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Biphenylene End-Capped Polyaromatics

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ABSTRACT

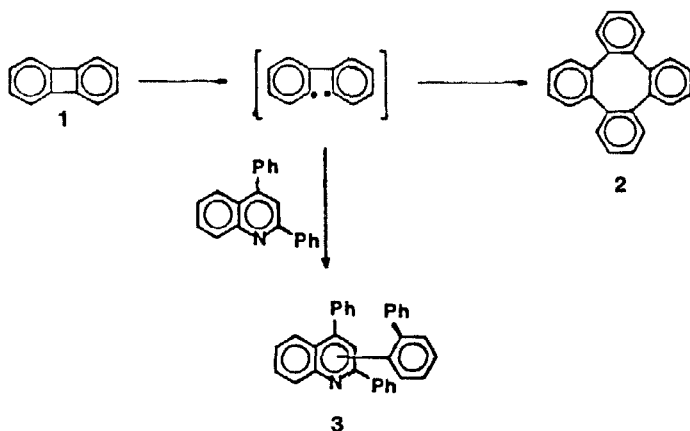
Biphenylene end-capped polyquinoline pre-polymers ($\overline{DP}=3,11$ and 22) were melt processed in the presence of a nickel catalyst at 325-340°C under 500 psi to give high quality transparent films. Very short cure times (~5 min) were realized, and the resulting films were insoluble, had increased Tg's, and showed improved mechanical properties both above and below the Tg as compared with the uncured resins. The main curing reaction is a chain extension by the conversion of the biphenylene ends to tetrabenzocyclooctatetraene, while a smaller amount of crosslinking takes place. Biphenylene end-capped polyimide, poly(keto-ether-sulfone) and polyphenylquinoxaline pre-polymers also were synthesized. The polyimide pre-polymer ($\overline{DP}=3$) was melt processed at 325°C and 500 psi (Ni catalyst) for 15 min to give films that showed good mechanical properties. Friedel Crafts polymerization to yield the biphenylene end-capped poly(keto-ether-sulfone) could not be adequately controlled to give reproducible oligomers. Polyphenylquinoxaline pre-polymers were similarly melt processed to give insoluble films with good mechanical properties. Graphite reinforced composites were prepared from biphenylene end-capped polyquinoline and polyimide pre-polymers. The composites showed 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.

INTRODUCTION

One approach to the problem of obtaining an easily processable polymer with a high end use temperature is to cross-link the

polymer after its fabrication. Because of the chemically inert structure and reduced chain mobility of polyaromatics, there are few good crosslinking reactions for them. In an effort to develop a high performance engineering plastic or a matrix resin for fiber reinforced composites, we utilized a thermal chain extension cross-linking reaction that depended on the ring opening of biphenylene (1)¹. This reaction has several distinct advantages: First, the reaction takes place without the evolution of volatiles. Second, the reaction produces a thermally stable link by dimerizing to tetrabenzocyclooctatetraene and by reaction with the main chain of the polyaromatics to generate an aryl-aryl link. Third, some control of the temperature can be exercised over the curing reaction.

At about 350°C, biphenylene undergoes a ring opening to yield mainly tetrabenzocyclooctatetraene (2) and some polymer. When the reaction is carried out in the presence of 2,4-diphenylquinoline, small amounts of biphenyl-substituted quinolines (3) in addition to 2 are obtained. The catalytic thermolysis of biphenylene containing small amounts of norbornadiene rhodium chloride dimer or bis(triphenylphosphine)dicarbonylnickel, takes place nearly 150°C lower, at 200°C.

