Phthalonitrile-Epoxy Blends: Cure Behavior and Copolymer Properties

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Received 27 February 2008; accepted 2 June 2008
DOI 10.1002/app.28817
Published online 20 August 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Binary blends composed of 4,4′-bis(3,4-dicyanophenoxy)biphenyl (biphenyl PN) and diglycidyl ether of bisphenol A (epoxy resin) and oligomeric $n = 4$ phthalonitrile ($n = 4$ PN) and epoxy resin were prepared. The cure behavior of the blends was studied under dynamic and isothermal curing conditions using differential scanning calorimetry, simultaneous thermogravimetric/differential thermal analysis, infrared spectroscopy, and rheological analysis. The studies revealed that phthalonitrile-epoxy blends exhibited good processability and that they copolymerized with or without the addition of curing additive. In the absence of curing additive, the blends required higher temperatures and longer cure times. The thermal and dynamic viscoelastic properties of amine-cured phthalonitrile-epoxy copolymers were examined and compared with those of the neat epoxy resin. The properties of the epoxy resin improved with increasing biphenyl PN content and with $n = 4$ PN addition. Specifically, the copolymers exhibited higher glass transition temperatures, increased thermal and thermo-oxidative stabililty, and enhanced dynamic mechanical properties relative to the commercially available epoxy resin. The results showed that the phthalonitrile-epoxy blends and copolymers have an attractive combination of processability and high temperature properties. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2504–2515, 2008

Key words: phthalonitrile; blends; curing of polymers; mechanical properties; thermal properties

INTRODUCTION

Polymer blending and copolymer formation is a well-established approach for tailoring the properties of polymeric materials for a particular application. The new materials generally have a useful combination of properties derived from the individual polymer components that can be tuned by changes in blend composition. Blending technology has resulted in a large number of high impact engineering thermoplastic materials.[1] Thermoplastics[2–7] have also been incorporated into thermosetting polymers, and blends of various thermosetting resins have been formulated to improve their toughness without sacrificing other desirable high temperature properties. Some examples of thermosetting systems that have been studied include epoxy/cyanate ester,[8–15] epoxy/bismaleimide,[16] epoxy/hyperbranched polymers,[17,18] epoxy/phenolic resin,[19–21] epoxy/benzoxazine,[22,23] cyanate ester/bismaleimide,[24,25] cyanate ester/cyanate ester,[26] cyanate ester/epoxy/phenolic,[27] phthalonitrile/epoxy,[28,29] and phthalonitrile/phthalonitrile.[30]

Phthalonitriles are an attractive class of high temperature thermosetting polymers that have been under investigation for over two decades. During this time, many different phthalonitrile monomers have been synthesized and the properties of the cured resins[31–38] and their composites[39–41] have been studied. The cured resins possess many useful properties which include high glass transition temperatures (T_g, above 450°C), outstanding thermal and thermo-oxidative stability, excellent mechanical properties, good moisture resistance, and superior fire resistance. In addition, the resins are processable into composite components by a wide range of methods that include prepreg consolidation, resin transfer molding, resin infusion molding, and filament winding. 4,4′-Bis(3,4-dicyanophenoxy)biphenyl (biphenyl PN, Fig. 1) was the first phthalonitrile-based, high-temperature resin reported[31,33] and has been the most extensively studied. Recently, the oligomeric $n = 4$ phthalonitrile monomer ($n = 4$ PN, Fig. 1) was designed and synthesized to achieve enhanced processability while maintaining high thermo-oxidative stability.[38]

Epoxy resins are also versatile thermosetting polymers and among the commercially most important. They have reasonable thermal, mechanical, and electrical properties, good chemical resistance and are easy to process. However, their utility is limited by their low softening temperature (~ 150°C).

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Contract grant sponsor: The Office of Naval Research.

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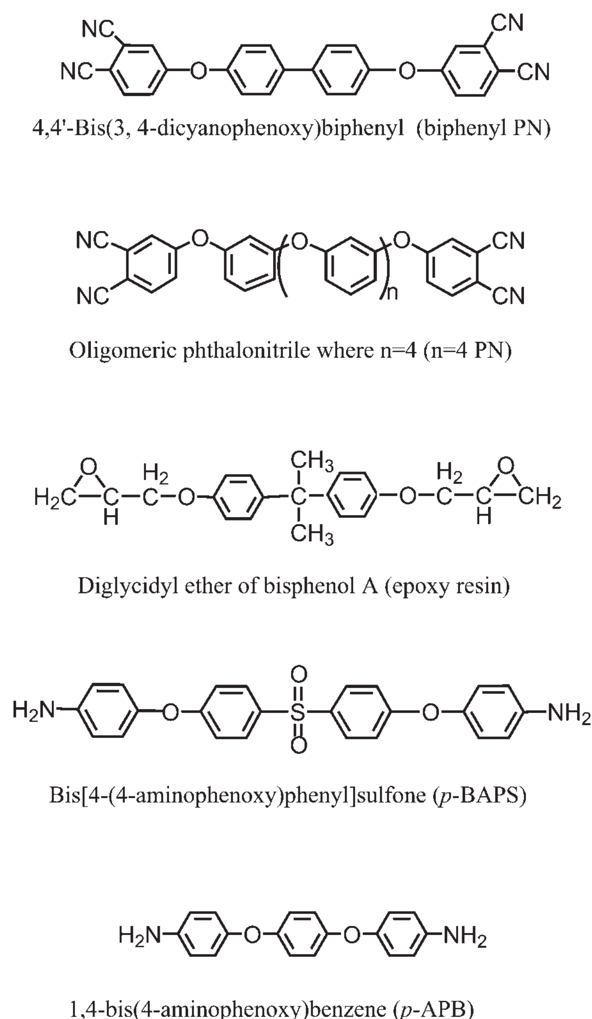

Figure 1 Chemical structures of the monomers and curing additives.

In this article, biphenyl PN and $n = 4$ PN were each blended with a diglycidyl ether of bisphenol A (epoxy resin, Fig. 1) and the cure behavior of the blends was investigated under dynamic and isothermal curing conditions using differential scanning calorimetry, simultaneous thermogravimetric/differential thermal analyses, infrared spectroscopy, and rheological analysis. The effect of the phthalonitrile addition on the thermal and mechanical properties of the epoxy resin was assessed. The results revealed that phthalonitrile-epoxy blends exhibited good processability and the copolymers have enhanced high temperature properties compared with the cured epoxy resin.

EXPERIMENTAL

Materials

The 4,4′-bis(3,4-dicyanophenoxy)biphenyl (biphenyl PN) and oligomeric $n = 4$ phthalonitrile ($n = 4$ PN) monomers were supplied by Dow Chemical Co. (Midland, MI) and JFC Technologies (Bound Brook, NJ), respectively. The diglycidyl ether of bisphenol A (epoxy resin) was acquired from Shell Chemical Co. (New Milford, CT) Bis[4-(4-aminophenoxy)phenyl]sulfone (*p*-BAPS, $T_m = 188°C$) and 1,4-bis(4-aminophenoxy)benzene (*p*-APB, $T_m = 170°C$) were purchased from ChrisKev Co. (Lenexa, KS) and Aldrich Chemical Co. (Milwaukee, WI), respectively. The monomers and *p*-APB were used as received. The *p*-BAPS was dried overnight at 175°C under vacuum before use. The chemical structures of the materials are shown in Figure 1.

