Synthesis, Characterization, and Properties of a Novel Epoxy Resin Containing both Binaphthyl and Biphenyl Moieties

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ABSTRACT: A new epoxy resin containing both binaphthyl and biphenyl moieties in the skeleton (BLBPE) was synthesized and confirmed by electrospray ionization mass spectroscopy, ^{1}H-nuclear magnetic resonance spectroscopy, and infrared spectroscopy. To evaluate the combined influence of two moieties, one epoxy resin containing binaphthyl moiety and another containing biphenyl moiety were also synthesized, and a commercial biphenyl-type epoxy resin (CER3000L) was introduced. Thermal properties of their cured polymers with phenol *p*-xylene resins were characterized by differential scanning calorimetry, dynamic mechanical, and thermogravimetric analyses. The cured polymer obtained from BLBPE showed remarkably higher glass transition temperature and lower moisture absorption, as well as comprehensively excellent thermal stability. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3889–3895, 2009

Key words: binaphthyl; epoxy resin; synthesis; thermal properties; thermosets

INTRODUCTION

Epoxy resins have been used as encapsulation materials in electronic components, such as integrated circuits, due to their good heat and chemical resistance, excellent electrical insulating and mechanical properties, and superior adhesive strength. Nowadays, the extensive application of surface mount technology demands high thermal resistance epoxy resins, especially when lead-free solder is used due to growing environmental concerns.[1,2] Moisture resistance is another key property. Absorbed moisture in packaging resin layers would be explosively vaporized during reflow soldering process, causing such package reliability problems such as package cracks, delamination, and package warpage.[3] Therefore, it is imperative to develop epoxy resins with high thermal resistance and low water absorption.

Many researches have been conducted to increase the heat resistance of epoxy resins, one effective approach among which is to incorporate rigid aromatic structures. Meanwhile, good moisture resistance property could be obtained due to the hydrophobic nature of aromatic structures. Kaji et al.[4,5] studied the incorporation of some polynucelar aromatic moieties, including biphenyl and naphthyl, in the skeleton of epoxy resins and found they markedly improved T_g and moisture resistance. Ho,[6] Pan et al.,[7] and Xu et al.[8] reported naphthalene-containing epoxy resins showed high heat resistance and low moisture absorption. Besides, introducing more than one rigid structure has been investigated, such as a naphthalene/dicyclopentadiene containing epoxy resin by Ren et al.,[9] and a naphthalene/limonene containing epoxy resin by Xu et al.[10] According to their reports, remarkably higher T_g, higher thermal stability, and better moisture resistance were acquired. Furthermore, increasing epoxy functionality while incorporating rigid aromatic structure has also been probed by some researchers. Wang and Lee[11,12] synthesized some multifunctional naphthalene-containing epoxy resins, which displayed superior thermal resistance but increased moisture absorption. This meant a trade-off between high T_g and low moisture absorption, due to the opposite effect of crosslinking density on the two properties.

However, epoxy resins containing binaphthyl moieties have not yet been reported. Because of extremely bulky rigid binaphthyl moieties, they expectedly should present superior thermal and moisture resistance, which may be further enhanced by extra incorporation of biphenyl moieties. So, in this work, incorporating both binaphthyl and biphenyl moieties as well as enhancing epoxy functionality were utilized to design a novel epoxy resin. Two other prepared epoxy resins containing only

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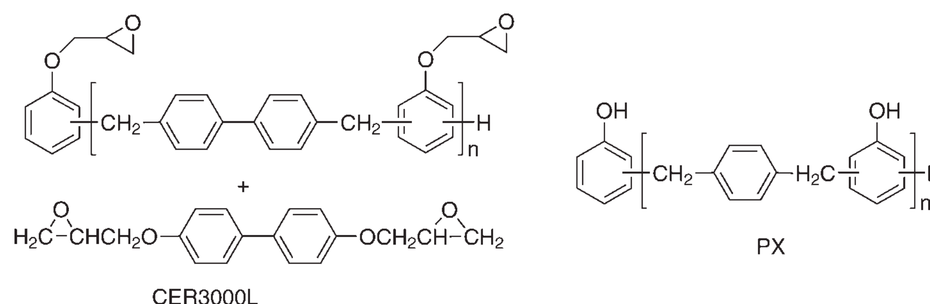


