

ALL-AROMATIC BIPHENYLENE END-CAPPED POLYQUINOLINE

AND POLYIMIDE MATRIX RESINS

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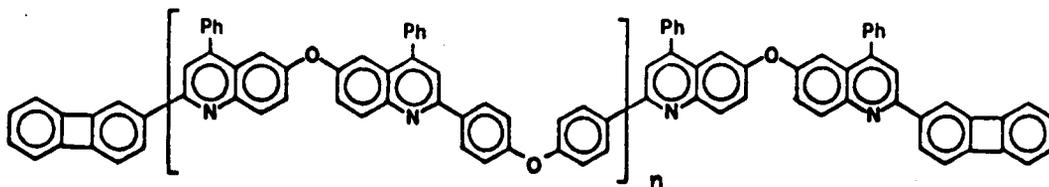
A promising approach to the processing of thermally stable polymers is the use of oligomeric pre-polymers containing reactive end-groups which undergo crosslinking/chain extension during processing and post-cure. Unfortunately, end-capped pre-polymers generally afford processed materials which show lower retention of properties for extended periods at high temperatures than would be expected had an all-aromatic, high molecular weight polymer been employed. Since the decreased thermo-oxidative stability is partly attributable, in some cases, to the use of aliphatic reactive end-groups (ref. 1), end-groups which afford more thermally stable structures are desired.

Biphenylene is an especially attractive reactive end-cap for high performance composite resins due to its all-aromatic structure. Biphenylene undergoes thermolysis above 350°C to afford tetrabenzocyclooctatetraene (tetraphenylene), aromatic polymer, or stable aromatic compounds depending on the reaction conditions (ref. 2 and fig. 1). Thus, any structure formed as a result of the thermolysis of a biphenylene unit in a thermally stable polymer would be expected to maintain the all-aromatic character and high temperature performance of the polymer. The temperature necessary for the ring opening reaction can be lowered by the addition of appropriate transition metal catalysts, such as (NBD Rh Cl)₂ and (PPh₃)₂ Ni(CO)₂ which are known to open strained cyclic hydrocarbons by an oxidative addition mechanism (ref. 3).

RESULTS AND DISCUSSION

Neat Resin Properties

Of the various polyquinolines that have been prepared (ref. 4), the ether-ether linked polyquinoline showed the greatest promise as a laminating resin due to its good solubility in common organic solvents (e.g. CHCl₃) and its relatively low



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T_g (266°C). We envisioned that the use of an oligomeric ether-ether linked polyquinoline would give a most processable thermoplastic resin, which could be converted to a thermosetting resin with a high T_g after processing by reaction of the biphenylene end-groups. Since it is desirable to use the least amount of the biphenylene end-cap possible (functionalized biphenylenes are only prepared with considerable difficulty), a series of biphenylene end-capped oligomeric polyquinolines having various degrees of polymerization were prepared.

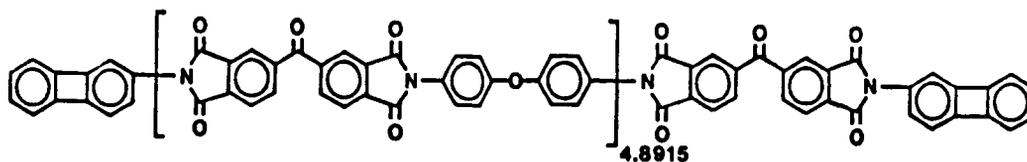
The neat resins, containing 2.5 wt% (Ph₃P)₂Ni(CO)₂, were melt pressed into thin films at 325° under 5000 lb. load for 15 minutes. All films after processing were insoluble (24 hours in CHCl₃) and had T_g's of 235°- 243°C. Young's modulus above T_g increased by an order of magnitude due to the crosslinking (Table 1). It was surprising that the T_g as well as the mechanical properties above T_g after processing were independent of the degree of polymerization and thus, the concentration of biphenylene end-caps. The results suggested that a limited and approximately equal amount of crosslinking was occurring in each of the three samples. As a control, phenyl end-capped polyquinolines of $\overline{DP} = 11$ and $\overline{DP} = 22$ were prepared and melt processed in the presence of the Ni° catalyst under the same conditions. The $\overline{DP} = 11$ material had very poor film qualities whereas the $\overline{DP} = 22$ material processed into a good quality, transparent film. However, both samples after processing were completely soluble in CHCl₃ and showed no increase in T_g indicating that no crosslinking/chain extension occurred in the absence of the biphenylene end-cap.