Preparation of the phthalonitrile-epoxy blends

Phthalonitrile-epoxy blends were prepared by stirring the phthalonitrile monomer and the aromatic diamine curing additive (*p*-BAPS or *p*-APB) into the viscous liquid epoxy resin under ambient conditions to form a homogeneous mixture. The biphenyl PN-epoxy blends were formulated with 25 : 75, 50 : 50, and 75 : 25 molar ratios of the biphenyl PN and epoxy monomers, respectively. An oligomeric $n = 4$ PN-epoxy blend was prepared with a 32 : 68 molar ratio of $n = 4$ PN and epoxy monomers. Phthalonitrile-epoxy blends were also prepared without the curing additive.

Preparation of the phthalonitrile-epoxy copolymers

Rectangular solid copolymer samples for dynamic mechanical analysis were made in aluminum molds with cavity dimensions 65 mm × 13 mm × 4 mm. Phthalonitrile-epoxy copolymers were prepared by weighing the respective monomers into the mold and stirring to achieve a homogenous blend. The blends were degassed under vacuum at 200°C for about 1 h. After the initial degassing, *p*-BAPS (2.5 mol %) or *p*-APB (24 mol %) was added to the biphenyl PN-epoxy or $n = 4$ PN-epoxy melt, respectively, and evenly dispersed with continuous stirring for about 2 min. The mixture was further degassed and heated at 200°C for another 1 h until gelation occurred. Biphenyl PN-epoxy and $n = 4$ PN-epoxy samples were thermally cured by heating in an oven at 325°C for 1 h, and stepwise at 325°C for 1 h, and 350°C for 8 h, respectively, under an atmosphere of argon. The cured copolymer samples were cooled gradually to room temperature in the oven, removed from the molds, and sanded to a thickness of ∼ 2 mm for the dynamic mechanical measurements. Cured copolymer samples were broken into small pieces for thermogravimetric analyses.

Biphenyl PN (*p*-BAPS, 2.5 mol %), $n = 4$ PN (*p*-APB, 24 mol %), and epoxy (*p*-BAPS, 33 mol % and *p*-APB, 33 mol %) polymer samples were similarly prepared with degassing at 250, 200, and 150°C,

respectively. The following temperature/time schedules were used to cure the polymer samples: biphenyl PN—250°C for 1 h, 325°C for 3 h, 350°C for 2 h, and 375°C for 8 h; $n = 4$ PN—280°C for 1 h, 325°C for 1 h, 350°C for 1 h, and 375°C for 8 h; and the epoxy resin—280°C for 1 h.

Characterizations

Dynamic differential scanning calorimetric (DSC) analysis was used to study the cure of the phthalonitrile-epoxy blends using a TA Instruments 2920 DSC at a heating rate of 10°C min^{-1} and a nitrogen flow rate of 100 mL min^{-1}. Data were recorded from 0 to 400°C on samples (1–2 mg) in sealed aluminum pans. T_gs were determined from the inflection points in the heat flow versus temperature curves.

A TA Instruments SDT 2960 simultaneous thermogravimetric/differential thermal analyzer (TGA/DTA) was employed to determine the thermal and thermo-oxidative stability of the cured polymer and copolymer samples. The thermal studies were carried out by heating small samples (25–50 mg) from room temperature to 1000°C at a heating rate of 10°C min^{-1} in an atmosphere of either nitrogen or air flowing at a rate of 100 mL min^{-1}. Degradation temperatures are reported as the temperature where a 5% sample weight loss was observed or as the temperature maximum of the peak seen in the DTA curve. Samples for oxidative aging studies were predried in the TGA chamber by heating from room temperature to 100°C where they were held for 30 min to remove absorbed moisture. After drying, the samples were heated in the TGA stepwise for 8 h at 260, 288, 316, and 343°C at a heating rate of 10°C min^{-1}.

The isothermal cure of the 50 : 50 biphenyl PN-epoxy blend was investigated using a Nicolet magna 750 Fourier transform infrared (FTIR) spectrometer. Infrared spectra in the optical range of 400–4000 cm^{-1} were recorded on a small quantity of sample compressed into a potassium bromide pellet.

Dynamic viscosity measurements were performed on a TA Instruments AR-2000 rheometer in conjunction with an environmental testing chamber for temperature control. Phthalonitrile-epoxy samples (0.5–1 g) were melted between 25 mm diameter parallel plates in the test chamber of the rheometer. Complex viscosity data were acquired at a fixed temperature in air as a function of time at a low strain (2.5×10^{-4}) and a frequency of 1 Hz. During a measurement, the gap between the plates was maintained at 0.5 mm. The rheometer was also used with torsion fixtures to measure the storage modulus (G') and damping factor ($\tan\delta$) of rectangular PN polymer and copolymer samples (dimensions 50 mm × 12 mm × 2 mm) in nitrogen over the temperature range of 40 to 400°C. Using a strain of 2.5×10^{-4} selected from within the linear viscoelastic region, an oscillatory temperature ramp of 3°C min^{-1} was used to determine G' and $\tan\delta$ at a frequency of 1 Hz. Normal force control was utilized throughout the tests to keep the samples taut.

RESULTS AND DISCUSSION

Cure studies on the biphenyl PN-epoxy blends under dynamic conditions

Based on its slow reactivity and high thermal stability, *p*-BAPS was selected as the preferred curing additive for the polymerization of the biphenyl PN-epoxy blends and 2.5 mol % *p*-BAPS was used to study the curing of the blends. DSC thermograms acquired while heating the biphenyl PN-epoxy blends to 400°C with *p*-BAPS are presented in Figure

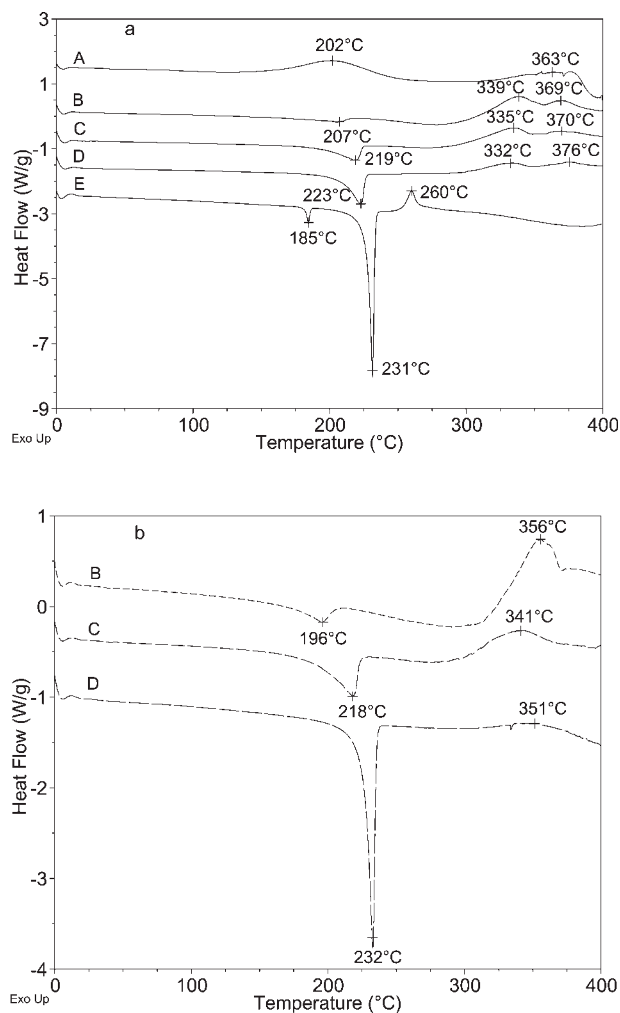

Figure 2 DSC thermograms of monomers and biphenyl PN-epoxy blends with (a) *p*-BAPS curing additive and (b) no curing additive. The samples are as follows : (A) epoxy resin, (B) 25 : 75 biphenyl PN-epoxy, (C) 50 : 50 biphenyl PN-epoxy, (D) 75 : 25 biphenyl PN-epoxy and (E) biphenyl PN.

