Preparation and Properties of Nadic-End-Capped Cyclotriphosphazene-Containing Polyimide/Carbon Fiber Composites

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ABSTRACT: New novel fire-resistant and heat-resistant cyclotriphosphazene-containing polyimide resins were prepared *in situ* by the polymerization of (*p*-aminophenoxy)-(phenoxy)cyclotriphosphazenes with 3,3′,4,4′-benzophenonetetracarboxylic acid or 3,3′,4,4′-diphenylsulfonetetracarboxylic acid and a crosslink agent, 5-norbornene-2,3-dicarboxylic acid and were used as polymer matrix compositing with a woven carbon fiber to prepare nadic-end-capped cyclotriphosphazene-containing polyimide/carbon fiber composites. The thermal stability, flame retardance, morphology of the surface fracture, and some physical properties of the composites were investigated by thermogravimetric analysis, scanning electron microscopy, and a material testing system, respectively. The composites had good thermal stability, flame retardance, and mechanical properties. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 810–818, 2003

Key words: polyimides; composites; flame retardance

INTRODUCTION

Because of their outstanding properties and high strength-to-weight ratio, fiber-reinforced polymer composites have been increasingly used in various structural components. Several types of matrices, including epoxy, polysulfone, phenolic, and polyimide resins, have been used in these composites.[1] Among them, high-performance polyimide composites are used in high-temperature applications, aerospace vehicles, military facilities, and so on because of their excellent properties, including thermooxidative stability, chemical resistance, and a low dielectric constant.[2–5] Nevertheless, there are still some problems that must be solved to make them more appropriate for use. One of them is that 4,4′-methylenedianiline (MDA), a monomer commonly used in the preparation of polyimides, has been shown as a potential occupational carcinogen. Therefore, much attention has been focused on finding a less toxic diamine to replace MDA.[6]

It has been reported that the phosphazene materials usually possess high thermooxidative stability and fire-retardance properties and are nontoxic compounds.[7,8] So, some cyclotriphosphazenes have been incorporated into polymers to improve their heat and flame resistance, and some were found to have potential for use as biomedical materials.[9] Several polymers based on cyclotriphosphazene have been reported in the literature,[10–13] but except for those in the work reported by Kumar et al.[14,15] few have been used for the preparation of composites. In these studies, Kumar et al. found that graphite fabric laminates with maleimido-substituted aromatic cyclotriphosphazene resin as a matrix had good thermal stability, good fire resistance, and good mechanical properties.

Because polyimide systems are capable of performing at high temperatures as bismaleimide systems,[16] in a previous study we synthesized two cyclotriphosphazene-containing polyimides by the reaction of bis(*p*-aminophenoxy)(tetraphenoxy)cyclotriphosphazene with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA) and found that the polyimides were also thermally stable and had high char yields at 600°C.[17] In this study, we prepared nadic-end capped cyclotriphosphazene-containing polyimide resins from bis(*p*-aminophenoxy)(tetraphenoxy)-cyclotriphosphazene, BTDA (or DSDA), and 5-norbornene-2,3-dicarboxylic anhydride (NA). These resins were then used to prepare the carbon-fiber-reinforced composites. The preparation and some physical properties of the composites were investigated.

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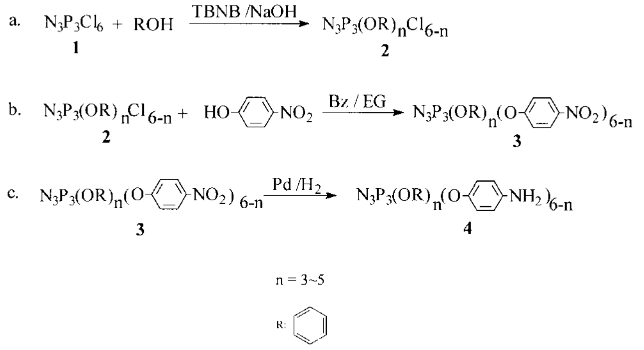


Scheme 1

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (**1**) was kindly provided by Nippon Fine Chemical Co. (Tokyo, Japan). Dichloromethane, benzene, methanol, phenol, 4-nitrophenol, and tetrabutylammonium bromide (TBNB) were purchased from Merck Chemical Co. (Darmstadt, Germany). NA was purchased from Eastman Kodak Co. (USA) and acted as a crosslinker. The dianhydrides, BTDA and DSDA, purchased from Chriskev Co. (USA), were purified by recrystallization from an acetic acid–acetic anhydride (1/1) solvent system before use.

