Highly Thermally Stable Novolac Derivatives and Their Properties in Epoxy Composites

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ABSTRACT: Two diazo-coupling novolac derivative resins (carbonyl phenyl azo novolac resin and carbonyl phenol–biphenylene azo novolac resin) were used as flame retardants. The cured resins exhibited elevated glass-transition temperatures from 115°C (blank) to 195 and 167°C, respectively. The char yield at 800°C was increased, which elaborated the effectiveness of flame retardancy with evaluated limiting oxygen indices around 36 to 40. This was mainly attributed to the increased crosslink densities and highly aromatic contents in the modified phenol novolac derivative resins, which exhibited higher thermal degradation energies.

Furthermore, the more effective flame retardancy was expected because of the loss of nitrogen during combustion. Through the evaluation of the cooperative flame retardancy in the organic/inorganic hybrid with char yield and increasing limiting oxygen index percentage, the effects of the filler showed cooperative flame retardancy only with the appropriate addition and with a difference in the crosslinking densities. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3782–3790, 2009

Key words: azo polymers; flame retardance; synthesis; thermal properties; thermodynamics

INTRODUCTION

Phenolic derivative resins are widely used in industrial applications, such as adhesives, coatings, construction, composite matrices, and electronics. Their popularity arises from their good dimensional stability, low cost, high resistance to chemicals, good thermal stability, and heat resistance.[1–3] The rapid growth of phenolic resin applications has also prompted extensive research to enhance the thermal properties of materials for versatile applications in the electrical and electronics industries. Currently, the commercial market is dominated by compounds containing halogens, notably chlorine and bromine, where exceptional flame-retarding efficiency is found when these compounds are incorporated as either additives or reactants. However, they are clearly disadvantageous, as toxic and corrosive gases are generated during their thermal degradation.

Recent developments in the chemistry of halogen-free, flame-retardant polymers involve polymers or reactive monomers that are inherently flame retardant, such as those containing P, Si, B, N, and other miscellaneous elements.[4] Silicon and phosphorus compounds have been reported to demonstrate effective flame retardancy by the formation of a foam layer.[5–9] These additives are somewhat toxic

and often show adverse effects in other material characteristics, such as humidity and heat resistance, when applied to epoxy resin compounds. Boric acid and borate salts are also effective flame retardants because impenetrable glass coatings are formed during thermal degradation to contribute to the intumescence effect. However, these additives have to be used at relatively high concentrations, which may affect the physical and mechanical properties of the polymers.[10–12] Recently, metal hydrates have been proposed to replace halogen compounds by water during combustion.[13,14] However, the extremely large quantity of additive mars the crosslinking properties of the epoxy resin. Nitrogen compounds are widely used as protective coatings because of their transparency, good adhesion, and heat and chemical resistance for effective intumescence in fire ignition. A recent study of a diazo-coupled novolac polymer has also made the addition of curable phenolic appealing because of the improved thermal stability.[15] However, the uses of the diazo-coupled novolac polymer in epoxy resin and the performance of cured resins has not been detailed previously.

In prior studies, researchers have also attempted to produce flame-retarding compounds mainly by restraining the movement of molecular segments in the epoxy resin, that is, by stiffening networks at high temperature to increase the heat resistance or inserting bulky substituents, such as aromatic groups, into the networks.[16] In this article, we present the syntheses of two kinds of epoxy-curable

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diazo-coupling phenol novolac (PN) derivatives; these gave rise to high crosslinking densities with reduced free volumes, tied up the molecular segments, and inserted bulky substituents, such as aromatic groups by inflammable N elements. The synthetic procedure and material characteristics are discussed, and the flame retardancy and thermostability were evaluated and compared against inorganic filler analogues.

EXPERIMENTAL

Materials

4-Aminobenzoic acid (Aldrich, 99%), sulfamic acid (Aldrich, 99.5%), sodium acetate trihydrate (Aldrich, 99.5%), ammonium hydroxide (Aldrich, 28–30%), sodium nitrite (Showa, 98.5%), hydrochloric acid (Aldrich, 37%), and acetic acid (Fluka, 99.8%) were used as received. Aluminum trihydrate (ATH) filler (particle size = 1–3 µm) was obtained from Industrial Technology Research Institute (Taiwan). O-Cresol–formaldehyde novolac epoxy (epoxy equivalent weight (eew) = 200–230) was purchased from Nan Ya Plastic Co. (Taiwan), phenol–formaldehyde novolac (OH equivalent = 106 g/equiv) was received from Bakelite Co. (Taiwan), and phenol–biphenylene novolac (PBN; OH equivalent = 200 g/equiv) was received from Meiwa Plastics Co. (Japan).

Techniques

^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra were recorded on a Varian Mercury VX model 200-MHz spectrometer in acetone or dimethyl sulfoxide (DMSO) as the solvent. The chemical shifts are reported in δ units (ppm). Fourier transform infrared (FTIR) spectra were recorded with a Bio-Rad model FTS-3000. Gel permeation chromatography (GPC) analysis was performed on a Waters model 600 with tetrahydrofuran as the eluent. Elemental analysis was performed on a Foss Heraeus model CHN-O-Rapid apparatus. The cure characterizations of the resins were studied with differential scanning calorimetry (DSC; DSC 7, PerkinElmer) at a heating rate of 10°C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a PerkinElmer TGA 7 at various heating rates (5, 10, 20, and 40°C/min) under a nitrogen or air atmosphere.