TABLE I
Thermal Properties of the Biphenyl PN-Epoxy (BPN : Epoxy) Blends

	DSC exotherm peak temperature (°C)		ΔH (J g^{-1})		Gelation time at 275°C (min)	
BPN : Epoxy (mole ratio)	With *p*-BAPS	No *p*-BAPS	With *p*-BAPS	No *p*-BAPS	With *p*-BAPS	No *p*-BAPS
0 : 100	202	–	173	–	–	–
25 : 75	339	356	69	86	19	28
50 : 50	335	341	48	56	24	48
75 : 25	332	351	26	56	40	76
100 : 0	260	–	26	–	40	76

2(a). DSC curves of the individual monomer/*p*-BAPS mixtures heated under similar conditions are included in the figure. The DSC trace of the biphenyl PN monomer exhibited two endothermic transitions centered at 185 and 231°C, which are attributed to the melting of the *p*-BAPS and the biphenyl PN monomer, respectively. In the thermograms of the blends, only the biphenyl PN monomer melting transition was observed (207–223°C) and the peak melting temperature was dependent on the blend composition. The biphenyl PN monomer/*p*-BAPS mixture had one exothermic transition which peaked at 260°C. The transition corresponds to triazine ring formation from the cyclotrimerization of phthalonitrile via its cyano groups.[33,35,39] The DSC thermogram of the epoxy resin had two well-resolved exothermic transitions centered at 202 and 363°C. The exotherms are attributed to reaction of the epoxy resin with the amine curing additive and to thermal degradation/decomposition of the polymer and/or excess epoxy resin, respectively. The latter was confirmed by thermal and dynamic mechanical analyses (*vide supra*). The exotherm at 202°C was absent in the thermograms of the biphenyl PN-epoxy blends, implying that the aforementioned *p*-BAPS-catalyzed cure reaction of the epoxy resin was not happening appreciably in the blends. Instead, the thermograms of the blends exhibited two exothermic transitions that peaked in the ranges of 332–339°C and 369–376°C. The first transition was due to the *p*-BAPS-catalyzed copolymerization reaction between the nitrile groups of the phthalonitrile and the epoxy resin. The overlapping higher temperature exotherm was again ascribed to the decomposition of unreacted epoxy resin, although copolymer decomposition and reaction between the less reactive nitrile group on the phthalonitrile and the epoxy resin may also be occurring. The exotherm peak intensities and temperatures are a function of the blend composition. As the biphenyl PN content of the blend increased, the exotherm peak intensities decreased and the exotherms separated from each other. Lower peak intensities indicated that the copolymerization and decomposition reaction rates had decreased. The enthalpy of cure for the 25 : 75, 50 : 50, and 75 : 25 molar blends with *p*-BAPS was estimated as 69, 48, and 26 J g^{-1}, respectively. The enthalpy of reaction for the epoxy resin/*p*-BAPS and biphenyl PN/*p*-BAPS mixtures was ~ 173 and 26 J g^{-1}, respectively. The exotherm peak shift to lower temperatures (<339°C) was evidence that the reactivity of the blends increased with higher biphenyl PN contents. The peak shift in the high temperature region (>369°) is due to an increase in the copolymer thermal stability with an increasing phthalonitrile content.

DSC analysis was used to study the cure of the biphenyl PN-epoxy blends without the curing additive and the thermograms obtained are depicted in Figure 2(b). The thermograms each show one broad exothermic transition in the 341–356°C range, assigned to the reaction of the phthalonitrile with the epoxy resin, with a trailing shoulder attributed to the continuation of the reaction and perhaps some thermal degradation of the epoxy resin and/or the copolymer. As expected, higher exotherm peak temperatures indicated that the uncatalyzed blends were less reactive than the catalyzed blends. The cure enthalpies for the uncatalyzed 25 : 75, 50 : 50, and 75 : 25 molar blends were estimated as 86, 56, and 56 J g^{-1}, respectively. DSC results obtained on the biphenyl PN-epoxy blends with and without *p*-BAPS are summarized in Table I.

Cure studies on the biphenyl PN-epoxy blends under isothermal conditions

The cure of the biphenyl PN-epoxy blends was evaluated under isothermal conditions. The temperatures of the isothermal curing experiments were chosen based on the DSC data displayed in Figure 2. The DSC data showed that the biphenyl PN and epoxy resin copolymerization onset temperature was around 300°C with or without the curing additive. As such, the isothermal cure of the blends was conducted at 250, 275, and 325°C and the progress of the copolymerization was examined by DSC, TGA/DTA, and rheological analyses and by infrared spectroscopy.

DSC thermograms acquired after heating the 50 : 50 biphenyl PN-epoxy molar blend with *p*-BAPS at 250°C for 10 min, 2 h, and 4 h are shown in Figure

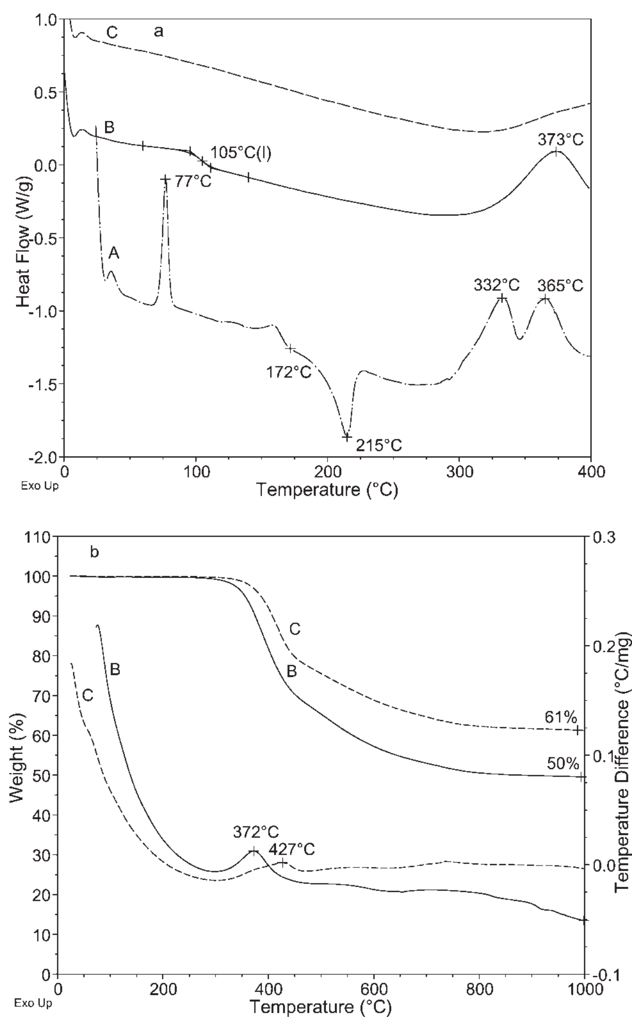

Figure 3 (a) DSC and (b) TGA/DTA thermograms of the 50 : 50 biphenyl PN-epoxy blend/*p*-BAPS mixture acquired after heating at 250°C for (A) 10 min, (B) 2h, and (C) 4h.