Analytical equipment

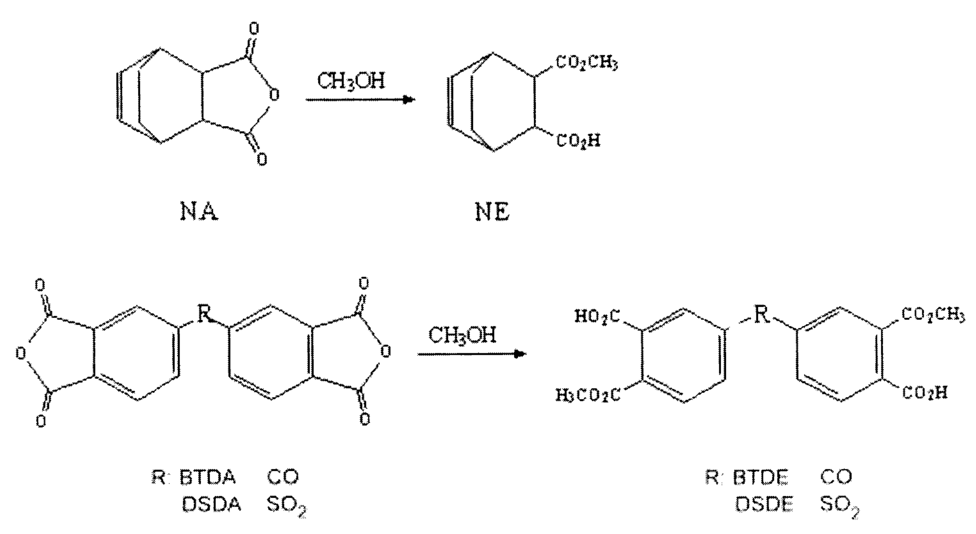
Fourier transform infrared spectroscopy (FTIR) was performed on a Bio-Rad FTS-7 FTIR spectrometer (Tokyo, Japan). A Seiko TG/DTA-220 thermal analyzer was used to measure thermal stability at a heating rate of 10°C min^{-1} both in nitrogen and in air. The mechanical properties were performed on a MTS BIONIX 850 material testing system (Minnesota). Tensile tests, flexural tests, and interlaminar shear strength tests of the composites were measured according to ASTM D 3093, ASTM D 790, and ASTM D 2344, respectively. The resin contents of the composites were determined by the ignition loss method according to ASTM D 2584-68.

Synthesis of (*p*-nitrophenoxy)(phenoxy)-cyclotriphosphazenes (3) and (*p*-aminophenoxy)-(phenoxy)cyclotriphosphazenes (4)

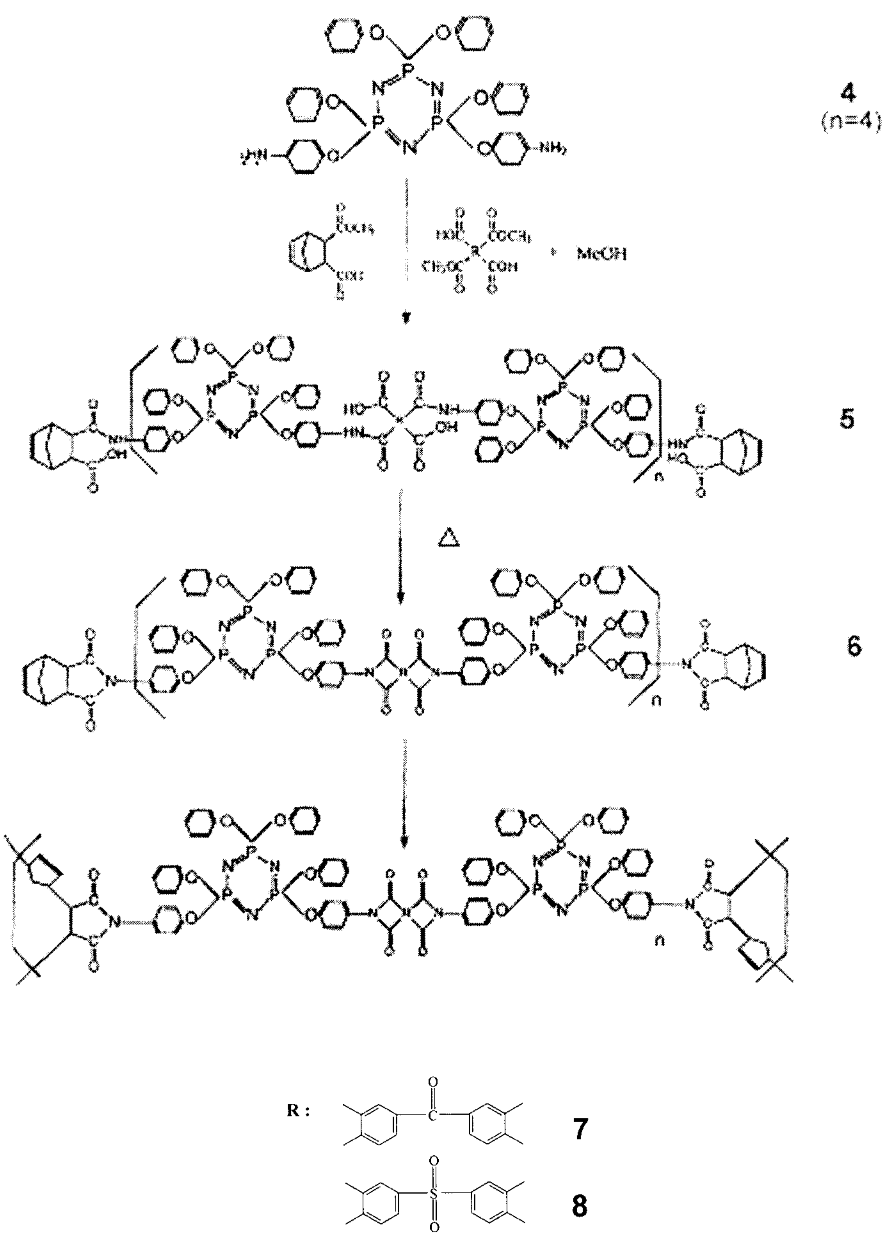
The cyclotriphosphazenes **3** and **4** were synthesized according to the procedures outlined in Scheme 1 by a phase-transfer catalysis reported previously.[17,18] Hence, a solution of **1** (27.98 g, 0.08 mol) in 150 mL of CH_2Cl_2 was stirred mechanically. To this solution, cooled with an ice bath, a basic solution prepared by sodium hydroxide (23.96 g, 0.60 mol), phenol (30.08 g, 0.32 mol), and the phase-transfer catalyst TBNB (10.0 g, 0.031 mol) dissolved in 200 mL of water was added dropwise. The reaction mixture was stirred at room temperature for 1 h. The dichloromethane layer was separated from the aqueous layer, washed with water, and dried over magnesium sulfate. The solution was then filtered and concentrated to produce a light yellow liquid, which was identified as (phenoxy)chlorocyclotriphosphazenes (**2**), or $N_3P_3(OC_6H_5)_nCl_{6-n}$, where $n = 3$–5.

