the preparation of test specimens was used. Small molds (1 × 2.7 in.) that required a minimum amount of resin per composite (1.5 g) were utilized. Each 1 × 2.7 in. composite afforded three flexural specimens and five interlaminar shear specimens.

Unidirectional graphite-fiber-reinforced composites were prepared from biphenylene end-capped polyquinoline prepolymer 1 containing 20 mol % (based on biphenylene)



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bis(triphenylphosphine)dicarbonylnickel(0). The pre-preg was prepared by brush coating a chloroform solution of the prepolymer and catalyst onto the graphite fiber reinforcement. Application from only one side did not afford suitable fiber wetting, and resin had to be applied to both sides of the fiber. The resultant pre-preg was boardy and of only fair quality due to shrinkage of the fiber bundle as a result of the inability to restrict the unidirectional reinforcement from all sides during application of the resin. The pre-preg was assembled in 7- or 8-ply stacks and melt processed in a 1 × 2.7 in. mold at 330 °C (625 °F) under 1500 psi for 2 h. The cured composites gave a metallic-like ring when dropped on a hard surface and exhibited good room-temperature flexural properties but only modest interlaminar shear strength (Table I). Thermoplastic breaks were observed in all cases, which suggested a low cross-link density. The T_g increased during postcuring in air; however, the mechanical properties severely diminshed as evidenced by a decrease in the room-temperature mechanical properties and the failure of the laminate to give a metallic-like ring when dropped on a hard surface.

In an effort to improve the pre-pregging of prepolymer 1, graphite cloth was employed in place of unidirectional graphite fiber. Brush coating of a chloroform solution of prepolymer 1 onto the fiber reinforcement restrained on all four edges gave a boardy but good quality pre-preg that showed minimum shrinkage upon solvent removal. The Ni(0) catalyst was not used in the preparation of the cloth composites in order to determine if the catalyst had a deleterious effect on the composite properties. Since the uncatalyzed ring opening of biphenylene occurs at ~440 °C (maximum exotherm), a higher cure temperature was required. The melt processing of 6-ply layups was conducted at 388 °C (730 °F) under 2000 psi for 3 h and gave composites that showed good resin flow as indicated by the presence of flash. The composites gave a metallic-like ring when dropped on a hard surface. Again, postcuring resulted in severely decreased mechanical properties (Table II) and thermoplastic breaks were observed. The thermoplastic (nonbrittle) breaks were attributable to a low cross-link density and a flexible polymer backbone.

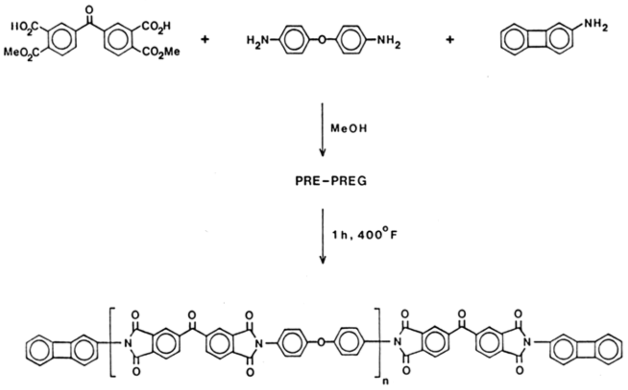
The PMR (polymerization of monomer reactants)[1] approach was employed in the preparation of biphenylene end-capped polyimide graphite-fiber-reinforced composites. A methanolic solution of 4,4′-diaminodiphenyl ether, 2-aminobiphenylene, and the dimethyl ester of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride was brush coated onto unidirectional Celion-6000 graphite fiber (Scheme I). The resultant pre-preg showed desirable tack and drape. (The Ni(0) catalyst was not used due to poor solubility in the binder solution and the previous observation that low-$\overline{DP}$ prepolymers showed restricted flow when melt processed in the presence of the Ni(0) catalyst.)