Synthesis of carbonyl phenyl azo novolac resin (CPAN) and carbonyl phenol–biphenylene azo novolac resin (CPBAN)

CPAN was prepared by a coupling reaction[17,18] between diazonium and PN resin in the presence of a base catalyst. 4-Aminobenzoic acid (24.5 g,

175 mmol) was dissolved in a mixture of water (344 g) and HCl (60.4 g, 613 mmol), which was cooled in an ice–acetone bath with stirring. A solution of sodium nitrite (13.15 g, 185 mmol) in water (25 g) was added dropwise into the mixed solution and remained stirring for overnight while the temperature was maintained below 5°C. Sulfamic acid (1.6 g, 0.17 mmol) was then added to neutralize the oxidant. Afterward, the solution was added slowly to a mixture of sodium acetate trihydrate (24.1 g, 175 mmol), ammonium hydroxide (42.3 g, 350 mmol), and phenol–formaldehyde novolac resin (31 g, 290 mmol) at 5°C. After the addition, the solution was kept at the same temperature for 8 h by stirring, and acetic acid (30 mL) was added to adjust the pH value. The solution was filtered, and the precipitated polymer was further purified by dissolution in methanol and precipitation in water. The obtained product was dried in vacuo at room temperature for 2 days at 60°C for 24 h. The product was characterized by elemental analysis, FTIR spectroscopy, ^{1}H-NMR spectroscopy, ^{13}C-NMR spectroscopy, and GPC.

CPBAN was prepared with the same procedures used for CPAN, and the product was also characterized by the aforementioned instruments.

Curing procedure of the epoxy resin with CPAN and CPBAN

A predetermined amount of CPAN or CPBAN was added to the solution of epoxy/novolac resin/acetone at various weight ratios, respectively. The mixtures were stirred until they were homogeneous, and the acetone solvent was removed by vaporization in vacuo. The mixed powders were subsequently cured in a mold at 200°C at 5 kg/cm^{2} for 2 h and were further postcured at 220°C for 3 h to obtain the cured specimens.

ATH filler was added to the mixture of novolac epoxy/novolac resin/CPAN (100/0.5/50) or novolac epoxy/novolac resin/CPBAN (100/0.5/50) at various weight ratios, respectively. The obtained cured specimens were obtained by the aforementioned procedures.

RESULTS AND DISCUSSION

Phenolic resins substituted with carbonyl functions linked through azo groups (CPAN and CPBAN) were synthesized by the reaction of 4-carbonyl phenyl diazonium salt with novolac resin, as per Scheme 1. The coupling of diazonium salt is known to occur preferentially at the para position of the phenol. Coupling at the ortho position practically does not take place if the para position is free.[19,20] From the N content (%) determined by elemental analysis (summarized in Table I), the ratio of diazo-
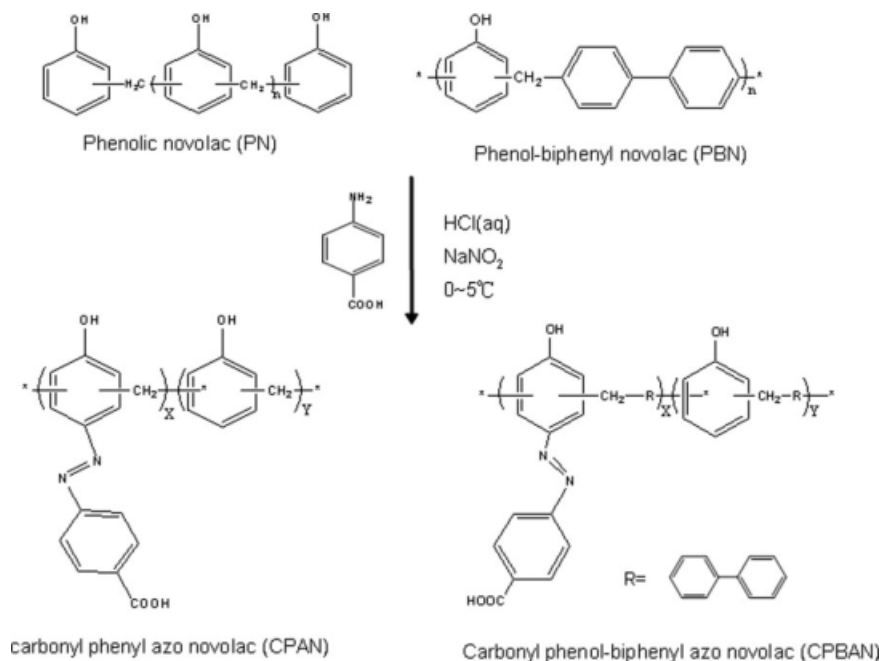
Scheme 1 Synthesis of CPAN and CPBAN.

coupling phenol groups (x) to unsubstituted phenol groups (y) was determined to be equal to 0.6/1 for CPAN and 0.26/1 for CPBAN with the following equation:

$$
\begin{aligned}
\text{N content (\%)} = {} & (\text{Molecular weight of N}_2) \times x \\
& / (\text{Molecular weight of the diazo-coupling} \\
& \qquad \text{phenol group}) \times x \\
& + (\text{Molecular weight of the unsubstituted} \\
& \qquad\qquad\qquad\qquad \text{phenol group}) \times y
\end{aligned}
$$

where x and y correspond to the monomer units depicted in Figure 1. The extents of diazo-coupling were estimated to be 40 and 20%, respectively. The difference in free para positions between PN and PBN was due to the higher repeat units (OH functionality = 12) and identical units in the polymer chain of the PN resin than in that of the PBN resin (OH functionality = 4).