To obtain **3**, the solution of **2** (31.0 g) in 100 mL of CH_2Cl_2 was reacted with 22.37 g (0.16 mol) of *p*-nitrophenol in 100 mL of a sodium carbonate ethylene glycol solution by phase-transfer catalysis as described before. After working up, **3**, or $N_3P_3(p\text{-}OC_6H_4NO_2)_{6-n}(OC_6H_5)_n$, where $n = 3$–5, was obtained:

FTIR (KBr, cm^{-1}): 770 and 1300–1600 (P=N), 949 (P—O—C), 1524 and 1346 (NO_2); ^{31}P-NMR ($CDCl_3$, δ, ppm): 8.5; ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.2–6.9 (OC_6H_5),



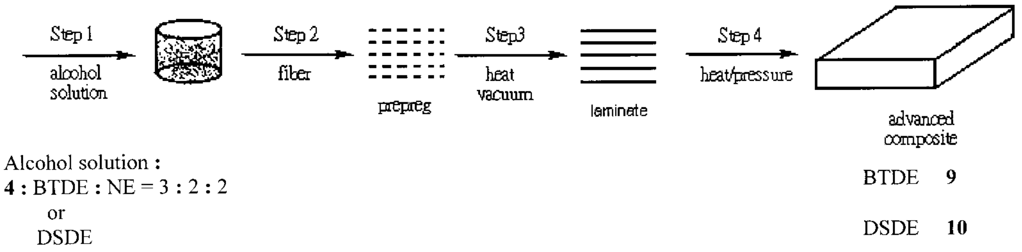
Scheme 2



Scheme 3

8.0–7.9 ($OC_6H_4NO_2$); ^{13}C-NMR ($CDCl_3$, δ, ppm): 120.6 and 155.0.

The reduction of **3** then followed to prepare the corresponding **4**. A 250-mL heater-equipped autoclave was charged with a solution of **3** (27.56 g) in CH_2Cl_2 (50 mL), which contained 0.5 g of a platinum oxide catalyst. The solution was agitated vigorously at 25°C and 50 psi of hydrogen for about 5 h until no further



Scheme 4

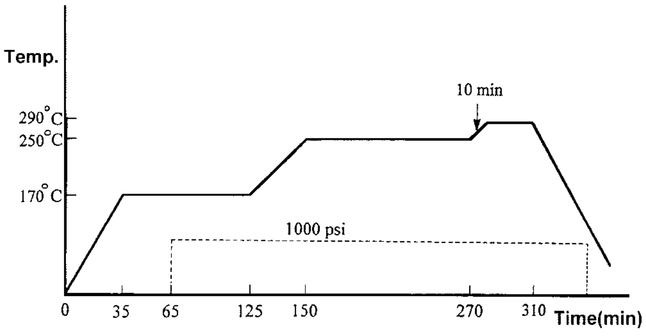


Figure 1 Temperature and heat-press time curing cycle.

pressure drop was observed. The reaction product was filtered and concentrated under reduced pressure to 5 mL and poured slowly into *n*-hexane to obtain a light brown solid that was identified as the amino-substituted aromatic **4**, or $N_3P_3(p\text{-}OC_6H_4NH_2)_{6-n}(OC_6H_5)_n$, where $n = 3$–5.

FTIR (KBr, cm^{-1}): 3365, 3460, and 1624 (NH_2); ^{31}P-NMR ($CDCl_3$, δ, ppm): 9.5; ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.2–6.9 (OC_6H_5), 3.4 (NH_2); ^{13}C-NMR ($CDCl_3$, δ, ppm): 115.3 and 151 ppm.

Synthesis of the nadic-end-capped cyclotriphosphazene-containing polyimide (6)

The nadic-end-capped poly(amic acid) (**5**) was prepared according to the procedure depicted in Schemes 2 and 3. Hence, the monomethyl esters of 5-norbornene-2,3-dicarboxylic acid (NE), 3,3′,4,4′-benzophenonetetracarboxylic acid (BTDE), and 3,3′,4,4′-diphenylsulfonetetracarboxylic acid (DSDE) were obtained by refluxing of the corresponding anhydrides, NA, BTDA, and DSDA, in methanol separately for about 2 h. A solution of **4** (5.0 g, 6.7 mmol) in methanol (30 mL) was added into a stirring solution of BTDE (1.5 g, 4.5 mmol) in methanol (100 mL) at room temperature for 1 h under a nitrogen atmosphere. Then, NE (0.87 g, 4.5 mmol) was added, and the mixture was heated at 70°C for 3 h. After the reaction, the product was precipitated in ice water. The precipitate obtained was then filtered, washed with water, and dried to yield **5**.

To prepare **6**, the powder of **5** was thermally cyclodehydrated at 170°C for 90 min. The bulk polymer **7** was obtained by the curing of **6** at 250°C for 2 h and at 290°C for 30 min.