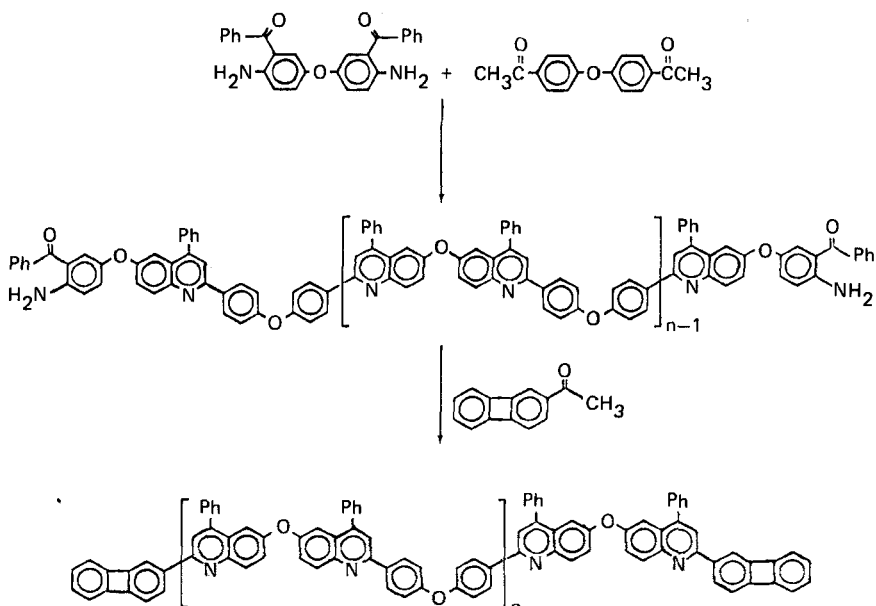


Thus, this reaction appeared to meet the criteria for cross-linking aromatic polymers.

A number of polymers, including polyquinolines, polyamides, polyquinoxalines and polybenzimidazoles, containing biphenylene units in the main chain have been synthesized. These polymers undergo thermal crosslinking reactions via the biphenylene ring-opening reaction either with or without a transition metal catalyst.²⁻⁶ Polyaromatics also have been crosslinked with bis-biphenylene crosslinking agents, that contained structures connecting the biphenylene units that mimicked the polymer to be crosslinked.⁷ In all of these curing reactions, although the reaction is faster and the curing temperature can be lowered in the presence of catalysts, no curing takes place below the glass transition temperature.

RESULTS AND DISCUSSION

Biphenylene End-Capped Polyquinolines.



Because of the good solubility of flexible, oxygen-linked polyquinolines in chloroform and their relatively low T_g 's, oligomers of this polymer capped with biphenylene, were prepared⁸ according to the relationship $DP=1+r/1+r-2rp$, where r =moles of ketomethylene monomer/aminoketone monomer and p =extent of the reaction (Table 1). The oligomers before processing showed glass transition temperatures consistent with the relationship $T_g=T_{\infty}-k/M_n$, ($k \sim 2.5 \times 10^5$).

The resins (4) containing a nickel catalyst could be melt pressed into thin films at 340°C under 500 psi for 15 minutes. After this relatively short processing time, the exotherm characteristic of the ring-opening reaction had disappeared (Fig. 1), and all films were insoluble. Young's modulus above T_g had increased by an order of magnitude. The T_g 's of the cured polymers were all relatively the same (234–243°C) as were the mechanical properties ($E'=2.8 \times 10^{10}$ dyn/cm² at 25°C and $1-2 \times 10^8$ dyn/cm² above T_g). This suggests that the chain extension reaction by conversion of biphenylene ends to tetrabenzocyclooctatetraene links proceeds until the different oligomers all reach about the same molecular weight, at which point further chain extension reactions by this mode stop due to the inaccessibility and reduced collision frequency of the biphenylene ends. Thereafter some cross-linking occurs by reaction of biphenylene units with the aromatic units in the polymer main chains.

Biphenylene End-Capped Polyimides, Poly(keto-ether sulfone)s and Polyquinoxalines.⁹

Phenyl end-capped polyimides of $DP=3$ and 11, were prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 4,4'-diaminodiphenyl ether and aniline in the appropriate ratios. Oligomers of $DP=3$ showed far superior melt flow properties at 325°C and 500 psi. Thus, a biphenylene end-capped pre-polymer (5) was similarly prepared, except that 2-amino-biphenylene was used as the end cap.