Table III
Properties of Composites Prepared from Polyimide Prepolymers Celion-6000 Unidirectional Graphite Fiber

			ILSS, psi		flex strength, psi		flex modulus, psi	
end cap	postcure conditions[a] (h/temp)	T_g,[b] °C (TMA)	room temp	316 °C (600 °F)	room temp	316 °C (600 °F)	room temp	316 °C (600 °F)
nadic[c]	16 h/316 °C (600 °F)	332 (630 °F)	17 000	7 300	250 000	140 000	17 400 000	16 200 000
biphenylene[d]		263 (505 °F)	14 000		287 000	90 000[e]	20 200 000	15 600 000[e]
biphenylene[d]	50 h/316 °C (600 °F)			6 000[e]	270 000	156 000[e]	18 300 000	16 700 000[e]
biphenylene	150 h/316 °C (600 °F)	337 (639 °F)	11 000	7 000[e]				
phenyl		246 (475 °F)	8 700	3 600[e]				
phenyl	47 h/343 °C (650 °F)[e]	250 (482 °F)	10 000	5 700[e]	139 000[d]		12 300 000[e]	

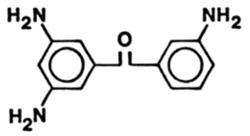
[a] In circulating air. [b] Thermal mechanical analysis. [c] Properties of PMR-15 composites for comparison. PMR-15 employs 4,4′-methylenedianiline as the diamine monomer and has $n = 2.09$. The other composites were prepared using 4,4′-diaminodiphenyl ether as the diamine monomer and have $n = 4.89$. All composites were prepared with the dimethyl ester of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride as the acid ester monomer. [d] 30% resin content by weight. [e] Thermoplastic (nonbrittle) breaks.

Scheme I



Staging of 9-ply layups at 204 °C (400 °F) permitted loss of volatiles prior to molding. Composites were prepared by processing the ply stack at 391 °C (735 °F) under 1500 psi for 3 h. The resultant composites showed excellent properties; however, testing at 316 °C (600 °F) indicated thermoplastic breaks even after postcuring (Table III), which suggested that only a moderate degree of cross-linking had been realized. As a control, a phenyl end-capped polyimide was prepared similarly, except aniline was used in place of 2-aminobiphenylene. The composite made from phenyl end-capped polyimide clearly showed inferior properties compared to composites prepared with biphenylene end-capped polyimide prepolymers (Table III).

To increase the cross-link density, a trifunctional amino monomer was used as a branching site. The pre-preg was prepared as before except 3–10 mol % of 4,4′-diaminodiphenyl ether was replaced with 3,3′,5′-triaminobenzophenone (**2**). The staged pre-preg was processed at 391 °C (735 °F) under 2000 psi for 3 h. The higher pressure (2000 compared to 1500 psi) was used since the branch site was expected to reduce polymer flow. The composites in which 3 and 5 mol % of 4,4′-diaminodiphenyl ether had been replaced with **2** showed excellent mechanical properties both at room temperature and at 316 °C (600 °F) (Table IV). All breaks were true thermoset (brittle) breaks, which confirmed that a sufficient cross-link density had been achieved. Particularly interesting was the observation that replacement of 10 mol % of 4,4′-diaminodiphenyl ether afforded a composite in which the desired biphenylene reaction had been inhibited, as evidenced by the lower T_g and the thermoplastic ILSS break. This was attributed to the reduced mobility of the polymer chains due to the high branch site concentration and gave a polymer with a low cross-link density that was primarily chain extended through the branch site.