Composite fabrication

The procedure for fabricating the cyclotriphosphazene-containing polyimide/carbon fiber composites is depicted in Scheme 4. Hence, a methanol solution with 25 wt % resin was prepared by the dissolution of **4**, BTDE (or DSDE), and NE in a 3:2:2 molar ratio in methanol and was used to prepreg the carbon fiber clothes [woven Toray 6K (0/90°)]. The *in situ* polymerization was carried out directly on the fiber surface, as described previously, to form polyimide **7,** and the resulting compound was dried by vacuum.

Lamination

Eight plies of the dried prepregs (150 × 150 × 3 mm) were B-staged at 200°C for 1 h in a vacuum oven and then stacked in a steel mold and heated from room temperature to 290°C. The condition of the temperature and the heat-press time at each stage was followed according to the curing cycle depicted in Figure 1. After holding at 170°C for 30 min, the temperature ramp rate set at 4°C/min was applied under a 1000 psi pressure and maintained at 170°C for 1 h, 250°C for 2 h, and 290°C for 0.5 h.

RESULTS AND DISCUSSION

Synthesis and characterization of 6

3 and the corresponding **4** were synthesized according to Scheme 1.

As indicated in Table I, the chemical shifts and the coupling constants showed that the ^{31}P-NMR spectra of the components in **2** were second order with $J/\Delta\nu$ values in the range 0.06–0.07, and these partially substituted compounds were predominantly nongeminal. Table I also shows that about 88% of the products was tetra(phenoxy)bis(chloro)cyclotriphosphazene. Nevertheless, because separation is a time-consuming pro-

TABLE I
^{31}P-NMR Data and Components of 2

Component of 2	Spectrum type	Chemical shift (ppm)[a] P_A	P_B	Jab (Hz)	Jab/$\Delta\nu$[b]	Composition (%)
$n = 3$	A_3	18.5				2.3
$n = 4$	AB_2	5.0	20.3	80.8	0.06	87.8
$n = 5$	A_2B	22.3	6.9	83.3	0.07	10

[a] $P_A = P(OC_6H_5)_2$; $P_B = PCl(OC_6H_5)$.
[b] J = coupling constant; $\Delta\nu$ = chemical shift difference.

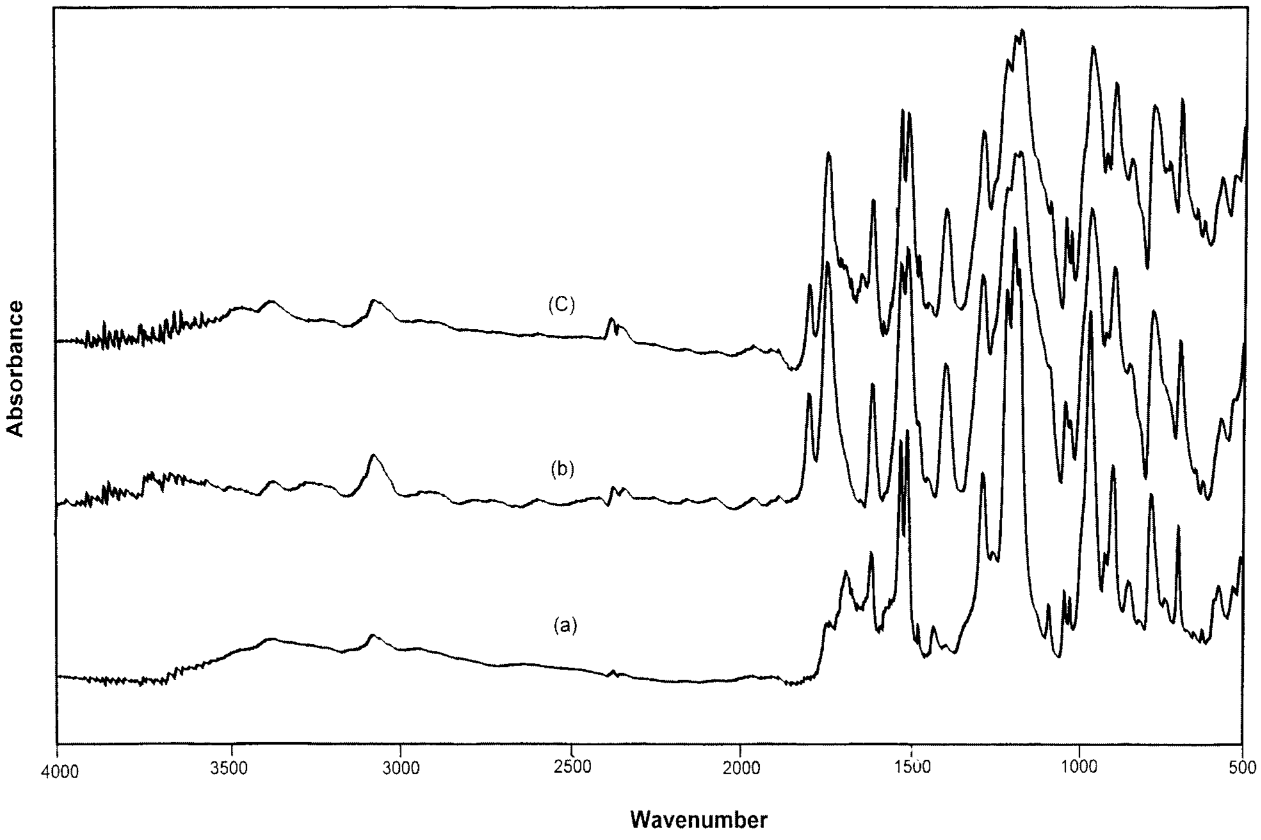


Figure 2 FTIR spectra of polymers (a) **5**, (b) **6**, and (c) **3**.

cess, for economic and practical reasons, mixture **2** rather than the pure tetra(phenoxy)cyclotriphosphazene was used in this study. Therefore, the as-prepared **4** was mainly nongeminal bis(*p*-aminophenoxy)tetra(phenoxy)cyclotriphosphazenes.