Thermal gravimetric analysis of melt pressed film samples of biphenylene end-capped polyquinoline ($\overline{DP} = 22$) containing 2.5 wt% (PPh₃)₂ Ni(CO)₂ showed breaks in air and nitrogen of 535°C and 570°C, respectively. These values are comparable to those obtained with film samples of high molecular weight polyquinolines cast from solution. However, oxidative isothermal aging at 300°C for 100 h showed 3% weight loss for the melt pressed film of biphenylene end-capped polyquinoline whereas the high molecular weight polyquinoline film showed 0% weight loss during the same aging.

Composite Properties

Graphite-reinforced composites were prepared from biphenylene end-capped polyquinoline of $\overline{DP} = 22$. This degree of polymerization was considered to be an optimum of processability with a minimum incorporation of the biphenylene end-cap since no gains were realized when a lower degree of polymerization polyquinoline (containing a corresponding higher concentration of the biphenylene end-cap) was used. Pre-pregs were prepared by brush-coating a chloroform solution of the polymer onto either unidirectional Celion^R - 6000 graphite fiber or Celion^R - 3000 graphite cloth. When the Ni° catalyst was used, processing was effected at 625°F (330°C) under 1500 psi for 2 hours. The uncatalyzed laminates were processed at 735°F (391°C) under 2000 psi for 3 hours, the higher temperature being necessary to effect the uncatalyzed ring opening of biphenylene. In both cases high quality void-free laminates were prepared but due to the relatively flexible polymer backbone and the moderate degree of crosslinking attributable to the biphenylene end-cap, thermoplastic breaks during room temperature interlaminar shear were observed. Furthermore, only 25% of the initial room temperature interlaminar shear strength was retained after oxidative aging at 650°F (343°C) for 50 h, even though the composite weight loss was only two percent during the aging.

Using the PMR (polymerization of monomer reactants) approach (ref. 5), unidirectional Celion^R - 6000 graphite fiber was impregnated with a methanolic solution of the diester of 3, 3', 4, 4' - benzophenonetetracarboxylic dianhydride, oxydianiline, and 2-aminobiphenylene in a calculated stoichiometry to give $\overline{DP} = 4.8915$ (FMW = 3000). The pre-preg showed desirable tack and drape. The pre-preg was staged at



400°F (204°C) for 1 hour and processed at 735°F (391°C) under 1500 psi for 3 hours. (The Ni° catalyst was not used since it was insoluble in the methanolic monomer solution.) The resultant 9-ply laminates were of high quality and had low void content but showed thermoplastic breaks during interlaminar shear testing even though the T_g of the composite (337°C) was well above the test temperature (316°C). In an effort to increase the crosslink density, 3, 5 and 10 mole % of the oxydianiline monomer was replaced with the appropriate amount of the triamine, 3, 3', 5' - triaminobenzophenone. Composites in which 3 and 5 mole % of the diamine was replaced with the triamine showed sufficient crosslink density as evidenced by true thermoset breaks during interlaminar shear testing at 600°F (316°C, Table 2). However, photomicrographs of the composites after oxidative isothermal aging at 600°F for 50 h showed the presence of voids. Polyimide composites isothermally aged at 650°F (343°C) under a nitrogen atmosphere for 71 h did not show degradative void formation.

CONCLUSION

Biphenylene end-capped polyquinoline and polyimide resins afforded low void content graphite-reinforced composites with good initial properties. However, with both resins, rapid degradation occurred during oxidative isothermal aging at elevated temperatures. The degradation was not observed during isothermal aging under a nitrogen atmosphere which suggests that the biphenylene end-cap (or the resulting crosslink/chain extension structures) are not particularly thermooxidatively stable. The nature of the thermooxidative instability is currently under investigation.