Scheme 1 Structure of CER3000L epoxy resin and PX hardener.

binaphthyl or biphenyl moieties and a commercial phenol biphenylene-type epoxy resin (CER3000L) shown in Scheme 1 were also encompassed for comparison. Their cured polymers with phenol *p*-xylene hardener (PX) were examined with thermal analysis means and moisture absorption measurements, and the effects of the two moieties were discussed.

EXPERIMENTAL

Materials

2-Naphthol was obtained from Shanghai Jinshanting Chemical Co., Shanghai, China to prepare 1,1′-binaphthyl-2,2′-diol (BINOL) according to the procedure of Refs. 13,14. Epichlorohydrin, tetrabutylammonium bromide (TBB), and *p*-toluene sulfonic acid (PTSA) were purchased from Shanghai Lingfeng Chemical Co., Shanghai, China. 4,4′-Bis(methoxymethyl)biphenyl (BMB), phenol *p*-xylene resin (HEW = 175 g eq^{-1}), CER3000L epoxy resin (EEW = 241 g eq^{-1}), and triphenylphosphine (TPP) were obtained from Henkel Huawei Electronics Co., Ltd. Lianyungang, China Phenol and methyl isobutyl ketone (MIBK) were obtained from Tianjing No.1 Chemical Co., China, Tianjing, China All reagents were analytical grade. Epichlorohydrin was distilled before usage, whereas all other reagents were used without further purification.

Synthesis of binaphthyl-containing epoxy resin (BLE)[15,16]

Into a 250 mL four-necked round-bottom flask equipped with a temperature controller, thermometer, stirrer, and a Dean-Stark trap with a reflux condenser, were charged 15.0 g (0.052 mol) BINOL, 0.1 g TBB, and 100 mL (1.3 mol) epichlorohydrin. With a temperature of 70°C and a pressure of 20 kPa, 9.0 g 48% sodium hydroxide solution was added dropwise over a period of 4 h, removing generated water by azeotropic distillation. On completion, excessive epichlorohydrin was distilled off from the solution, and MIBK was added to dissolve the product. To this solution, 1.5 g of 20% sodium hydroxide was added dropwise with stirring at 80°C for another 2 h. After washing with water three times, and MIBK was distilled to give 20.5 g of BLE as a light yellow half solid: yield 98.1%. Its epoxy equivalent weight (EEW) was 287 g eq^{-1}.

IR (KBr): 3058 (aromatic = C—H); 1618, 1596, 1506 (s, aromatic C=C); 1223 (versus, C—O); 901 cm^{-1} (m, oxirane ring).

Synthesis of biphenyl novolac resin (BPN)

Into a 250 mL four-necked round-bottom flask equipped with a temperature controller, nitrogen inlet, thermometer, stirrer, and a Dean-Stark trap with a reflux condenser, were charged 36 g (0.15 mol) BMB, 42 g (0.45 mol) phenol, and 0.6 g PTSA. Under nitrogen atmosphere, the mixture was stirred at 120°C for 3 h, removing generated methanol. After neutralization with sodium carbonate, phenol was distilled under reduced pressure to give a light brow solid.

IR (KBr): 3417 (s, OH); 3021 (aromatic = C—H); 2903 (saturated C—H); 1610, 1594, 1510 (s, aromatic C=C); 1238 cm^{-1} (s, C—O).