To assure that the *in situ* crosslink polymerization occurred in the composite, a similar process for the synthesis of **6** was carried out. As indicated in Scheme 2, the monomethyl esters, BTDE and NE, were synthesized by the reaction of the corresponding anhydrides, BTDA and NA, with methanol. According to Scheme 3, **5** was then prepared by the reaction of **4** with BTDE and NE in a methanol solution. Finally, **5** was imidized to form the corresponding **6** by heating at 170°C.

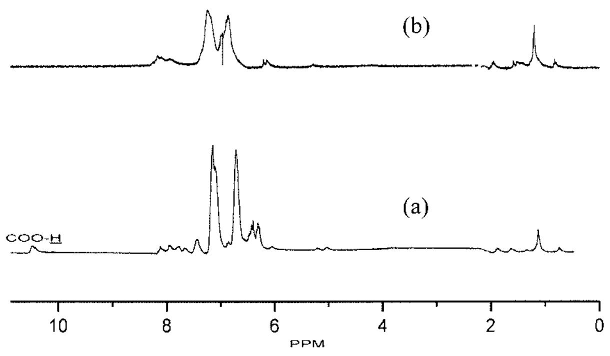


Figure 3 ^{1}H-NMR spectra of (a) **5** and (b) **6**.

The structures of **5** and **6** were characterized by a combination of FTIR and NMR spectroscopies. As seen in the FTIR spectrum for **5** [Fig. 2(a)], except that the absorbances of the NH_2 vibrations of **4** [Fig. 2(c)] peaks at 3460, 3365, and 1624 cm^{-1} were significantly reduced, the other characteristic absorbances of **4** were preserved. Also, the absorbances of the amic $C{=}O$

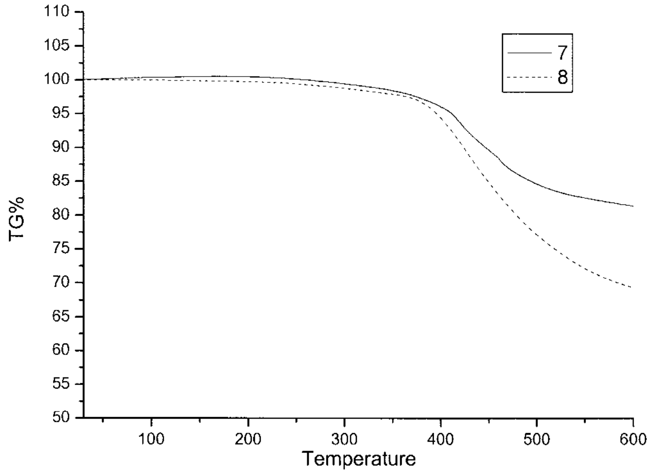


Figure 4 Dynamic TGA thermograms of composites **7** and **8**.

TABLE II
Dynamic TGA Data of the Composites

Composite	$T_{5\%}$ (°C)	T_{max}[a] (°C)	Char yield (%) 600°C	Char yield (%) 1000°C	Atmosphere
7	413	428	81		Nitrogen
8	397	421	69		Nitrogen
9	403	852		82	Nitrogen
9	432	839		78	Air
10	380	866		83	Nitrogen
10	405	871		82	Air

[a] T_{max} = maximum degradation temperature.

(1661 and 1728 cm^{-1}), acidic O—H (3371 cm^{-1}), and aromatic C═C groups (1588 cm^{-1}) from BTDE and NE were observed. This result confirmed the structure of **5** as expected. In the FTIR spectrum of **6**, as shown in Figure 2(b), the characteristic absorbances of the O—H and N—H groups of **5** between 3100 and 3600 cm^{-1} disappeared, whereas the characteristic imide C═O absorbances (1779 and 1728 cm^{-1}) and the C—N—C absorbance (1378 cm^{-1}) were observed, confirming that **6** was the imidization product of **5**.

However, as shown in Figure 3(a), the ^{1}H-NMR spectrum of **5** showed the characteristic peaks for the aromatic protons between 6.3 and 8.0 ppm (OC_6H_5 and OC_6H_4) and for the norbornene protons at 6.0–6.3 ppm (HC═CH) and 1.0 ppm (CH_2). Also, the peak at 10.2 ppm indicated the presence of the COO—*H* of the amic acid. The spectrum of **6**, as shown in Figure 3(b), showed that the peaks for the aromatic protons and the norbornene protons were preserved with slight shifts. However, the peak of COO—*H* at 10.2 ppm disappeared, confirming the imidation of **5** and the structure of **6** as expected.