Molecular characteristics of CPAN and CPBAN

The ^{1}H-NMR spectra (acetone-d_6) of the CPAN resin are shown in Figure 2, with signals at 7.4–8.2 and 6.6–7.2 and with signals at 6.7–8.4 ppm of CPBAN due to aromatic protons. The methylene bridge appeared as broad signals at 3.5–4.0 ppm for CPAN, and sharp doublets appeared at 3.8–4.2 ppm for CPBAN. The ^{13}C-NMR spectra of CPAN showed the signal of —C=O at 167 ppm; multitudes of signal due to various C—N=N and C—O groups were found at 145–160 ppm, and other signals were due to aromatic carbons at 115–135 ppm and methylene bridge carbons at 30–35 ppm. For CPBAN, the signal at 168 ppm corresponded to —C=O; multitudes of signal from various C—N=N and C—O groups were found at 152–158 ppm, and other signals from aromatic carbons at 115–142 ppm and methylene bridge carbons at 36–41 ppm were found. The FTIR spectra of CPAN and CPBAN are shown in Figure 3, with characteristic absorptions of hydroxyl groups at 3300–3600 cm^{-1} and Ar—C=O groups at 1693 cm^{-1};

TABLE I
Molecular Characteristics of CPAN and CPBAN

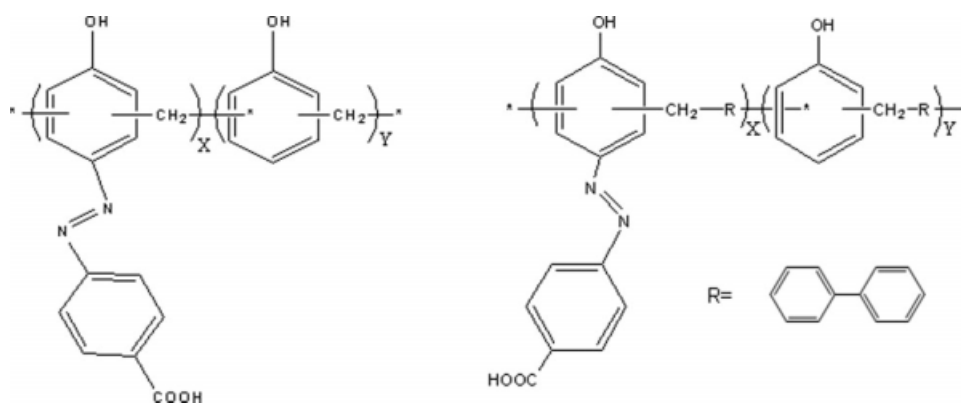| Polymer	N content (wt %)	Molecular weight by GPC (g/mol)			OH equiv	
		M_w	M_n	M_p	Calculated	Measured
PN	0	2059	1940	1987	106	112
CPAN	6.5	608	587	583	162	162
PBN	0	992	981	965	200	200
CPBAN	2.5	909	879	846	230	230

Figure 1 Illustration of estimated polymers CPAN and CPBAN.

the absorption increased at 1600 cm^{-1} due to azo groups.

The average molecular weight of the synthesized polymers was determined by GPC and is given in Table I. The number-average molecular weight (M_n) of the grafted polymer CPAN computed from GPC data decreased from 1940 to 587 g/mol, and that of CPBAN decreased from 981 to 879 g/mol. Also, the weight-average molecular weight (M_w) of CPAN decreased from 2059 to 608 g/mol, and that of