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Although composites with state-of-the-art initial properties had been prepared, loose surface fiber was observed in all composites prepared from biphenylene end-capped prepolymers oxidatively aged for 50–100 h at 316 °C (600 °F), even though the composite weight loss during aging was only 1–2.5% (polyquinoline and polyimide composites). Furthermore, aged composites no longer gave a metallic-like ring when dropped on a hard surface. These

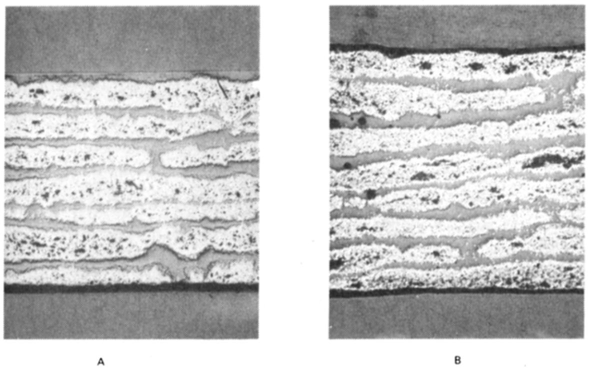

Figure 1. Photomicrographs (20×) of composites prepared from biphenylene end-capped polyquinoline prepolymers in the presence of bis(triphenylphosphine)dicarbonylnickel(0): (A) before aging; (B) after oxidative aging for 51 h at 343 °C (650 °F). (Light gray areas are fiber, darker gray areas are resin, and very dark areas in resin are voids).

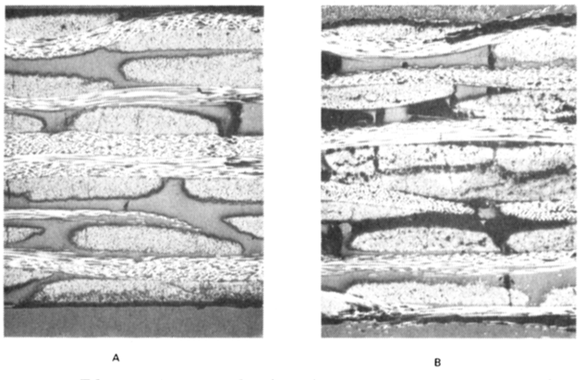

Figure 2. Photomicrographs (20×) of composites prepared from biphenylene end-capped polyquinoline prepolymers without added catalyst (graphite cloth reinforcement): (A) before aging; (B) after oxidative aging for 96 h at 316 °C (600 °F).

Table IV
Properties of Composites Prepared from Biphenylene End-Capped Polyimide Prepolymers Containing 3,3′,5′-Triaminobenzophenone

mol % diamine replaced with triamine	postcure conditions[a] (h/temp)	T_g,[b] °C (TMA)	ILSS, psi room temp	ILSS, psi 316 °C (600 °F)	316 °C (600 °F) flex strength, psi	316 °C (600 °F) flex modulus, psi
3		298 (568 °F)	13 000			
3	14 h/343 °C (650 °F)	325 (617 °F)	12 000	7 300		
5[c]	47 h/316 °C (600 °F)	328 (622 °F)	13 000	6 800	186 000	17 300 000
10	43 h/316 °C (600 °F)	310 (590 °F)	9 600[d]	5 400[d]		

[a] In circulating air. [b] Thermal mechanical analysis. [c] 26% resin content by weight. [d] Thermoplastic (nonbrittle) break.

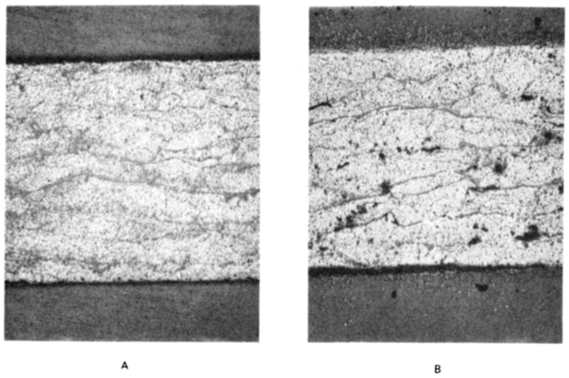

Figure 3. Photomicrographs (20×) of composites prepared from biphenylene end-capped polyimide prepolymers without added catalyst: (A) before aging; (B) after oxidative aging for 50 h at 316 °C (600 °F).