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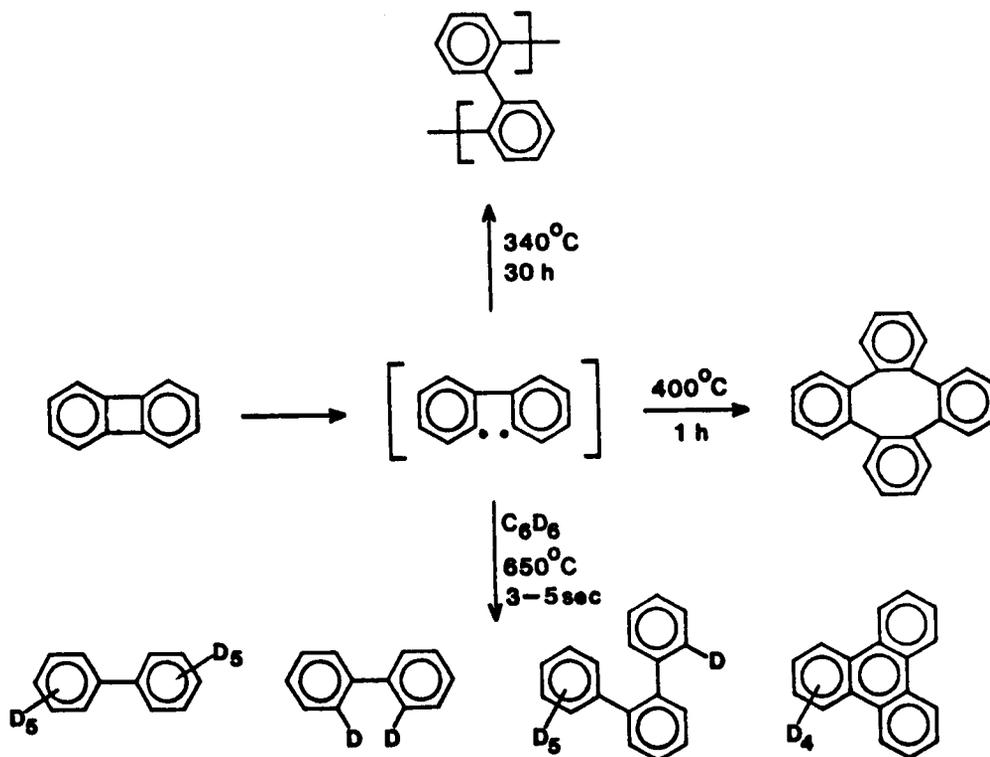


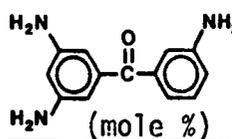
Figure 1. The products of the pyrolysis of biphenylene under various conditions.

Table 1. Biphenylene End-Capped Polyquinoline.

DP	Wt % biphenylene	Neat Resin Processing		ΔT_g	Solubility (CHCl ₃ , 24h)	E' above T _g (dynes/cm ² @ T°C)
		T _g (°C) before processing	T _g (°C) after processing			
3	23	153	235	+82	26%	-----
11	7.5	212	243	+31	i	1.4 x 10 ⁸ (285-335°C)
22	3.5	232	243	+11	i	1.0 x 10 ⁸ (291-330°C)
22*	0	232	232	0	s	-----

*phenyl end-cap

Table 2. Biphenylene End-Capped Polyimide/Celion^R-6000 Unidirectional Graphite Composite.

 (mole %)	POST-CURE	T _g (°C, TMA) after pc	ILSS		% wt loss 48 h / 600°F
			RT	600°F (psi)	
0	150 h / 600°F	337	14370	7098 pc*	1.4
3	14 h / 650°F	325	12261	7316 pc	—
5	47 h / 600°F	328	13294 pc	6842 pc	1.2
10	43 h / 600°F	310	9628 pc*	5422 pc*	1.7

* Thermoplastic break