CPBAN decreased from 992 to 909 g/mol. The average molecular weight showed a decreased result with added diazonium to the phenolic resins. The apparent decrease in the average molecular weight was the consequence of the reduced hydrodynamic volume of the macromolecules with increasing extent of diazo coupling. The incorporation of the carbonyl phenyl azo groups in a regular and comb-like fashion to the novolac backbone must have been conducive to the decrease of the hydrodynamic
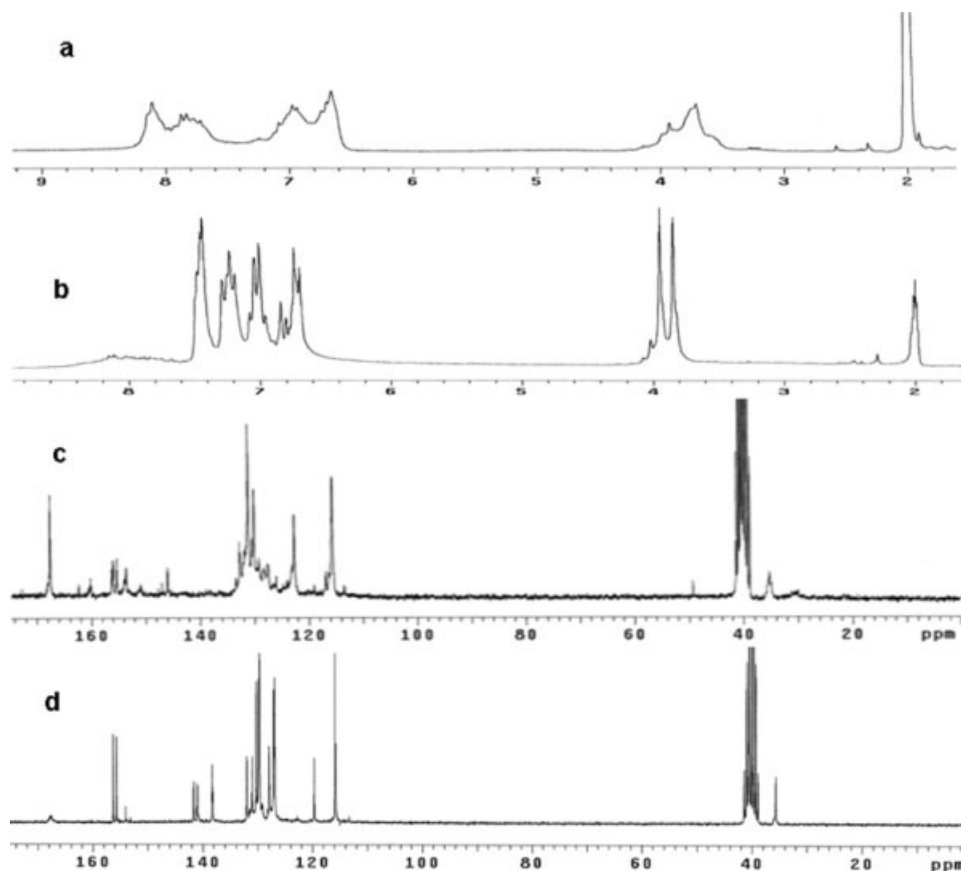

Figure 2 ^{1}H-NMR spectra of (a) CPAN and (b) CPBAN in acetone-d_6 and ^{13}C-NMR spectra of (c) CPAN and (d) CPBAN in DMSO-d_6.
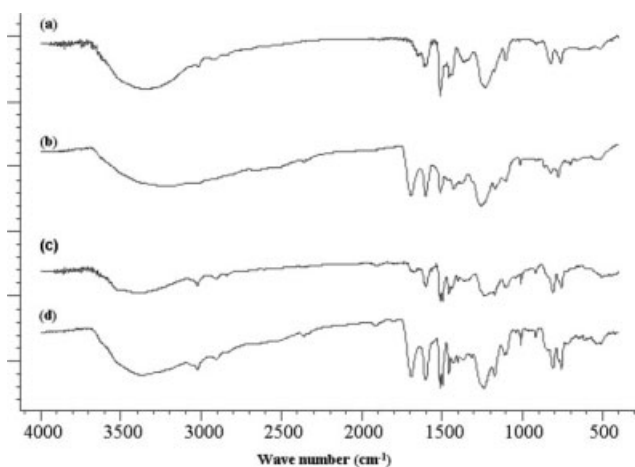
Figure 3 FTIR spectra of (a) PN, (b) CPAN, (c) PBN, and (d) CPBAN.

volume of the polymer, which led to longer retention times. Compared with CPAN, the decrease in the average molecular weight of CPBAN was much lower; it should have been the lower change in the hydrodynamic volume caused by the previously mentioned lower extent of diazo coupling. A reduction in hydrodynamic volume is common in branched polymers.[21] Because the polymer was isolated in good yield, we ruled out the possibility that the decrease in average molecular weight was caused by the selective isolation of the low-molar-mass components.

The OH equivalent was evaluated from the content derived from elemental analysis and the average molecular weights [M_w, M_n, and peak average molecular weight (M_p)] determined by GPC analysis. Because x/y was determined to be equal to 0.6/1 for CPAN and 0.26/1 for CPBAN by the previous equation, the theoretical OH equivalent weight could be calculated from the following equation with the average molecular weights measured by GPC analysis:

$$[(\text{Molecular weight of the diazo-coupling}$$
$$\text{phenol group}) \times x$$
$$+ (\text{Molecular weight of the unsubstituted}$$
$$\text{phenol group}) \times y]/x + y$$

The fact that the calculated OH equivalent weight and the measured value for the starting materials, PN and PBN, were almost identical indicated that the GPC measurement was accurate.