In addition, **5** and **6** were soluble in dimethyl sulfoxide, dimethylformamide, and so on, but with further thermal heating, the specimens became tough unsoluble materials, indicating that **6** was thermally cured. The possible structure of the cured specimen is believed to be like the structure of **7** as found in a similar reported reaction.[19]

Thermal properties of 7 and 8

The glass-transition temperatures of polyimides **7** and **8**, as measured by DSC, were at 160–180°C. This revealed that the polyimides were processable at relatively lower temperatures than that of the conventional polyimide, which are usually in the range 200–215°C. In addition, the thermal stabilities of polyimides **7** and **8** in a N_2 atmosphere were investigated by thermogravimetric analysis (TGA; Fig. 4). As listed in Table II, the temperatures of 5% weight loss ($T_{5\%}$'s) were 397 and 412°C, and the temperatures at which major thermal decomposition occurred were at 420–430°C. This suggested that the synthesized polymers were thermally stable up to about 400°C.

Properties of the composite laminates

The composite laminates were prepared according to the procedure described in the Experimental section. As discussed previously, the polymer matrix, formed directly on the fiber surface during the heat-pressing process in the as-prepared composites was the cured nadic-end-capped phosphazene-containing polyimide with a structure similar to **7**.

Figure 5 shows the thermograms of the composites investigated by dynamic TGA. As listed in Table II,

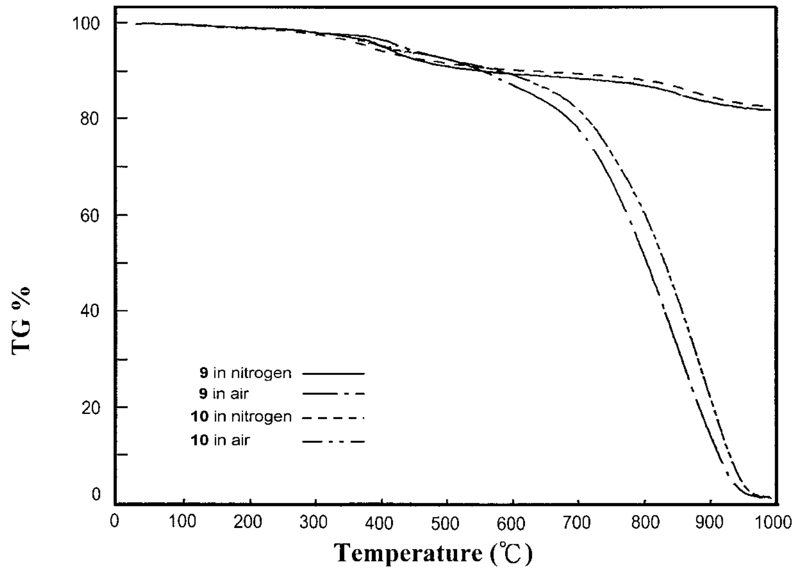


Figure 5 Dynamic TGA thermograms of composites **9** and **10**.

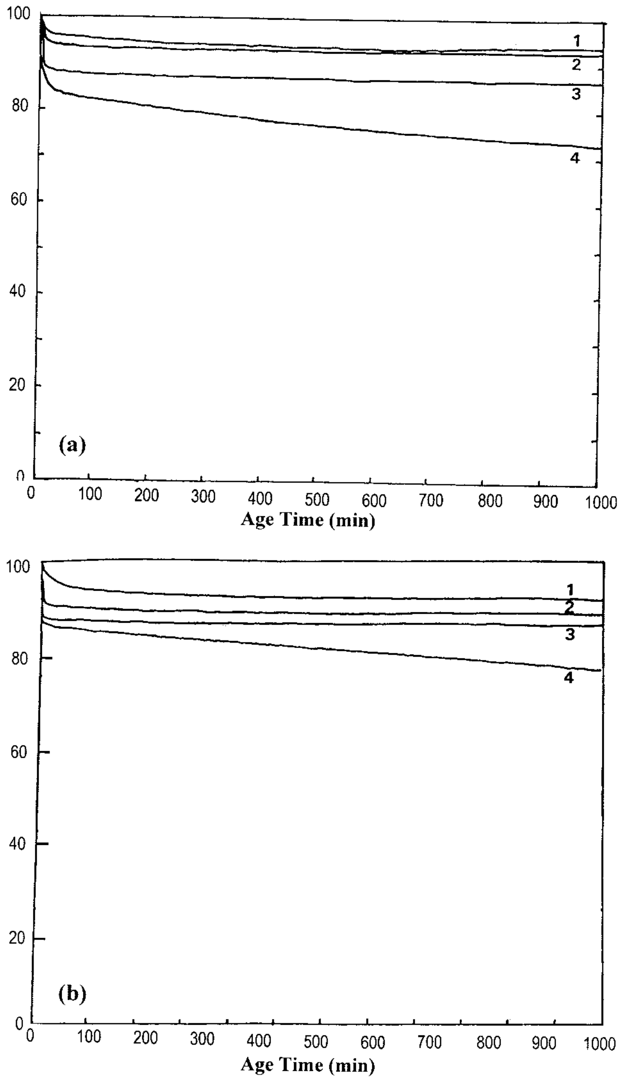


Figure 6 Isothermal TGA thermograms of composites (a) **9** and (b) **10** aging in nitrogen at (1) 316, (2) 400, (3) 500, and (4) 700°C.