3(a). Similarly, TGA/DTA thermograms obtained after heating the monomer blend/*p*-BAPS mixture at 250°C for 2 h and 4 h are presented in Figure 3(b). The figures show the thermal property evolution as the copolymerization progressed. Figure 4 compares TGA/DTA thermograms of the 50 : 50 biphenyl PN-epoxy blend/*p*-BAPS mixture obtained after heating for 1 h at three temperatures (250, 275, and 325°C). The results showed that the thermal properties of the copolymers improved when the blends were heated at the higher temperatures.

TGA/DTA data for the three biphenyl PN-epoxy blend compositions are compared in Table II after the blends were heated at 275°C in air for various lengths of time with and without *p*-BAPS. The table presents the decomposition peak temperatures and the residual char yields of the copolymers at 1000°C when heated under a flow of nitrogen. The data showed the cure progression of the copolymers and their thermal stability as a function of the heating time and biphenyl PN content. The data also revealed that the epoxy resin effectively advanced the phthalonitrile cure without the curing additive.

FTIR spectroscopy was used to monitor the cure of the 50 : 50 biphenyl PN-epoxy molar blend/*p*-BAPS mixture after heating at 250°C for 2 h and at 325°C for 1 h. The FTIR data showed that as the copolymerization advanced, the characteristic absorptions of the phthalonitrile nitrile band at 2232 cm^{-1} and the epoxy groups at 917 and 860 cm^{-1} disappeared. The phthalonitrile-epoxy copolymerization reaction was predicted to result in oxazoline ring formation. Spectral subtraction was used to observe the appearance and growth of this band at 1608 cm^{-1}.

The cure of the biphenyl PN-epoxy blends was also investigated by rheological analysis. The study was carried out by heating the blends between parallel plates in a rheometer at 275°C and following the complex viscosity, η*, change over time as the cure progressed. Initially, the viscosity of the blends increased gradually until gelation occurred. Then, a rapid increase in sample viscosity was observed until a glassy material formed. From these data, the gelation time (gel point) that characterizes the sample cure was determined. The gel point corresponds to the start of copolymer network formation. Figure 5(a,b) compare the complex viscosity (η*) changes with cure time at 275°C for the three biphenyl PN-epoxy blend compositions with and without *p*-BAPS, respectively. The data revealed that all the biphenyl PN-epoxy blend samples exhibited a dramatic increase in viscosity when heated at 275°C. The observed viscosity changes are evidence that the monomers are coreacting to form crosslinked networks. The influence of biphenyl PN concentration on the gelation time is evident. As the biphenyl

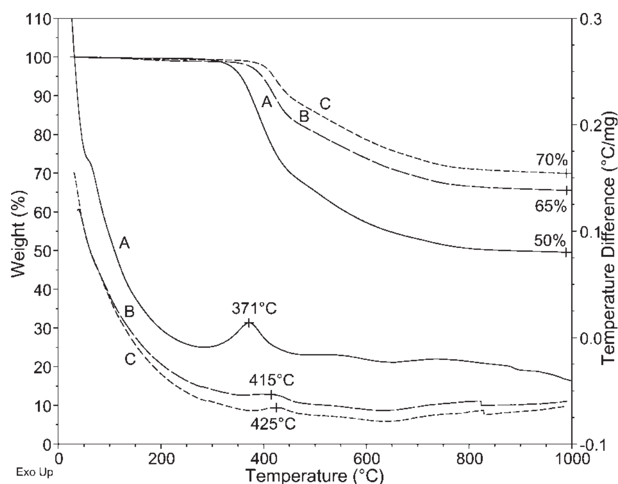

Figure 4 TGA/DTA thermograms of the 50 : 50 biphenyl PN-epoxy blend/*p*-BAPS mixture acquired after heating for 1 h at (A) 250 °C, (B) 275 °C, and (C) 325 °C.

TABLE II
Thermal Properties of the Biphenyl PN-Epoxy (BPN : Epoxy) Copolymers Heated at 275°C in Air

BPN : epoxy (mole ratio)	Heating time at 275°C (h)	DTA peak temperatures (°C)		Char yield at 1000°C (%)	
		With *p*-BAPS	No *p*-BAPS	With *p*-BAPS	No *p*-BAPS
25 : 75	1	377	301, 366	43	39
	2	395	374	42	42
	4	>400	>400	54	41
50 : 50	1	373	336	50	51
	2	373	365	46	58
	4	>400	378	61	63
	6	>400	>400	59	60
75 : 25	1	>400	>400	71	69
	2	>400	>400	70	69
	4	>400	>400	71	70

PN content of the sample increased, the gelation time increased. This result was expected since the DSC data showed that higher biphenyl PN concentrations in the blend decreased the rate of copolymerization. The effect of the curing additive on the copolymerization rate is also apparent. For a given blend composition, the gelation time increased when no *p*-BAPS was added. The gelation times (determined from the G', G'' crossover points[19,42]) for the biphenyl PN-epoxy blends and for biphenyl PN at 275°C, with and without the addition of *p*-BAPS, are summarized in Table I. The rheological data revealed that the biphenyl PN-epoxy blends may offer some processing advantages relative to biphenyl phthalonitrile.

Cure studies on the oligomeric $n = 4$ PN-epoxy blends under dynamic conditions

The oligomeric $n = 4$ PN has a larger average molecular weight, lower density of reactive nitrile groups, lower melting point, and larger processing window than the biphenyl PN. Although the biphenyl PN-epoxy blends were cured in the presence of 2.5 mol % of *p*-BAPS, similar amounts of curing additive did not result in gelation of the $n = 4$ PN-epoxy blend in a timely manner. As a result, the aromatic amine *p*-APB, a curing additive more reactive than *p*-BAPS, and a higher additive concentration (24 mol %) were used to affect the $n = 4$ PN-epoxy cure. DSC thermograms obtained on heating the $n = 4$ PN-epoxy molar blend and the individual monomers to 400°C with *p*-APB are presented in Figure 6(a). The $n = 4$ PN monomer exhibited a small, crystalline melting transition centered at 42°C which was also observed in the DSC trace of the blend. In addition, the thermogram of the $n = 4$ PN/*p*-APB mixture showed one exothermic transition with a peak at 265°C