Thermal characteristics of the cured resins

Thermal degradation was characterized by TGA, as shown in Figure 4. The heating process showed a single-stage degradation process under a nitrogen

atmosphere [Fig. 4(a,b)] due to the high thermo-stability of increasing crosslink densities and aromatic units. The degradation of the blank matrix and epoxy/PN/CPAN (or epoxy/PN/CPBAN) cured resins almost overlapped at temperatures around 350–450°C. Moreover, the diazo-coupling groups generated heat-resistant residues to achieve a high char yield at 800°C. With heating under air, the TGA curves were different [Fig. 4(c,d)]. The cured resins showed similar weight loss behaviors below 400°C to that under a nitrogen atmosphere. However, a second-stage degradation occurred because of the oxidative reaction at temperatures greater than 500°C. As aromatics were reported to exhibit significant char formation under heating with air,[22–24] the cured resins with diazo-coupling groups (epoxy/PN/CPAN and epoxy/PN/CPBAN series) incorporated in various contents showed an increasing char yield at 800°C. This retardation effect on weight loss was further enhanced because of the diazo-coupling group in the synthesized PN resin.

The degradation temperatures are summarized in Table II. The downward shift in the onset temperature of degradation (T_{onset}), temperature at 5% weight loss (T_d), and temperature at the maximum weight loss (T_{max}) displayed the same trend, which may have been because the azo group decomposed at lower temperatures and they were proportional to the extent of diazo coupling. The decrease was more pronounced in CPAN but less so in CPBAN because of the lower extent of diazo coupling in the phenol–biphenylene structures. All factors play some critical roles in flame-retarding polymeric materials through condensed-phase mechanisms and gas-phase mechanisms. In this case, CPAN and CPBAN advanced the temperatures (T_{onset}, T_{max}, and T_d), because of the nitrogen gas or releasing volatile nitrogen oxidants, through the mechanisms believed to dilute the ambient oxygen gas and decrease heat absorption in heated conditions or fire environments. Furthermore, the increased char yield at 800°C showed the effect of thermostability caused by the noncombustible gas when highly thermostable aromatic products were formed.

The limiting oxygen index (LOI) was calculated according to Gracik and Long[25] with the following equation:

$$\text{LOI} = 16.9 + 0.5 \times [\text{Char at } 800°C \text{ in } N_2 \text{ (wt \%)}]$$

The addition of CPAN or CPBAN both increased the LOI values from 30 to 40 or 28 to 36, respectively. These results directly reflected the flame-retarding efficiency; the LOI value was enhanced in cured resins and gradually increased the CPAN and CPBAN contents.
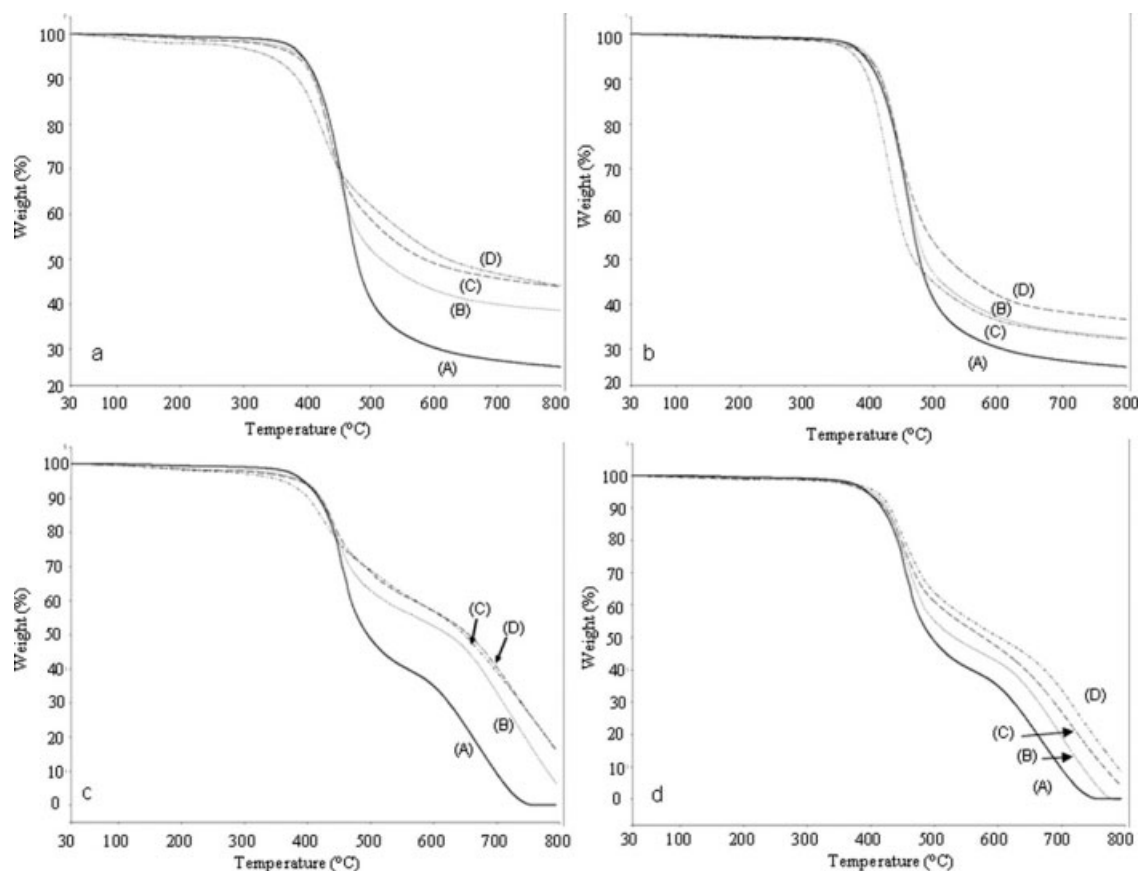
Figure 4 TGA curves of cured resins: (a) epoxy resin/PN/CPAN, (b) epoxy resin/PN/CPBAN under nitrogen, (c) epoxy resin/PN/CPAN, and (d) epoxy resin/PN/CPBAN under air. The compositions were as follows: (A) 100/0.5/0, (B) 100/0.5/30, (C) 100/0.5/50, and (D) 100/0.5/100.