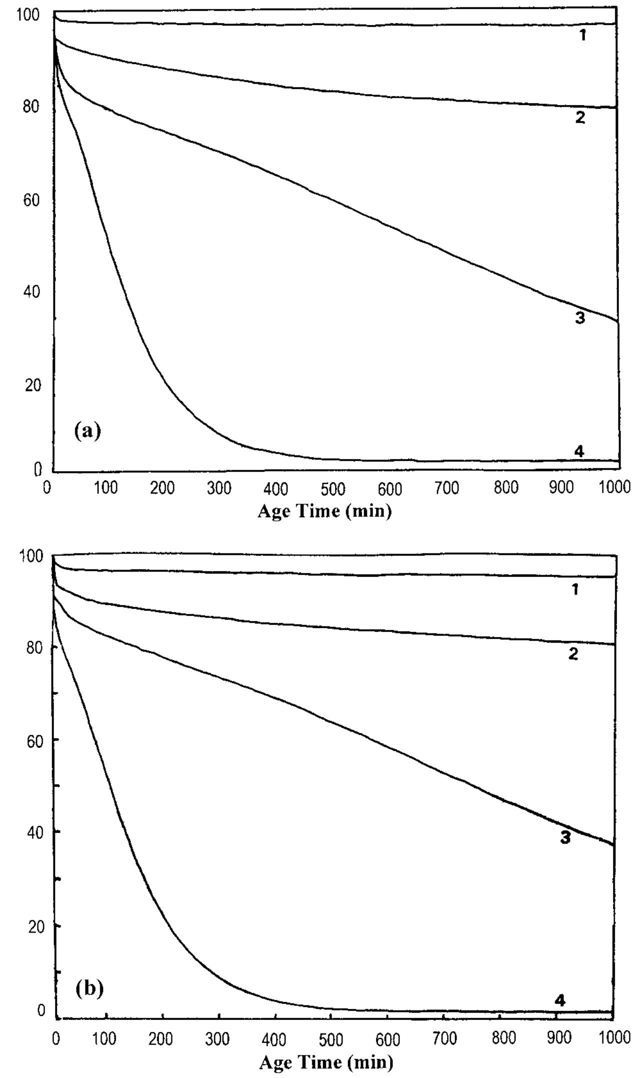


Figure 7 Isothermal TGA thermograms of composites (a) **9** and (b) **10** aging in air at (1) 316, (2) 400, (3) 500, and (4) 700°C.

the $T_{5\%}$ values were 403 and 380°C in nitrogen and 432 and 405°C in air for composites **9** and **10**, respectively. This suggests that the composites were thermally stable above 380°C in nitrogen and above 400°C in air. Also, the composites had high char yields (> 80% at 1000°C in nitrogen and close to 80% at 700°C in air), implying that the composites had good flame-retardant properties.

In addition, the isothermal TGA thermograms of the composites were performed in nitrogen (Fig. 6) and in air (Fig. 7) at 316, 400, 500, and 700°C. As shown for 1000 min of aging in a nitrogen atmosphere, the weight loss of the composites was 6.1–8.3% at 316°C, 7.1–11.7% at 400°C, 13.5–13.9% at 500°C, and 23.7–27.2% at 700°C. This indicated that in nitrogen, the composites had less than a 14% weight loss at temperatures lower than 500°C, and after the temperature was kept constant for about 10 min, no further significant weight loss was observed. However, in air, after the temperature was kept for 1000 min, the weight loss was 3.9–4.9% at 316°C, 19.2–22.3% at 400°C, 62.5–68.0% at 500°C, and 98.7–98.5% at 700°C, as shown in Table III. This indicated that after 1000 min of heating, the composites were still thermooxidatively stable at 316°C,

TABLE III
Isothermal TGA Data of the Composites

Composite	Char yield (%) in nitrogen (1000 min) 316°C	400°C	500°C	700°C	Atmosphere
9	94	93	87	73	Nitrogen
9	96	78	32	2	Air
10	92	88	86	76	Nitrogen
10	95	81	38	1	Air

TABLE IV
Mechanical Properties of the Composites

Property	Composite 9 (GPa)	 10 (GPa)
Tensile strength		
0/90°	0.299	0.337
±45°	0.026	0.024
Tensile modulus		
0/90°	5.000	4.500
±45°	1.450	1.100
Flexural strength	0.334	0.149
Flexural modulus	44.50	31.30
Short-beam shear	14.80	10.80
Resin content (wt %)	59	58

which is the upper-use temperature of the well-known polymerization of monomeric reactants type polyimides (PMR) system.[5] Also, the results of both the dynamic TGA and the isothermal TGA show that composite **9** had better thermal stability than composite **10**, but both had similar flame-retardant properties.

The resin contents of the composites were determined by the ignition loss method. As shown in Table IV, the resin content of both composites **9** and **10** were close to 60%. The mechanical properties of the composites were also measured before and after aging at 316°C in air (Table V). As shown in Table IV, the tensile strength (0/90°) of composite **10** was a little bit higher than that of composite **9**. However, the other mechanical properties of composite **9**, which included tensile strength (±45°), flexural strength, flexural modulus, and short-beam shear, were all higher than that of composite **10**. In addition, as indicated in Table V, after aging at 316°C for 24 h in air, both the composites still retained 80–90% of their original strengths. This result implies that the composites prepared in this study have the potential for use at high temperature.

Figure 8 shows the scanning electron microscopy (SEM) photograph of the original composite **9**. The resin strongly adhered to the fibers. Figure 9 shows the SEM photographs of the fractured section of the composites after the tensile test. The resin still strongly adhered to the fibers. In addition, the SEM

TABLE V
Tensile Strength of the Composites Before and After the Aging Process

Composite	Tensile strength (0/90°) Before aging	 After aging
9	0.299	0.270
10	0.337	0.251

[a] The composites were aged at 316°C for 24 h before measurement.