TABLE I
Biphenylene End-Capped Oligomers 14

| n^a | \bar{M}_n^b | $[\eta]$ | \bar{M}_n^c | \bar{M}_n^d | \bar{M}_w/\bar{M}_n^d | $T_g, ^\circ\text{C}$ (DSC) |
|------------------|---------------|----------|---------------|---------------|-------------------------|--------------------------------|
| 3 | 2100 | 0.09 | 1100 | 600 | 5.7 | 153 |
| 11 | 6800 | 0.25 | 5000 | 6500 | 2.9 | 212 |
| 22 | 13,000 | 0.47 | 13,000 | 12,000 | 2.9 | 232 |
| 68 ^e | — | 1.00 | 40,000 | 51,000 | 3.8 | 266 |
| 270 ^e | — | 2.47 | 160,000 | — | — | 266 |

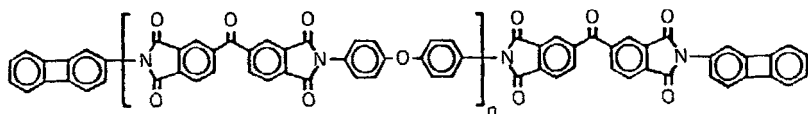
c. $[\eta] = K \bar{M}_n^a$

a. $n = 1+r/1-r$
r = AA/BB

d. GPC

b. $n[590] + 2[151]$

e. No End-Cap



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Oligomeric imide 5, melt processed at 325°C under 500 psi for 15 min in the presence of a nickel(0) catalyst gave a film with $T_g=261^\circ\text{C}$, 86°C higher than the phenyl end-capped polyimide of $DP=3$. Although Young's modulus measured as a function of temperature showed that the cured film maintained mechanical properties above T_g , the film quality indicated some restricted flow during melt processing.

Poly(keto-ether-sulfone)s pre-polymers (calculated $DP=11, 22, 6$) were obtained from isophthaloyl chloride and 4,4'-diphenoxysulfone (excess) under Friedel-Crafts conditions

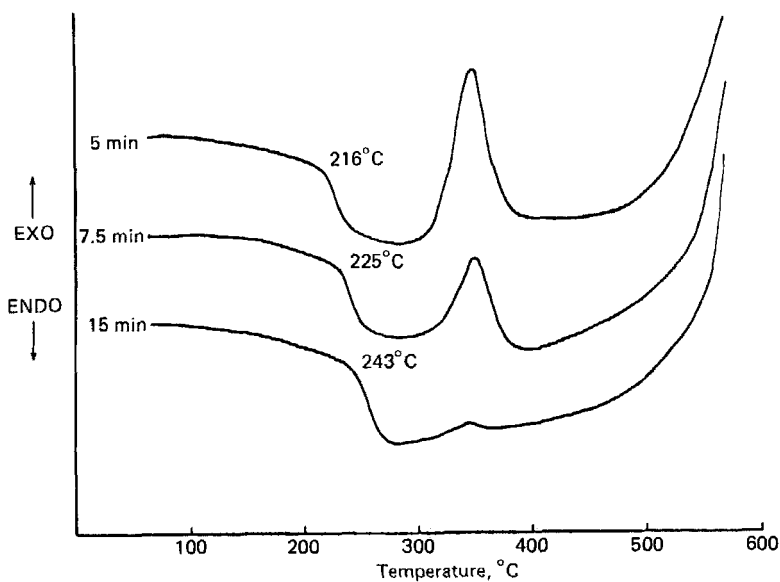
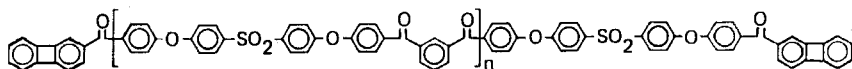


Figure 1. Differential Scanning Calorimetry of 4 ($\overline{DP}=11$) Melt Processed in the Presence of Bis(triphenylphosphine)dicarbonyl nickel(0) for Various Times at 340°C under 500 psi

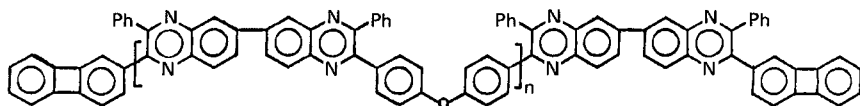
(methylene chloride, aluminum chloride) and then the isolated polymer was subjected to a Friedel-Crafts reaction with biphenylene 2-carboxylic acid chloride. GPC of both polymer samples revealed that they were actually polymers of about the same molecular weight ($M_n=15-20,000$). The molecular weight could not be readily controlled, and melt pressed films had poor properties.