Curing behaviors and thermal degradation kinetic by DSC and TGA

The glass-transition temperature (T_g) values of the cured resins were determined from DSC (N2; 10°C/min), as shown in Figure 5 and summarized in Table III. For both the epoxy/CPAN and epoxy/CPBAN series, the introduction of a diazo-coupling group to

the PN derivative compounds increased the T_g value, which suggested the incorporated carbonyl group in the diazo-coupling group reacted with epoxy, which led to higher crosslinking densities and raised the T_g.

The thermostability could be further judged from the decomposition activation energy (E_a) values

TABLE II
Characterization of Cured Resins by TGA

|	In air (10°C/min)				In N$_2$ (10°C/min)				
	T_{onset}	T_d	T_{max}	Char yield[c]	T_{onset}	T_d	T_{max}	Char yield[c]	LOI
Epoxy/PN[a]/CPAN[b]									
100/0.5/0	421	393	456	0	417	392	460	25.6	30
100/0.5/30	411	392	442	6.5	405	384	438	38.0	37
100/0.5/50	402	387	438	16.0	400	383	432	43.4	39
100/0.5/100	377	361	427	16.5	372	341	424	44.0	40
Epoxy/PN/CPBAN[b]									
100/0.5/30	421	400	454	0	413	399	454	32.5	33
100/0.5/50	420	392	454	4.2	411	400	453	34.6	34
100/0.5/100	413	409	445	8.6	406	396	443	36.6	36

[a] Equivalent weight.
[b] Weight.
[c] At 800°C (%).
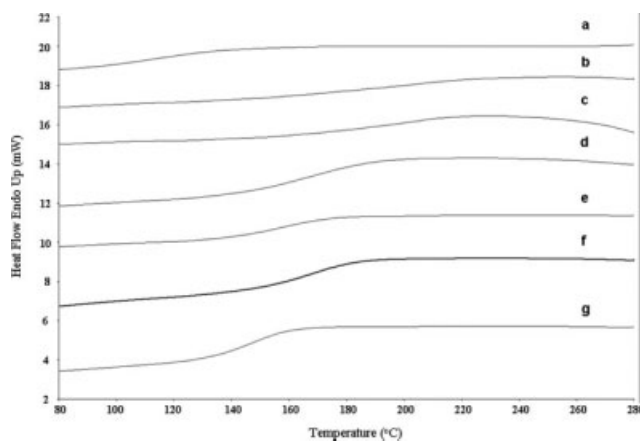
Figure 5 DSC curves of (a) 100/0.5/0, (b) 100/0.5/30, (c) 100/0.5/50, and (d) 100/0.5/100 epoxy resin/PN/CPAN and (e) 100/0.5/30, (f) 100/0.5/50, and (g) 100/0.5/100 epoxy resin/PN/CPBAN (N_2 and 10°C/min).
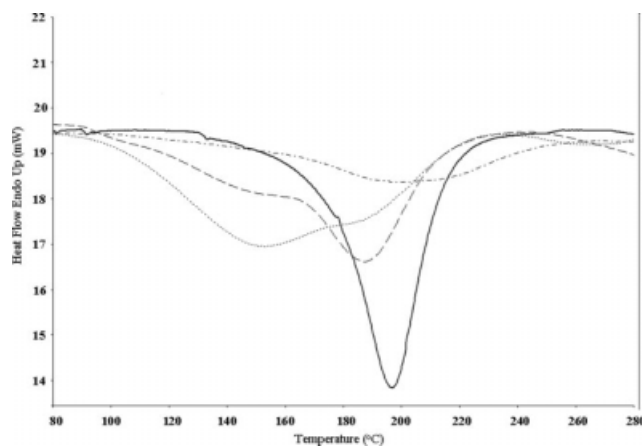

Figure 6 DSC curves of epoxy resin/PN/CPAN: (—) 100/0.5/0, (- · -) 100/0.5/30, (- - -) 100/0.5/50, and (· · ·) 100/0.5/100 (N_2 and 10°C/min).

derived from TGA measurements with various heating rates (5, 10, 20, and 40°C/min). Two common approaches proposed by Kissinger[26] and Ozawa[27] were used to derive the activation energies of the thermal degradation reactions. In theory, a higher E_a implies a higher thermostability. The analysis showed that both methods yielded similar results where the cured resins containing either the CPAN or CPBAN all displayed a higher thermostability (higher E_a) than the blank resin. This corroborated the higher crosslinking densities and enriched aromatic amounts. However, an excessive amount of carbonyl group led to a lower E_a and lower T_g.