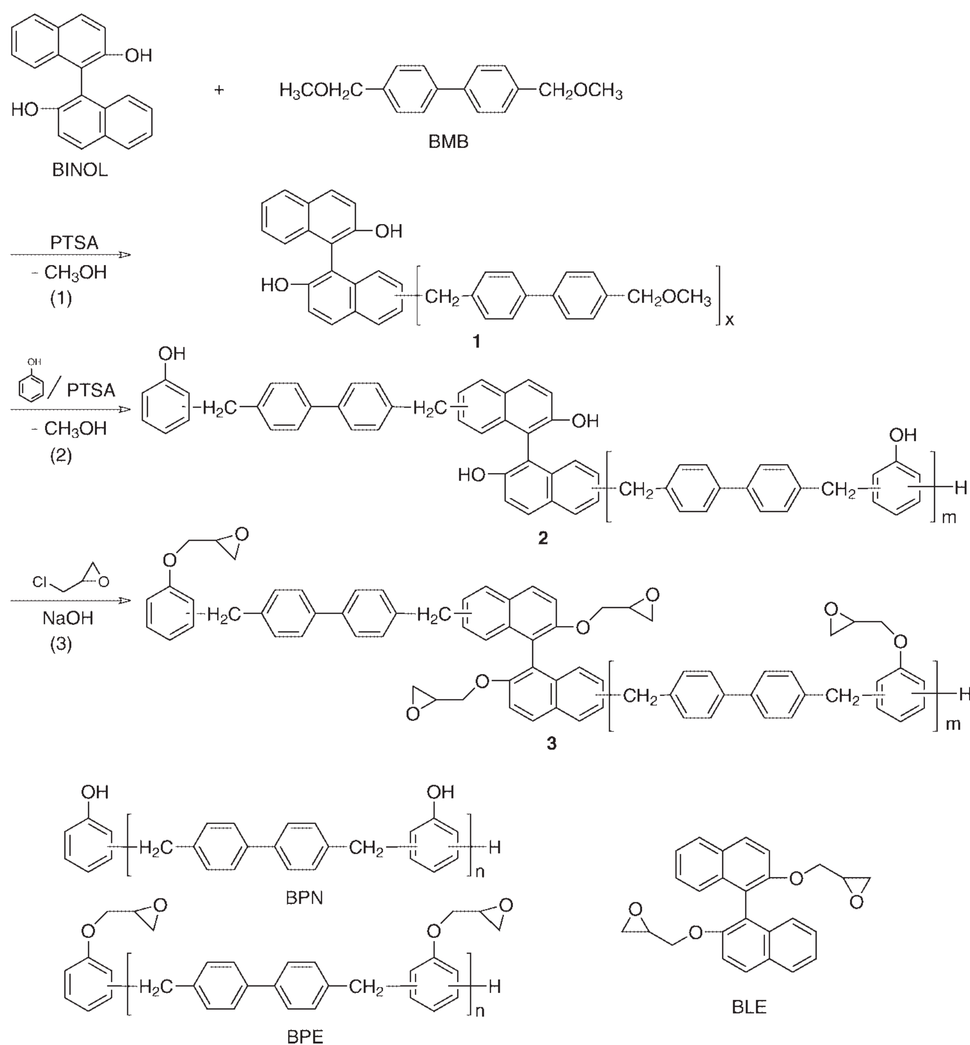
Synthesis of biphenyl novolac epoxy resin (BPE)

BPE was prepared from BPN in the same way as BLE. EEW: 326 g eq^{-1}.

IR (KBr): 3022 (aromatic = C—H); 2921 (saturated C—H); 1607, 1499 (s, aromatic C=C); 1244 (versus, C—O); 914 cm^{-1} (m, oxirane ring).

Synthesis of binaphthyl/biphenyl-containing novolac resin (BLBPN)

Similar to preparation of BPN, a mixture of 14.5 g (0.05 mol) BINOL, 48.5 g (0.2 mol) BMB, and 1.7 g PTSA was stirred at 120°C under nitrogen atmosphere. When 3.2 g (0.1 mol) methanol was obtained, 94 g (1 mol) phenol was added to the system and reaction proceeded for another 4 h. Subsequent neutralization and distillation gave a brown solid.



Scheme 2 Synthesis of epoxy resins.