observations suggested that the biphenylene end-capped matrix resins were not particularly thermooxidatively stable. Photomicrographs of polyquinoline and polyimide composites before and after oxidative isothermal aging at 316 °C (600 °F) confirmed that the resins degraded during aging (Figures 1–4). Photomicrographs of composites prepared from biphenylene end-capped polyquinoline prepolymer 1 containing 20 mol % (based on biphenylene) of the Ni(0) catalyst showed the least degradative void formation even though the composite properties had diminished considerably and the weight loss during aging was comparable to the other laminates (Figure 1). The composite also had the lowest amount of loose surface fiber after aging. While it is not possible to explain the observations with certainty, the results suggest that the Ni(0) catalyst does not necessarily have a deleterious effect on the thermooxidative stability of the composites and actually may impart some desirable characteristics.

While the actual mechanism of degradation of the composites is not known, high-energy aromatic radicals are undoubtedly involved due to the rapid and catastrophic nature of the degradation. In an effort to determine if unreacted biphenylene was responsible for the degradation, higher processing temperatures were employed in an attempt to complete the reaction of the biphenylene end groups. However, polyimide composites melt processed at 427 °C (800 °F) for 3 h showed more rapid degradation when oxidatively aged at 316 °C (600 °F) than those processed at 391 °C (735 °F). A polyimide prepolymer in which 25 mol % of 4,4′-diaminodiphenyl ether was replaced with 4,4′-methylenedianiline also afforded an inferior composite. The benzylic hydrogens in methylenedianiline did not improve the thermooxidative stability by acting as a sink for high-energy aromatic radicals. Finally, isothermal aging of a polyimide composite for 71 h at 343 °C (650 °F) under a nitrogen atmosphere showed low composite weight loss and no loose surface fiber. However, aging of the resultant composite under oxidative conditions at 316 °C (600 °F) resulted in rapid and severe degradation.

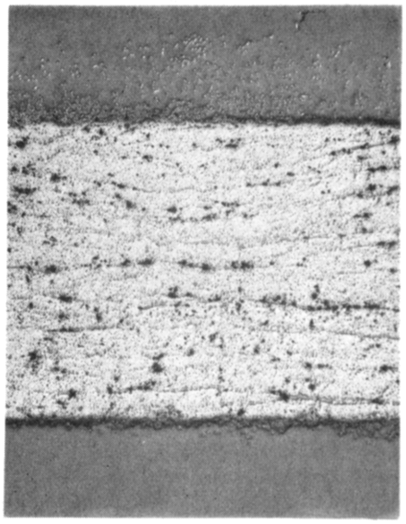

Figure 4. Photomicrograph (30×) of a composite prepared from a biphenylene end-capped polyimide prepolymer in which 5 mol % of 4,4′-diaminodiphenyl ether was replaced with 3,3′,5′-triaminobenzophenone. After aging 47 h at 316 °C (600 °F).

Conclusions

The high thermooxidative stability of resins prepared from biphenylene end-capped polyquinolines and polyimides was not realized. Curing takes place primarily by a chain extension reaction in which biphenylene ends give tetrabenzocyclooctatetraene linkages. A limited amount of cross-linking takes place by attack of a biphenyl diradical (obtained from the opening of biphenylene) on the backbone of a neighboring polymer chain. The amount of cross-linking is sufficient to provide insolubility but not sufficient to avoid thermoplastic breaks. Thus, the use of a small amount of trifunctional monomer to give some branched polymer containing three biphenylene ends was necessary to give sufficiently cross-linked resin.

The two most probable sources of degradation are the biphenylene end caps, which remain unreacted during postcuring, and the product of the biphenylene chain extension reaction, tetrabenzocyclooctatetraene. When biphenylene is pyrolyzed at 430–445 °C, the yield of tetrabenzocyclooctatetraene decreases at the expense of polymeric products.[10,11] In this pyrolysis, either the biphenylene is leading to the polymeric products or the initially formed tetrabenzocyclooctatetraene is underoging further degradation to yield polymer. In the latter case, tetrabenzocyclooctatetraene may be the source of high-energy radicals which, on aging, pick up oxygen from the air. Alternatively, because polymer chain motion is restricted as curing progresses, the biphenylene ends may become isolated and be unable to undergo appreciable further reaction in the polymer matrix. As a result, on isothermal aging, the remaining biphenylene ends can react with oxygen and lead to rapid degradation.