The DSC results displayed in Figures 6 and 7 reveal the enthalpy changes (ΔH) during the crosslinking reaction for epoxy resins containing the two types of diazo-coupling agent, CPAN and CPBAN.

The results are summarized in Table III. For both cases, the addition of diazo-coupling agent initiated a broader ΔH peak. This result suggests that the crosslinking reaction occurred across a broader temperature range when a diazo-coupling agent was present, which also implied that the diazo-coupling agent mediated the epoxy–phenolic crosslinking. However, substantial differences were still detected between the two series. Figure 6 revealed two major heat change regions, and from the evolution of the two peaks with the change of CPAN content, they were attributed to the crosslinking reaction between epoxy and PN ($\sim$ 195°C) and between epoxy and CPAN ($\sim$ 150°C). The carboxylic group in the diazo compound seemed to display easier crosslinking than that of hydroxyl group with the epoxy group, as suggested by the lower heat change temperature. On the other hand, the additional heat change peak
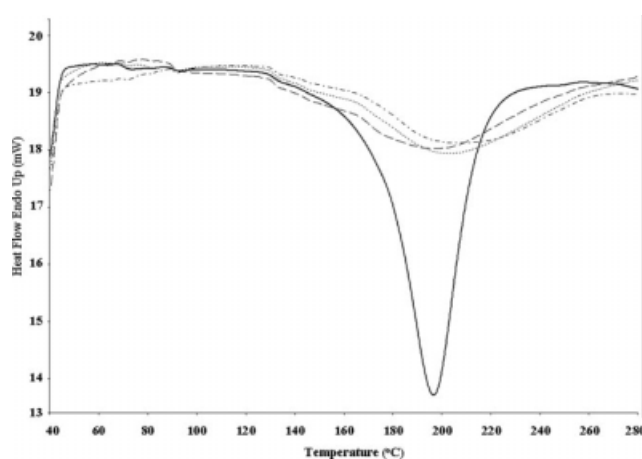
TABLE III
Curing Behavior and Thermal Degradation Kinetics by DSC and TGA

	DSC			E_a (kJ/mol × K) by TGA	
	T_g (°C)	T_p	ΔH (J/g)	Ozawa's method	Kissinger's method
Epoxy/PN[a]/CPAN[b]					
100/0.5/0	115	196	154	177	174
100/0.5/30	189	199	115	200	200
100/0.5/50	195	187	120	196	195
100/0.5/100	173	151	116	194	192
Epoxy/PN/CPBAN[b]					
100/0.5/30	160	202	99	200	198
100/0.5/50	167	198	67	187	185
100/0.5/100	147	194	47	183	181

[a] Equivalent weight.
[b] Weight.

Figure 7 DSC curves of epoxy resin/PN/CPBAN: (—) 100/0.5/0, (- · -) 100/0.5/30, (· · ·) 100/0.5/50, and (- - -) 100/0.5/100 (N_2 and 10°C/min).

appeared less pronounced in the resin containing CPBAN. This may have been due to the diluted carboxylic group available for crosslinking in CPBAN. The heat change (Table III) in this compound was much lower compared to that in CPAN, and a lower crosslinking density was expected. Both the diverseness of the reaction and overabundant functional group led to the increase in residual nonreactive functional groups and an increase in free volume. CPAN showed the lower maximum reaction temperature (T_p) because of higher amounts of diazo-coupling compounds, which led to higher crosslinking densities when a large amount of CPAN was present, and displayed a smaller increase in E_a when excessive amounts of CPAN were added. The mechanism and structural details are documented in a separate report.

$$LOI\ increase\ \% = \left[\frac{LOI\ value\ of\ cured\ resin\ containing\ filler - LOI\ value\ of\ blank\ cured\ resin}{LOI\ value\ of\ blank\ cured\ resin}\right] \times 100\%$$

The char yields all increased with increasing filler, possibly because of the effective oxidation barrier formed by the inorganic under high ambient air temperature according to recent studies. Interestingly, the effects of the filler were more pronounced in the CPBAN series than in the CPAN series. However, the LOI values tapered off at high filler contents for both the CPAN and CPAN experiments. The efficiency was saturated at levels of 33.3 and 58.9%, respectively, for CPBAN and CPAN, when the filler content reached 100 g of equivalent weight. It stands to reason that the lower crosslinking densities of the CPBAN/filler series led to more pronounced thermal-resistance and flame-retardance improvements by the filler, whereby the oxidation layer was formed more completely. On the basis of this evidence, we deduced that higher crosslinking

Effects of the filler on the thermostability

Finally, the effects of the filler (3-μm ATH particles) in the CPAN- and CPBAN-modified series were examined, and the results are summarized in Table IV with the parent polymer epoxy/PN/CPAN or epoxy/PN/CPBAN (100/0.5/50). All char yield and LOI increasing percentages were evaluated by TGA under air condition at a heating rate of 10°C/min. The LOI was calculated according to Van Krevelen[28] with the following equation:

$$LOI = 17.5 + 0.4 \times [Char\ at\ 850°C\ in\ air\ (wt\ \%)]$$

The efficiency brought about by the filler was evaluated from the difference or LOI between the cured resin with the filler and the resin without the filler with the following equation:

densities dominated the thermostability, which was characterized by higher thermal degraded activation energies.