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The polymerization of 4,4'-oxydibenzil and 3,3'-diaminobenzidine, with the tetraamine in excess, gave a pre-polymer which was phenyl end-capped by the addition of benzil to the polymerization mixture late in the reaction. The resulting polymer ($[\eta]_{inh} = 0.52$ dL/g, 0.5 percent solution, w/w, sulfuric acid), was melt processed at 325°C under 500 psi for 15 min to give a high quality, transparent film, confirming that the pre-polymer had a suitable DP for melt processing.

A biphenylene end-capped polyphenylquinoxaline pre-polymer (7) was prepared similarly except 2-(phenylglyoxalyl)biphenylene was used as the end-cap. Pre-polymer 7 had an inherent viscosity of 0.44 dL/g (0.5 percent solution (w/w), sulfuric acid). Differential scanning calorimetry of 7 showed $T_g = 267^\circ\text{C}$ and an uncatalyzed ring opening exothermic maximum for the biphenylene end-group at 480°C.



7

Melt processing in the presence of a nickel catalyst at 340°C under 500 psi for 15 min gave an insoluble film that showed

an increased T_g relative to uncured 7 (T_g 299°C and 267°C, respectively, DSC). However, the film quality clearly demonstrated that restricted flow was present during processing. A higher quality film was obtained by employing a step-wise processing approach. Pre-polymer 7 containing the Ni(0) catalyst was introduced into a 225°C press, 500 psi was applied, the temperature was increased over 15 min to 370°C, and maintained at 370°C for 15 min. The resulting film was suitable for dynamic mechanical testing (Rheovibron) which demonstrated a light to moderate crosslink density [$E'_{25^\circ\text{C}} = 2.5 \times 10^{10}$ dyn/cm², E' above $T_g = 7.2 \times 10^7$ dyn/cm² (measured at 365°C), $E''_{\text{max}}(T_g) = 268^\circ\text{C}$]. The degree of crosslinking was about the same as that observed in cured polymers prepared from the biphenylene end-capped polyquinoline and polyimide pre-polymers.

Graphite Fiber Reinforced Composites¹⁰

Unidirectional graphite fiber-reinforced composites were prepared from biphenylene end-capped polyquinoline pre-polymer 4 (DP=22) containing 20 mole % (based on biphenylene) bis(triphenylphosphine)(dicarbonyl)nickel(0). The pre-preg was prepared by brush coating a chloroform solution of the pre-polymer and catalyst onto the graphite fiber reinforcement. The pre-preg was laid-up in 7 or 8 stacks and melt processed in a 1 in. by 2.5 in. mold at 330°C (625°F) under 1500 psi for 2 hours. The cured composites had excellent ring and reasonable room temperature flex properties but only modest interlaminar shear strength (Table 2). Post-curing increased the T_g but a decrease in the mechanical properties at room temperature was observed. However, improved properties at 316°C (600°F) were achieved as a result of the higher T_g .

In an effort to improve the pre-pegging of pre-polymer 4, graphite cloth was employed in place of unidirectional graphite fiber. Brush coating of a chloroform solution of pre-polymer 4 onto the fiber reinforcement restrained on all four sides gave a boardy but good quality pre-preg which showed minimum

Table 2
 Properties of Polyquinoline Composites Prepared in the Presence
 of Bis(triphenylphosphine)(dicarbonyl)nickel(0)
 Unidirectional Ceion-6000[®] Graphite Fiber^a

| Post-Cure Conditions ^b (h/temperature) | T _g , °C(TMA) ^c | RT ILSS, psi ^d | | Flex Strength, psi ^d | | Flex Modulus, psi ^d | |
|--|---------------------------------------|---------------------------|---------------------|---------------------------------|---------------------|--------------------------------|--------------|
| | | RT | 316°C(600°F) | RT | 316°C(600°F) | RT | 316°C(600°F) |
| - | 222 (432°F) | 9000 | 36,000 ^e | 228,000 | 36,000 ^e | 16,200,000 | 3,400,000 |
| 100h/316°C(600°F) | 261 (502°F) | 6800 | 59,000 | 182,000 | 59,000 | 14,800,000 | 7,900,000 |
| 51h/343°C(650°F) | - | 2200 | 52,000 | 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.