Experimental Section

Thermal analyses were performed with a DuPont 990 thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base (heating rate 10 °C/min) and a 943 thermal mechanical analyzer (TMA, heating rate 20 °C/min). Oxidative isothermal aging was performed in a circulating-air oven. Unless otherwise noted, all monomers and solvents were obtained from commercial suppliers and used without further purification.

Biphenylene End-Capped Polyquinoline (1 ($\overline{DP}$ = 22)). This oligomer was prepared as described in the first paper in this series.

Unidirectional Graphite-Fiber-Reinforced Composites Prepared from Biphenylene End-Capped Polyquinoline Prepolymer 1. A chloroform solution of 1 and 2.5 wt % (based on the prepolymer) of bis(triphenylphosphine)dicarbonylnickel(0) was brush coated onto Celion-6000 unidirectional graphite fiber wound on a rotating drum. After air-drying, 7- and 8-ply 1 × 2.7 in. layups were staged for 1 h at 121 °C (250 °F) and melt processed in a steel mold at 330 °C (625 °F) under 1500 psi for 2 h. The composite properties are given in Table I.

Graphite-Cloth-Reinforced Composites Prepared from Biphenylene End-Capped Polyquinoline Prepolymer 1. A chloroform solution of 1 was brush coated onto both sides of a piece of Celion-3000 graphite cloth restrained on all four edges. After air-drying, 6-ply 1 × 2.7 in. layups were staged for 1 h at 121 °C (250 °F) and melt processed in a steel mold at 388 °C (730 °F) under 2000 psi for 3 h. The composite properties are reported in Table II.

Unidirectional Graphite-Fiber-Reinforced Composites Prepared from Biphenylene End-Capped Polyimide Prepolymers. PMR Approach.[1] A methanolic solution of 4,4′-diaminodiphenyl ether, 2-aminobiphenylene, the dimethyl ester of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, and, in some cases, 3,3′,5′-triaminobenzophenone was brush coated onto Celion-6000 unidirectional graphite fiber wound on a rotating drum. The resultant pre-preg showed desirable tack and drape. After air-drying, 9-ply 1 × 2.7 in. layups were staged at 204 °C (400 °F) for 1 h and melt processed at 391 °C (735 °F) under 1500–2000 psi for 3 h. The composite properties are given in Tables III and IV.

Composite Resin Content. The resin content of selected composites was determined by digestion of weighed composite samples in hot sulfuric acid, with the periodic addition of 30% hydrogen peroxide.[12] The digestion afforded recovered resin-free fiber, which permitted the calculation of resin content by the relation % resin content = 100 × {1 − [(weight of resin-free fiber)/(weight of composite sample)]}. The resin contents of polyquinoline and polyimide composites are reported in Tables I–IV.

Composite Properties. (a) Interlaminar Shear Strength (ILSS). The interlaminar (or short beam) shear strength was determined by applying a load to a short (span/depth of 5/1) composite specimen supported lengthwise in a chuck. The specimen was pushed against a pin until failure. The pressure at failure was measured by an Instron equipped with a high-temperature oven. (Since the specimen is short, failure occurs between plies. Thus, the ILSS affords a measure of the resin's ability to transfer the load from one ply to the next in a composite.) The ILSS of the composites as determined by ASTM D2344-76 are reported in Tables I–IV.

(b) Flex Strength and Flex Modulus. An analysis similar to the above was performed except longer (2 in.) specimens were used. In this test, failure occurs perpendicular to the fiber axis in the specimen. 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. The flex strengths and flex moduli of the composites as determined by ASTM D790-71 are reported in Tables I–IV.

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Registry No. 1, 85884-44-2; biphenylene end-capped polyimide, 87829-09-2; 2-aminobiphenylene, 55716-75-1.

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