IR (KBr): 3396 (s, OH); 3021 (aromatic = C—H); 2903 (saturated C—H); 1594, 1510 (s, aromatic C=C); 1170 cm^{-1} (s, C—O).

Synthesis of binaphthyl/biphenyl-containing novolac epoxy resin

Binaphthyl/biphenyl-containing novolac epoxy resin (BLBPE) was prepared from BLBPN in the same way as BLE. EEW: 309 g eq^{-1}.

IR (KBr): 3022 (aromatic = C—H); 2922 (saturated C—H); 1599, 1587, 1508 (s, aromatic C=C); 1242 (versus, C—O); 915 cm^{-1} (m, oxirane ring).

Sample preparation

With a 1 : 1 equivalent ratio, epoxy resin and PX hardener were mixed, heated, and stirred under 120°C to yield a homogeneous solution. Then, it was placed in 80°C oil bath and 2 wt % of TPP was added under agitation. The thermosettable samples were immediately cooled and stored in refrigerator before DSC experiment. For dynamic mechanical thermal analysis (DMTA) test, samples were cured in a mold at 120°C for 2 h and postcured at 180°C for 6 h.

Characterization and measurement

FTIR spectra were obtained with Bruker Vector 22 spectrometer. ^{1}H-NMR spectra were recorded on Bruker DRX 500 NMR spectrometer using tetramethylsilane as internal standard. The electrospray ionization (ESI) MS was determined by Thermo Scientific LCQ spectrometer (Finnigan). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were conducted on PerkinElmer Pyris 1 DSC and TGA, respectively, both with a heating rate of 20°C min^{-1} under nitrogen atmosphere. DMTA was performed on Rheometric Scientific DMTA V with 20 mm × 5 mm × 1 mm samples at a heating rate of 3°C min^{-1} from 40

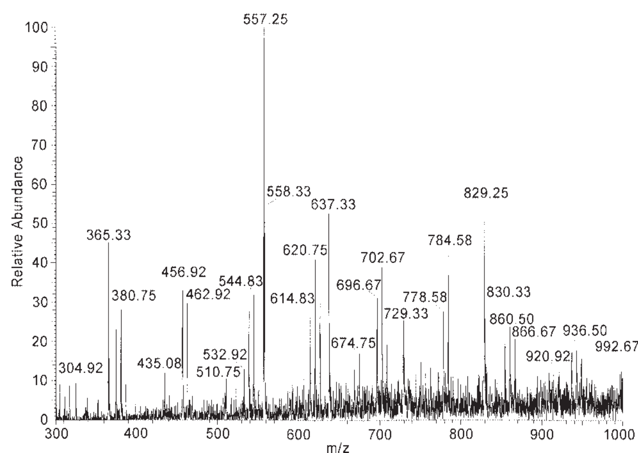


Figure 1 ESI-MS spectrum of BLBPN.

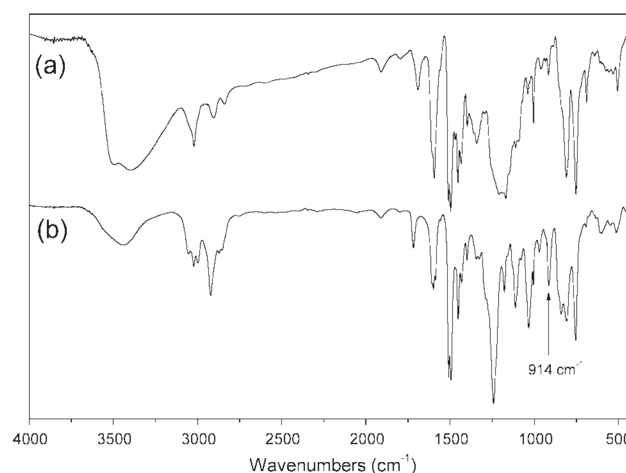


Figure 3 IR spectra of (a) BLBPN and (b) BLBPE.