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 400°C, a higher cure temperature was required. The melt processing of 6-ply lay-ups was conducted at 388°C (730°F) under 2000 psi for 3 hours and gave composites which showed good flow as indicated by the presence of flash. The composites had good ring and appearance. The initial room temperature properties were comparable to the polyquinoline composites prepared with the Ni(0) catalyst considering that only half of the fibers are oriented in one direction in the cloth.

Again, post-curing resulted in decreased mechanical properties, and thermoplastic breaks were observed in all samples. The thermoplastic (non-brittle) breaks were attributed to a low crosslink density and a flexible polymer backbone.

Biphenylene end-capped polyimide pre-polymers were also used in the preparation of graphite fiber-reinforced composites. Employing the PMR (polymerization of monomer reactants) approach,

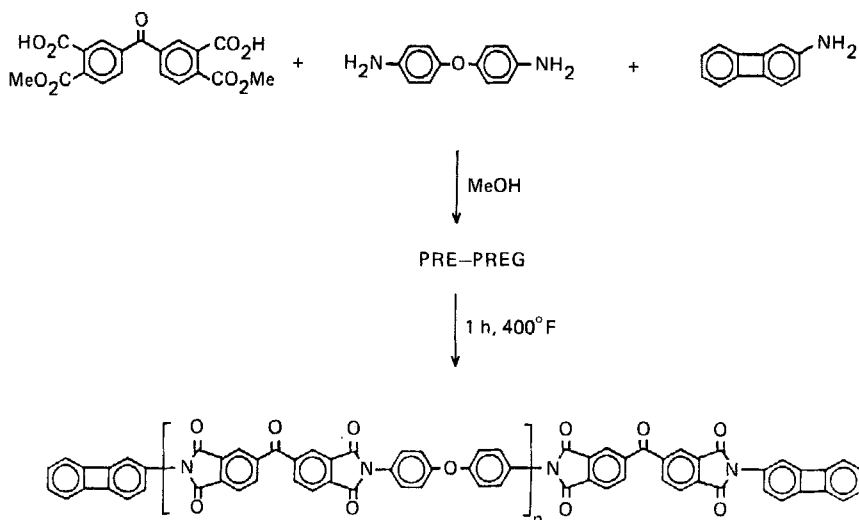


Table 3

Properties of Polyquinoline Composites Prepared without Added Catalyst.
Celion[®]-3000 Graphite Cloth

| Post-cure Conditions ^b (h/temperature) | T _g , °C (TMA) ^c | ILSS, psi ^d | | RT Flex Strength, psi ^d | RT Flex Modulus, psi ^d |
|--|--|------------------------|--------------|---------------------------------------|--------------------------------------|
| | | RT | 316°C(600°F) | | |
| - | 219 (426°F) | 5000 | - | 88,000 | 10,500,000 |
| 100h/316°C(600°F) | 242 (468°F) ^e | 3900 | 1300 | - | - |

a. 30% resin content by weight.

b. In circulating air.

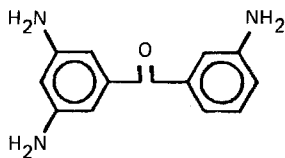
c. Thermal mechanical analysis.

d. Thermoplastic (nonbrittle) breaks observed in all cases.

e. After 48 h at 316°C (600°F).

a methanolic solution of 4,4'-diaminodiphenyl ether, 2-aminobiphenylene and the dimethylester of 3,3',4,4'-benzophenone tetracarboxylic dianhydride was brush coated onto unidirectional Celion-6000® graphite fiber. The resultant pre-preg showed desirable tack and drape. Staging of 9-ply lay-ups at 204°C (400°F) permitted loss of volatiles prior to molding. Composites were prepared by processing at 390°C (735°F) under 1500 psi for 3 hours. These composites showed excellent room temperature properties. Testing at 316°C (600°F) indicated thermoplastic breaks even after post-curing (Table 4), which suggested that only a moderate degree of crosslinking 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 clearly showed inferior properties compared to composites prepared with biphenylene end-capped polyimide pre-polymers.