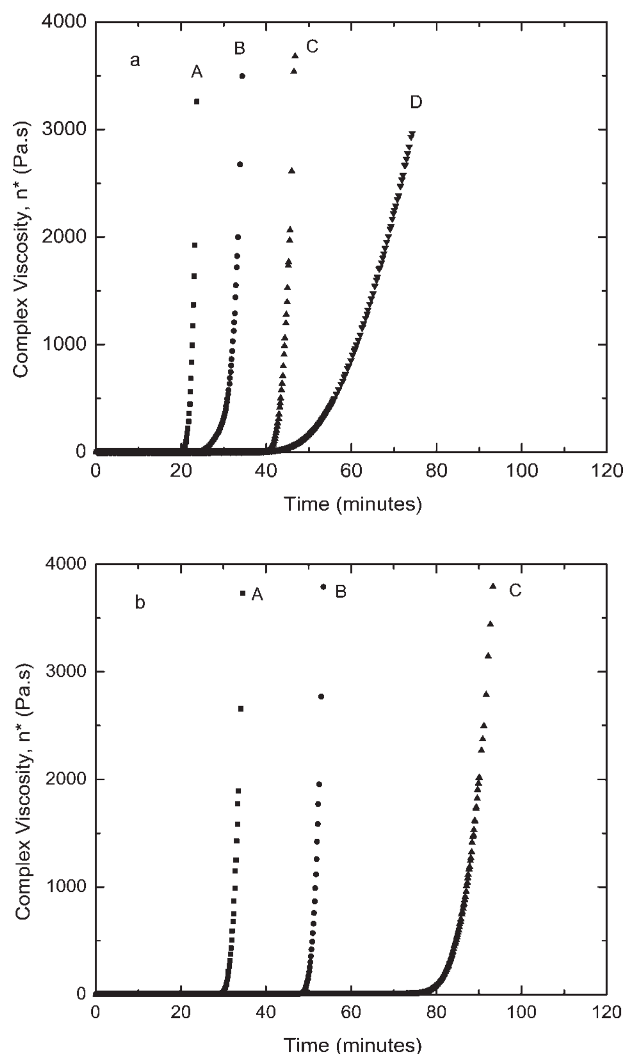

Figure 5 Complex viscosity (η*) at 275°C as a function of time for the biphenyl PN monomer and biphenyl PN-epoxy blends with (a) *p*-BAPS curing additive and (b) no curing additive. The samples are (A) 25 : 75 biphenyl PN-epoxy, (B) 50 : 50 biphenyl PN-epoxy, (C) 75 : 25 biphenyl PN-epoxy, and (D) biphenyl PN.

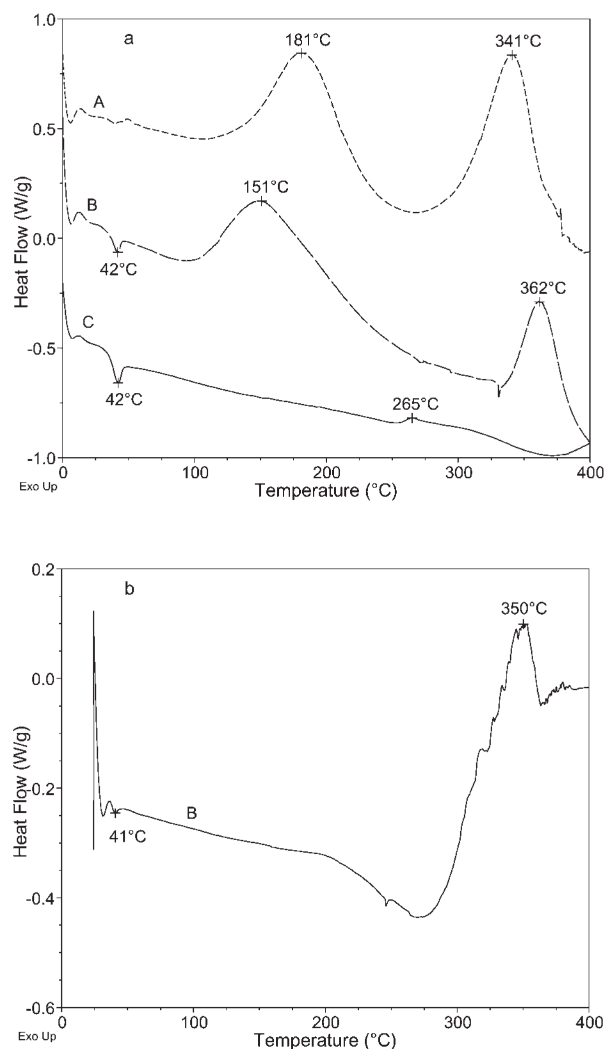

Figure 6 DSC thermograms of the monomers and the $n = 4$ PN-epoxy blend with (a) *p*-APB curing additive and (b) no curing additive. The samples are (A) epoxy resin, (B) 32 : 68 $n = 4$ PN-epoxy and (C) $n = 4$ PN.

which was not seen in the thermogram of the blend. The exotherm is attributed to the *p*-APB-catalyzed phthalonitrile polymerization reaction. Two broad exothermic transitions centered at 181 and 341°C are shown in the DSC trace of the epoxy/*p*-APB mixture. The transitions correspond to the reaction of the amine curing additive with the epoxy group and to the thermal decomposition of the polymer and/or excess epoxy resin, respectively. The DSC thermogram of the $n = 4$ PN-epoxy blend/*p*-APB mixture displayed two exothermic transitions shifted to lower (151°C) and higher temperatures (362°C), respectively. The low temperature shift was attributed to the catalytic affect of the phthalonitrile on the polymerization of the epoxy and the high temperature shift was probably caused by the higher thermal stability of the copolymer relative to the epoxy resin.

DSC was also employed to investigate the copolymerization of the $n = 4$ PN-epoxy molar blend with no *p*-APB addition. The thermogram shown in Figure 6(b) exhibited a single broad exotherm that peaked at 350°C. The exotherm peak temperature is in the range of that observed for the copolymerization of the biphenyl PN-epoxy blend in the absence of a curing additive and close to the decomposition temperature of the epoxy resin. As such, the single broad exotherm probably reflects competing copolymerization and decomposition reactions.

Cure studies on the oligomeric $n = 4$ PN-epoxy blends under isothermal conditions

The cure of the $n = 4$ PN-epoxy blend was investigated by heating the blends with *p*-APB under