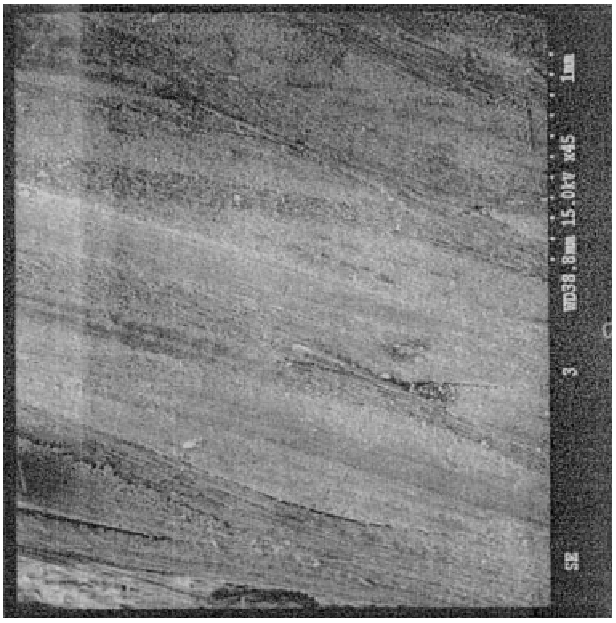
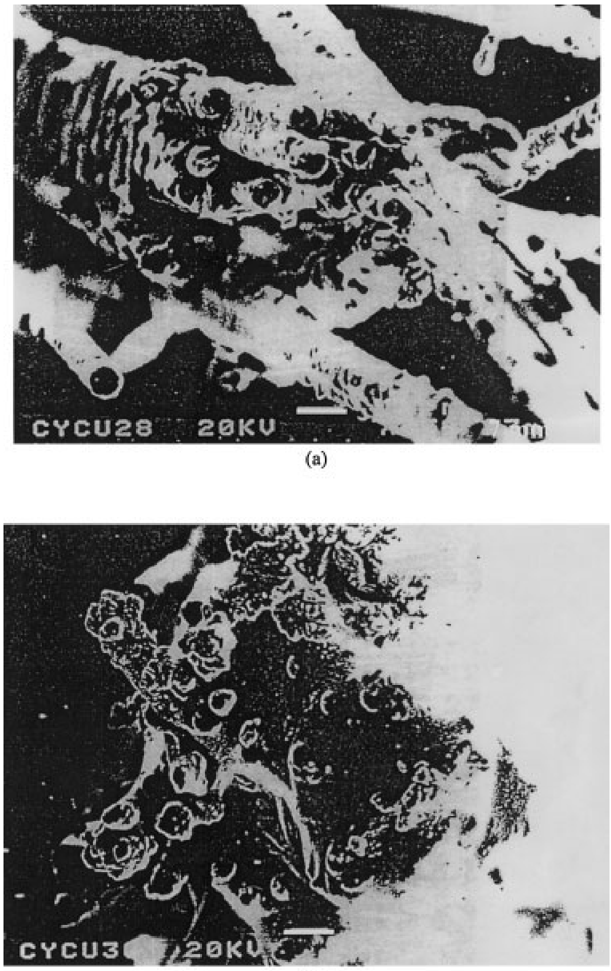


Figure 8 SEM micrograph of the original composite **9**.



(a)

(b)

Figure 9 SEM micrograph of the tensile test for the fractured section of composites (a) **9** and (b) **10**.

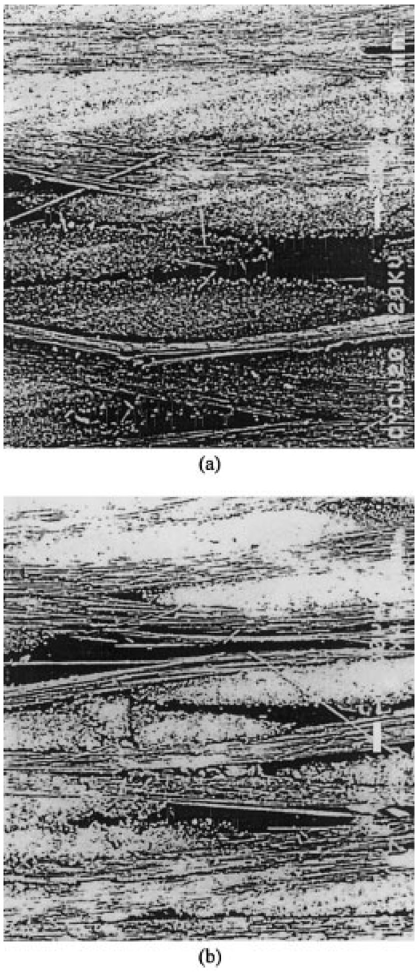


Figure 10 SEM micrograph of the shear test for the fractured section of composites (a) **9** and (b) **10**.

photograph of the fractured surface after the shear test shown in Figure 10 demonstrates the matrix cracks and the delamination of the composites. Again, this indicates that for both of the composites, the adhesion strength between the resin and the fibers observed was strong, but the matrices were brittle.

CONCLUSIONS

In this study, two nontoxic nadic-end-capped cyclotriphosphazene-containing polyimide resins were synthesized and were used to prepare carbon-fiber-reinforced composites. The results of the dynamic TGA and the isothermal TGA indicate that the composites had good thermooxidative stability and flame retardance and retained excellent tensile strength after aging at 316°C for 24 h. The char yields of these composites were higher than 85% at 1000°C in nitrogen and close to 80% at 700°C in air. The SEM photographs showed that both the resins had a strong adhesion to the carbon fiber. These results suggest that the composites prepared were useful at 316°C and also indicate that composite **9** had better thermal stability and mechanical properties than composite **10**.

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