To increase the crosslink density, a trifunctionalized monomer was used as a branching site. The pre-preg was prepared as before except 3-10 mole % of 4,4'-diaminodiphenyl ether was replaced with 3,3',5'-triaminobenzophenone (8). The staged pre-preg was processed at 319°C (735°F) under 2000 psi for 3 hours. The higher pressure (2000 psi vs 1500 psi) was used since



8

the branch site was expected to reduce polymer flow. The composites in which 3 and 5 mole % of 4,4'-diaminodiphenyl ether had been replaced with **8** showed excellent mechanical properties both at room temperature and 316°C (600°F) (Table 5). All breaks were now true thermoset (brittle) breaks which confirmed that a sufficient crosslink density had been achieved.

Table 4

Properties of Composites Prepared from Polyimide Pre-polymers
Celion-6000 Unidirectional Graphite Fiber

| End-Cap | Post-cure conditions ^a (h/Temperature) | T _g , °C(THA) ^b RT | ILSS, psi 316°C(600°F) RT | Flex Strength, psi 316°C(600°F) RT | Flex Modulus, psi 316°C(600°F) RT |
|--------------------------|--|---|---------------------------------|--|---|
| Nadic ^c | 16h/316°C (600°F) | 332°C (630°F) | 17,000 | 250,000 | 17,400,000 |
| Biphenylene ^d | - | 263 (505°F) | 14,000 | 287,000 | 20,200,000 |
| Biphenylene ^d | 50h/316°C (600°F) | - | - | 6000 ^e | 15,600,000 ^e |
| Biphenylene | 150h/316°C (600°F) | 337 (639°F) | 11,000 | 7000 ^e | 18,300,000 |
| Phenyl | - | 246 (475°F) | 8700 | 3600 ^e | - |
| Phenyl | 47h/343°C (650°F) ^e | 250 (482°F) | 10,000 | 5700 ^e | 12,300,000 ^e |

a. In circulating air.

b. Thermal mechanical analysis.

c. Properties of PHR-15 composites for comparison. PHR-15 employs 4,4'-methylene dianiline 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 using 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.

Table 5
 Properties of Composites Prepared from Biphenylene End-capped
 Polyimide Pre-polymers Containing 3,3',5'-triaminobenzophenone

| Mole % Diamine Replaced with Triamine | Post-cure Conditions ^a (h/Temperature) | T _g , °C (TMA) ^b | RT | ILSB, 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 | 14h/343°C (650°F) | 325 (617°F) | 12,000 | 7300 | - | - |
| 5 ^c | 47h/316°C (600°F) | 328 (622°F) | 13,000 | 6800 | 186,000 | 17,300,000 |
| 10 | 43h/316°C (600°F) | 310 (590°F) | 9600 ^d | 5400 ^d | - | - |

a. In circulating air.

b. Thermal mechanical analysis.

c. 26% resin content by weight.

d. Thermoplastic (nonbrittle) break.

Although composites with state-of-the-art initial properties had been prepared, some loose surface fiber was observed in all composites oxidatively aged for 50-100 hours at 316°C (600°F), even though the composite weight loss during aging was only 2-3% (polyquinoline and polyimide composites). Furthermore, aged composites no longer showed ringing when dropped on a hard surface. The observations suggested that the biphenylene end-capped matrix resins were not thermooxidatively stable as might have been expected. Photomicrographs of polyquinoline and polyimide composites before and after oxidative isothermal aging at 316°C (600°F) confirmed that the resins had degraded during aging. Photomicrographs of composites prepared from biphenylene end-capped polyquinoline pre-polymer 3 containing 20 mole % (based on biphenylene) of the Ni(O) 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. This composite also had the lowest amount of loose surface fiber after aging. Although the observations may not be explained with certainty, the results suggest that the Ni(O) 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 may be involved. These could arise either from unreacted biphenylene end groups or from the decomposition to tetrabenzocyclooctatetraene. A possible explanation for the observation that the nickel-catalyzed curing reaction gave a laminate that showed the least degradation, is that the ring opening reaction was more complete in the presence of the catalyst.

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