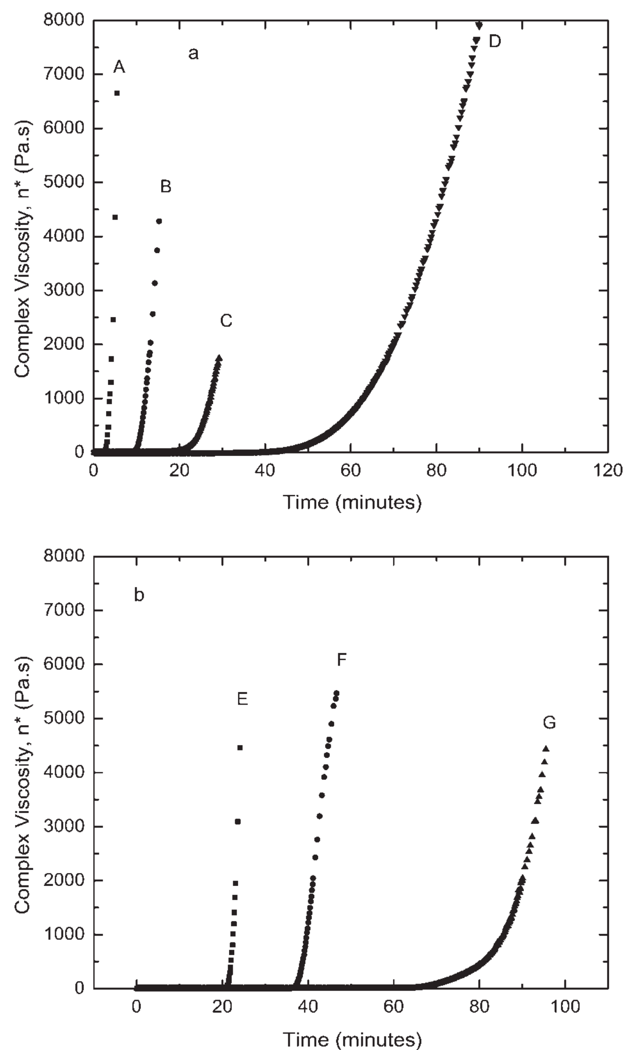

Figure 7 Complex viscosity (η*) as a function of time at various temperatures for the 32 : 68 $n = 4$ PN-epoxy blend with (a) *p*-APB curing additive and (b) no curing additive. The temperatures were (A) 200°C, (B) 150°C, (C) 125°C, (D) 100°C, (E) 300°C, (F) 270°C and (G) 250°C.

TABLE III
Thermal Properties of the $n = 4$ PN-Epoxy Copolymers as a Function of the Cure Conditions

Maximum cure (temperature/time)	DTA peak temperatures (°C)	Char yield at 1000°C (%)	DSC peak temperatures (°C)
150°C/22 h	306, 361	39	79, 301, 363
200°C/22 h	354	42	99, 353
250°C/8 h	364	50	45, 356
250°C/22 h	369	46	150, 365
300°C/3 h	359	48	80, 358
350°C/8 h	>400	73	>400

isothermal conditions. The curing temperatures were determined from the DSC data presented in Figure 6(a). According to the data, copolymerization in the presence of *p*-APB occurred between 100 and 250°C. Thus, the blend was initially heated in air at 150, 200, and 250°C and the progress of the copolymerization was examined by TGA/DTA and DSC analyses. The results, shown in Table III, provided evidence that the cure was progressing very slowly at these temperatures as the copolymers still exhibited relatively low decomposition temperatures, char yields and T_gs after heating for 22 h. Eventually, higher temperatures (300–350°C) and shorter reaction times were used to cure the blend. The TGA/DTA and DSC results of the high temperature cures are included in Table III. The data showed that the most effective cure of the $n = 4$ PN-epoxy blend was achieved by heating the blend at 350°C for 8 h. The cures at 300 and 350°C were carried out in an atmosphere of argon to avoid oxidative degradation of the copolymer.

Rheological analysis was performed on the $n = 4$ PN-epoxy blend to further characterize the curing behavior under isothermal conditions. Figure 7(a,b) compare the complex viscosity versus time variations that occurred while heating the blend at various temperatures with and without *p*-APB, respectively. In each case, abrupt viscosity increases were observed which indicated that the copolymerization was progressing. The rheological data showed that effective cure temperatures for the blend with and without *p*-APB were 100–200 and 250–300°C, respectively. As expected, the gelation time decreased with an increase in temperature and a higher rate of reaction. Plots of the logarithm of the gelation time versus temperature $(K)^{-1}$ are presented in Figure 8. The linearity of the plots reveals good agreement with Flory's gelation theory.[43] From the linear fit of these data, the slopes of the line, $-E_a/2.303R$ (where R is the gas constant equal to 8.314 J mol^{-1} deg^{-1}), were determined and the apparent activation energies of the crosslinking reactions were calculated.[19,20,42,44,45] The apparent activation energies of the copolymerization reaction with and without *p*-APB were 52 and 47 kJ mol^{-1}, respectively. These apparent activation energies agree well with literature values (42–50 kJ mol^{-1}) for the ring opening of an epoxy resin by the active amine hydrogen of an aromatic amine.[16]

Phthalonitrile-epoxy copolymer properties

Thermal properties

Using conditions determined by the DSC, TGA/DTA, and rheological analyses, biphenyl PN-epoxy and $n = 4$ PN-epoxy copolymers were cured with *p*-BAPS and *p*-APB, respectively. For comparison, biphenyl PN (*p*-BAPS), $n = 4$ PN (*p*-APB), and epoxy (*p*-BAPS and *p*-APB) polymers were prepared and the properties of the cured polymers and copolymers were evaluated. Results of the thermal studies on the biphenyl PN-epoxy and $n = 4$ PN-epoxy copolymers are presented in Tables IV and V, respectively. Included in the tables are the compositions of the cured resins, curing conditions, and

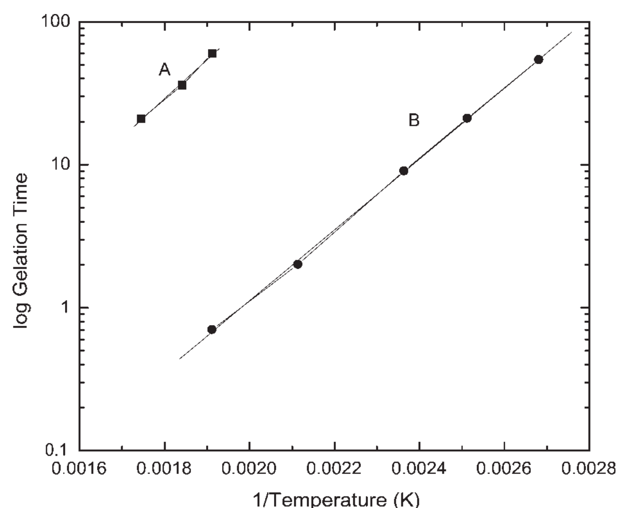

Figure 8 Plots of the logarithm of the gel time versus cure temperature $(K)^{-1}$ for the 32 : 68 $n = 4$ PN-epoxy blend with (A) no curing additive and (B) curing additive. The slopes of the lines give the apparent activation energies of the crosslinking reaction.

TABLE IV
Thermal Properties of the Biphenyl PN-Epoxy (BPN : Epoxy) Copolymers

BPN : epoxy (mole ratio)	(Mole %) *p*-BAPS	Maximum cure (temperature/time)	Cure atmosphere	$T_{5\%}$ (°C)	Char yield at 1000°C (%)	$TOS_{5\%}$ (°C)
0 : 100	28	280°C/1 h	Air	378	19	375
25 : 75	2.5	325°C/1 h	Air	403	61	448
50 : 50	2.5	325°C/1 h	Air	419	70	456
75 : 25	2.5	325°C/1 h	Air	479	74	493
100 : 0	2.5	375°C/8 h	Argon	500	71	496

thermal degradation temperatures ($T_{5\%}$) where 5% weight loss was measured and percentage of residue remaining (char yield %) after heating the samples to 1000°C in nitrogen. Also listed in the tables are the 5% weight loss degradation temperatures ($TOS_{5\%}$) determined in air.