to 200°C with a frequency of 1 Hz under nitrogen atmosphere. The EEW of epoxy resins was measured by HCl/acetone titration method. By dipping DMTA shaped samples into boiling water for 48 h, moisture absorption was calculated with the formula: $(w - w_0)/w_0 \times 100\%$, in which w_0 and w corresponded to weight of samples before and after boiling, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization

As shown in Scheme 2, the novel epoxy resin was prepared with three steps: (1) synthesis of **1** by condensing BINOL with BMB; (2) synthesis of **2** by condensing **1** with an excess amount of phenol; (3) epoxidation reaction of **2** with epichlorohydrin to yield **3**. During the synthesis, BMB (0.2 mol) was fourth the amount of BINOL (0.05 mol). Step (1) reaction was continued until 0.1 mol methanol was generated, which meant all BINOL had reacted with 0.1 mol BMB, and with one BINOL molecule linking two BMB moieties in an ideal case. In step (2) reaction, introduced phenol would react with both **1** and unreacted BMB to yield **2** and BPN, respectively. This novolac resin mixture was indicated as BLBPN. In step (3) reaction, produced novolac epoxy resin was a mixture of **3** and BPE, indicated as BLBPE. This result was verified by the ESI-MS spectrum of BLBPN shown in Figure 1. The molecular weight of **2** was: $558 + 272 \times m$, so $m/z = 557.25$ and 829.25 were corresponding to $m = 0$ and 1 in Scheme 2. In comparison, the molecular weight of BPN was: $94 + 272 \times n$, thus $m/z = 365.33$ and 637.33 were corresponding to $n = 1$ and 2.

BLBPE was characterized with ^{1}H-NMR and infrared spectroscopy. ^{1}H-NMR spectrum of BLBPE was shown in Figure 2. After epoxidation, three new groups of signals attributable to H_a, H_b, and H_c of glycidyl groups were observed at 4.0–4.3 ppm, 3.2–3.4 ppm, and 2.6–3.0 ppm, respectively. In IR

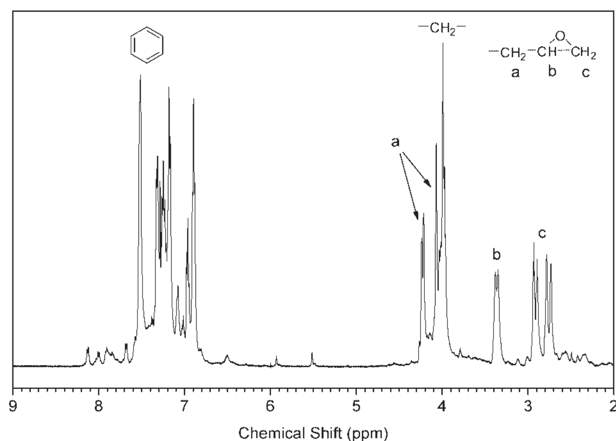


Figure 2 ^{1}H-NMR spectrum of BLBPE in $CDCl_3$.

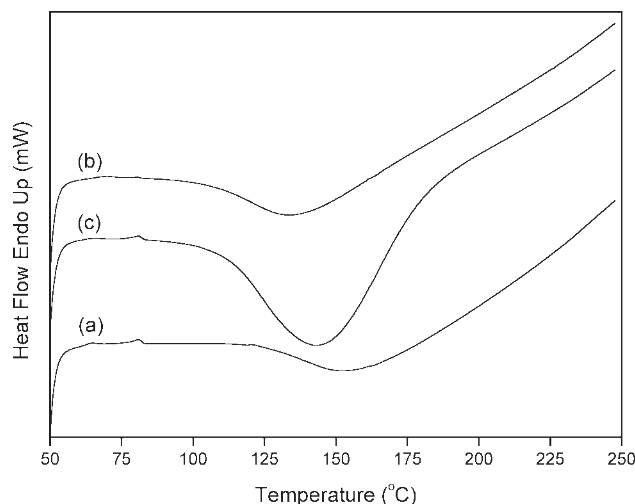


Figure 4 DSC thermograms of (a) BLE/PX, (b) BPE/PX, and (c) BLBPE/PX.