CONCLUSIONS

The thermostabilities of epoxy resins containing flame-retardant components bearing diazo-coupling functional groups in two types of PN derivative resins were examined by DSC and TGA. The degradation pattern, temperature, and rates of maximum weight loss were all affected by the flame-retardant components. Evaluating the LOI value, enthalpy, and activation energies, we concluded that the incorporation of CPAN or CPBAN into epoxy resins improved the thermal properties of the cured resins. The PN and PBN resins reached higher LOI and char yield values with increasing aromatic amounts and azo groups, had better flame retardancy, and suggested higher thermostability. However, excessive CPAN or CPBAN led to an increased amount of nonreacted functional group, a reduced T_g, and a lower increase in the degradation activation energy. Further addition of micrometer-size inorganic filler (ATH particles) showed cooperative flame-retardant behavior, which was saturated at a certain amount of inorganic addition. With this study, we concluded that the use of highly aromatic contents with higher crosslinking entities can lead to inflammable and low volatile compounds without the use of halogen or phosphorus elements.

TABLE IV
Characterization of Cured Resins with Fillers

	Filler content (g)	Char yield (%)	LOI	LOI increase (%)
Epoxy/PN[a]/CPAN[b]				
100/0.5/50 (blank)	0	16.0	24.0	—
100/0.5/50	30	18.6	25.0	4.2
100/0.5/50	50	34.7	31.0	29.1
100/0.5/50	100	37.2	32.0	33.3
Epoxy/PN/CPBAN[b]				
100/0.5/50 (blank)	0	4.2	19.2	—
100/0.5/50	30	29.5	29.3	52.6
100/0.5/50	50	30.0	29.5	53.6
100/0.5/50	100	32.5	30.5	58.9

[a] Equivalent weight.
[b] Grams.

References

1. Gardziella, A.; Pilato, L. A.; Knop, A. Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology; Springer-Verlag: Berlin, 2000.
2. Hshieh, F. Y.; Beeson, H. D. Fire Mater 1997, 21, 41.
3. Seo, K.; Kim, J.; Bae, J. Y. Polym Degrad Stab 2006, 91, 1513.
4. Lu, S. Y.; Hamerton, I. Prog Polym Sci 2002, 27, 1661.
5. Espinosa, M. A.; Galia, M.; Cádiz, V. J Polym Sci Part A: Polym Chem 2004, 42, 3516.
6. Liu, Y. L.; Chiu, Y. C.; Wu, C. S. J Appl Polym Sci 2003, 87, 404.
7. Wu, C. S.; Liu, Y. L.; Chiu, Y. S. Polymer 2002, 43, 4277.
8. Wu, C. S.; Liu, Y. L.; Chiu, Y. S. Polymer 2002, 43, 1773.
9. Shieh, J. Y.; Wang, C. S. Polymer 2001, 42, 7617.
10. Martin, C.; Ronda, J. C.; Cádiz, V. Polym Degrad Stab 2006, 91, 747.
11. Martin, C.; Ronda, J. C.; Cádiz, V. J Polym Sci Part A: Polym Chem 2006, 44, 1701.
12. Martin, C.; Ronda, J. C.; Cádiz, V. J Polym Sci Part A: Polym Chem 2006, 44, 3503.
13. Camino, G.; Costa, L. Polym Degrad Stab 1988, 20, 271.
14. Cullis, C. F. J Anal Pyrolysis 1987, 11, 451.
15. Reghunadhan Nair, C. P.; Bindu, R. L.; Ninan, K. N. Polymer 2002, 43, 2609.
16. Masatoshi, I.; Yukihiro, K. Polym Adv Technol 2001, 12, 393.
17. Leclair, S.; Mathew, L.; Giguere, M.; Motallebi, S.; Zhao, Y. Macromolecules 2003, 36, 9024.
18. Francois, A.; Yue, Z. J Polym Sci Part A: Polym Chem 2004, 42, 3445.
19. Szele, I.; Zollinger, H. Top Curr Chem 1983, 112, 1.
20. Hegarthy, A. F. In The Chemistry of Diazonium and Diazo Groups; Patai, S., Ed.; Wiley: New York, 1978; Part 2.
21. Burchard, W. Adv Polym Sci 1999, 143, 113.
22. Masatoshi, I.; Yukihiro, K.; Makoto, S. Polym Adv Technol 2003, 14, 638.
23. Chen, C. S.; Bulkin, B. J.; Pearce, E. M. J Appl Polym Sci 1982, 27, 3289.
24. Masatoshi, I.; Shin, S. Polym Adv Technol 1998, 9, 593.
25. Gracik, T. D.; Long, G. L. Thermochim Acta 1992, 212, 163.
26. Kissinger, H. E. Anal Chem 1957, 29, 1702.
27. Ozawa, T. Therm Anal 1970, 2, 301.
28. Van Krevelen, D. W. Polymer 1975, 16, 615.