When heated in nitrogen, the neat epoxy resin started to degrade at temperatures ($T_{5\%}$) of 378 and 356°C when cured with *p*-BAPS or *p*-APB, respectively, whereas the biphenyl PN and $n = 4$PN resins began to degrade at 500 and 534°C, respectively. The degradation temperatures for the phthalonitrile-epoxy copolymers improved in comparison to the epoxy resin. $T_{5\%}$ for the copolymers (403–508°C) was intermediate between those of the epoxy resin and the phthalonitrile. Char formation was also greatly enhanced in the copolymers relative to the cured epoxy resin. The neat epoxy resin exhibited a char yield of only 19–20% at 1000°C. With the addition of a phthalonitrile, the residual char yields of the copolymers at 1000°C increased to 61–74%. The $TOS_{5\%}$ of the copolymers (448–510°C) was also enhanced relative to the epoxy resin ($TOS_{5\%}$ 375 and 359°C with *p*-BAPS and *p*-APB, respectively). The thermal degradation temperatures and char yields increased when a phthalonitrile was blended and reacted with the epoxy resin because the phthalonitriles have significantly better thermal properties. Data acquired on the biphenyl PN-epoxy copolymers showed that the thermal properties of the copolymers increased as the biphenyl PN content increased.

Thermo-oxidative aging of the cured polymers and copolymers was carried out to assess the long term stability of the materials at elevated temperatures. The aging data for the biphenyl PN-epoxy and $n = 4$ PN-epoxy copolymers are presented in Figure 9(a,b), respectively. For comparison, data on the neat polymers are included in the figures. The data revealed that the phthalonitrile-epoxy copolymers retained 93–97% of their initial weight at the completion of the aging. The majority of the copolymer weight loss (2–5%) occurred while heating at 343°C. Most of the weight loss at 343°C is attributed to decomposition of the epoxy resin within the copolymer. In contrast, the residual weight retained for the *p*-BAPS- and *p*-APB-cured epoxy resins was 64–65%. The data clearly indicated that the phthalonitrile-epoxy copolymers exhibited improved oxidative stability compared to the neat epoxy resin.

Dynamic mechanical properties

The dynamic mechanical properties of the cured biphenyl PN-epoxy copolymers were evaluated to ascertain changes in the sample modulus as a function of temperature and to determine the T_gs of the cured copolymers. Plots of the storage modulus (G') and damping factor ($\tan\delta$) are presented in Figure 10(a,b), respectively. G' and $\tan\delta$ plots generated on biphenyl PN and epoxy polymers are included in the figures for comparison. It is evident from the plots that the *p*-BAPS-cured epoxy resin exhibited the largest modulus change and the lowest T_g (160°C). The peak observed at 353°C in the $\tan\delta$ plot of the *p*-BAPS-cured epoxy resin is attributed to the thermal decomposition of the resin. In contrast, no viscoelastic transition characteristic of a T_g was observed in the $\tan\delta$ plot of the biphenyl PN indicating that a stable crosslinked polymer network had formed on curing and that the polymer remained in the glassy state to at least 400°C.

TABLE V
Thermal Properties of $n = 4$ PN-Epoxy (n = 4PN : Epoxy) Copolymers

$n = 4$PN : epoxy (mole ratio)	(Mole %) *p*-APB	Maximum cure (temperature/time)	Cure atmosphere	$T_{5\%}$ (°C)	Char yield at 1000°C (%)	$TOS_{5\%}$ (°C)
0 : 100	27	280°C/1 h	Air	356	20	359
32 : 68	24	350°C/8 h	Argon	508	73	510
100 : 0	24	375°C/8 h	Argon	534	73	538

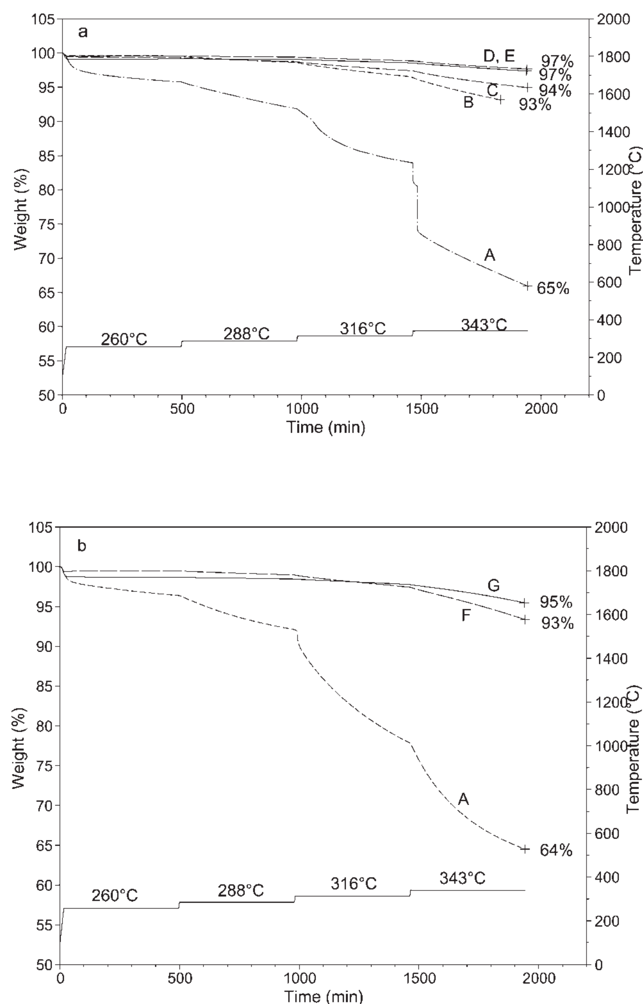

Figure 9 Weight loss as a function of time for (a) *p*-BAPS-cured polymers and copolymers and (b) *p*-APB-cured polymers and copolymers heated stepwise at various temperatures up to 343°C for 8 h intervals in air. The samples are (A) epoxy resin (B) 25 : 75 biphenyl PN-epoxy, (C) 50 : 50 biphenyl PN-epoxy, (D) 75 : 25 biphenyl PN-epoxy, (E) biphenyl PN, (F) 32 : 68 n - 4 PN-epoxy, and (G) $n = 4$ PN.

Biphenyl PN-epoxy copolymers exhibited moduli and tan δ changes intermediate between those of the biphenyl PN and epoxy polymers. At 40°C, the storage moduli of biphenyl PN, the biphenyl PN-epoxy copolymers and the epoxy resin were 1470, 1140, and 1070 MPa, respectively. Upon heating to 400°C, the storage moduli of the 25 : 75, 50 : 50, and 75 : 25 biphenyl PN-epoxy copolymers decreased from 1140 MPa to 10, 60, and 400 MPa, respectively, and the biphenyl PN modulus decreased from 1470 to 740 MPa. The data showed that the extent of the moduli changes with temperature decreased as the biphenyl PN content of the copolymer increased. In the damping factor versus temperature plots of the copolymers, only one relaxation peak was observed. The presence of a single tan δ peak indicated that the individual components in the resin mixture coreacted to form a network and that no phase separation occurred. Figure 10(b) shows that the tan δ peak height decreased and shifted to higher temperatures as the biphenyl PN content of the copolymer increased. The changes in the tan δ curves are attributed to oxazoline ring formation from reaction of the phthalonitrile and the epoxy groups which caused a reduction in polymer segmental motion. The cured biphenyl PN-epoxy copolymers showed a substantial increase in T_g (up to 240°C) in comparison to the neat epoxy resin.

Dynamic mechanical analysis was also performed on the cured $n = 4$ PN-epoxy copolymer and on neat epoxy and $n = 4$ PN polymers. G' and tan δ plots for these materials are presented in Figure 11(a,b), respectively. As seen from these curves, a

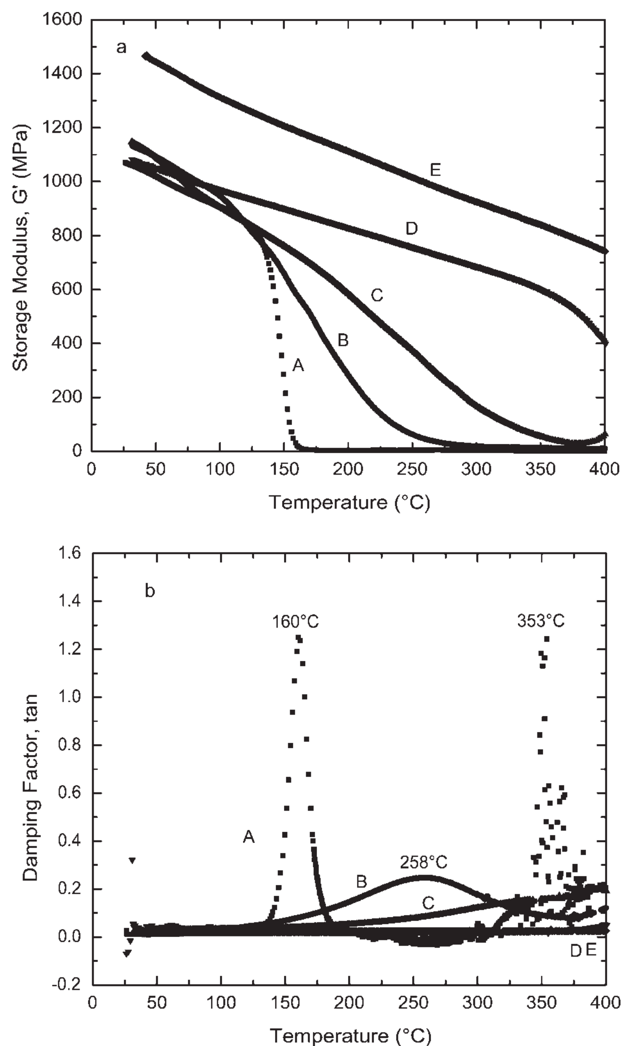

Figure 10 (a) Storage modulus (G') and (b) damping factor (tan δ) as a function of temperature for *p*-BAPS-cured polymers and copolymers heated in nitrogen: (A) epoxy resin, (B) 25 : 75 biphenyl PN-epoxy, (C) 50 : 50 biphenyl PN-epoxy, (D) 75 : 25 biphenyl PN-epoxy and (E) biphenyl PN.

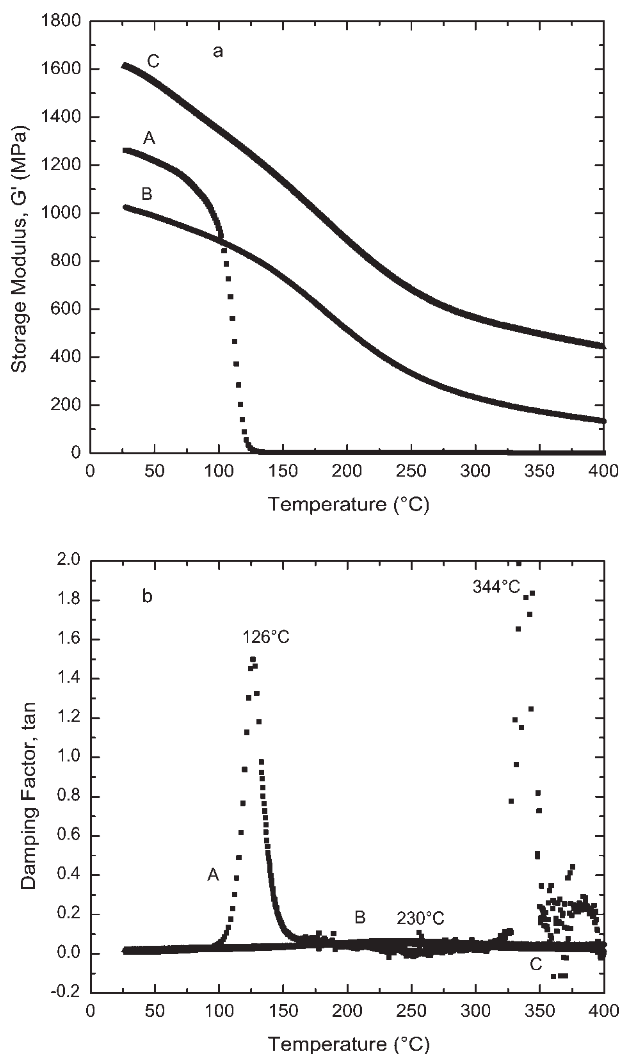

Figure 11 (a) Storage modulus (G') and (b) damping factor ($\tan\delta$) as a function of temperature for *p*-APB-cured and copolymers heated in nitrogen: (A) epoxy resin, (B) 32 : 68 $n = 4$ PN-epoxy and (C) $n = 4$ PN.

large modulus change and a low T_g (126°C) are again observed for the epoxy resin. The peak at 343°C in the $\tan\delta$ plot of the *p*-APB-cured epoxy resin is attributed to the thermal decomposition of the resin. The room temperature storage modulus of the $n = 4$ PN, the $n = 4$ PN-epoxy copolymer, and the epoxy resin were 1610, 1020, and 1260 MPa, respectively. Upon heating to 400°C, the storage modulus of the copolymer and the $n = 4$ PN polymer gradually decreased to 10–30% of their room temperature values due to stress relaxation of the polymer network, whereas the storage modulus of the epoxy resin decreased by almost three orders of magnitude. Inspection of the damping curve for the $n = 4$ PN-epoxy copolymer again showed a single $\tan\delta$ peak indicating homogeneous phase morphology. The addition of $n = 4$ PN to the epoxy resin increased its T_g by $\sim$ 100°C.

CONCLUSIONS

Biphenyl PN-epoxy and $n = 4$ PN-epoxy blends were prepared and the cure behavior of the blends was studied under dynamic and isothermal curing conditions with and without a curing additive. The studies revealed that phthalonitrile-epoxy blends have good processability and that they will copolymerize in the absence of a curing additive, although higher temperatures and longer cure times are needed. The thermal and dynamic mechanical properties of the amine-cured phthalonitrile-epoxy copolymers were evaluated. The phthalonitrile-epoxy copolymers exhibited improved high temperature properties relative to the epoxy resin.

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