TABLE I
Results of DSC Measurements

Sample	T_o[a] (°C)	T_p[b] (°C)	ΔH[c] (J g^{-1})	$T_{g\text{-DSC}}$ (°C)
BLE/PX[a]	122	155	32.4	77
BPE/PX[b]	100	135	58.4	93
BLBPE/PX[c]	106	145	177.8	112

[a] Onset temperature of curing reaction.
[b] Temperature corresponding to exothermic peak.
[c] Calorific value of curing reaction.

spectrum shown in Figure 3, the characteristic absorption band of oxirane ring at 914 cm^{-1} was observed, as a result of the epoxidation reaction. Meanwhile, although not disappearing completely, the characteristic absorption band of hydroxyl group at 3400–3500 cm^{-1} declined significantly, indicating a major conversion of hydroxyl groups to glycidyl ether groups.

DSC measurements

The curing behaviors of three prepared epoxy resins were probed by DSC, after which each cured sample was re-scanned to acquire glass transition temperature (T_g). The results were shown in Figure 4 and Table I. Judging from T_p and width of exothermic peak, BLE/PX had the lowest curing reactivity whereas BPE/PX had the highest. This was due to different content of bulky binaphthyl moiety, which may lead to low molecular chain mobility and hinder the diffusion of reactive sites, like epoxy groups. BLBPE/PX gave the highest calorific value, which should ascribe to its enhanced epoxy functionality due to extra epoxidation reaction with hydroxyl groups of BINOL. Besides, the fact that BLBPE had higher content of bulky moieties while lower EEW value than BPE also lent credence to the above presumption.

Dynamic mechanical thermal analysis

The DMTA results of cured BLBPE polymer were compared with those of BPE and the commercial CER3000L epoxy resin. BLE/PX was too fragile to perform DMTA test, but it should have the lowest T_g taken $T_{g\text{-DSC}}$ data from Table I into account. As shown in Figure 5, BLBPE/PX showed the highest T_g, which was indicated from the peak of tan δ. According to the rubber elasticity theory,[5,17] crosslinking density was calculated from storage modulus of rubbery region, summarized in Table II. BLBPE/PX had higher crosslinking density than BPE/PX, in agreement with its higher epoxy functionality. Factors that enhanced chain stiffness or lowered chain flexibility would increase T_g, like introducing rigid structure,[18] or increasing crosslinking density.[19] Although with a lower crosslinking density, BLBPE/PX had higher T_g than CER3000L/PX, which was attributed to the incorporation of bulky binaphthyl moieties. This rigid structure may increase the difficulty of chain rotation and constrain the thermal movement of polymer backbone, and thus led to higher T_g.

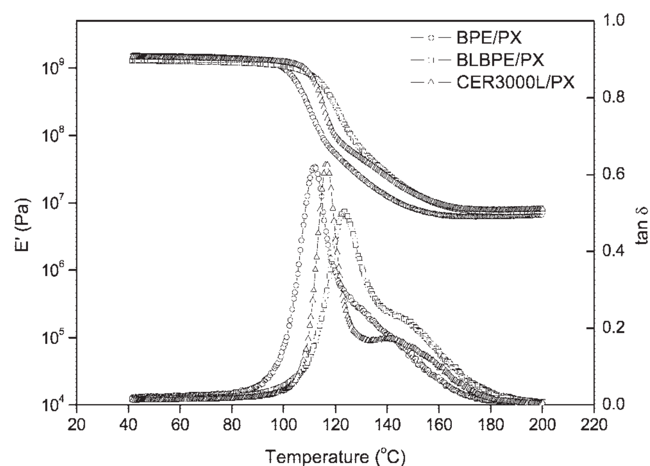


Figure 5 DMTA tests of cured polymers.

In addition, BLBPE/PX and CER3000L/PX also showed another peak at a higher temperature around 150 and 140°C, respectively. This may be due to the existence of denser crosslinking phases, which were scattered in looser crosslinking bulk. BLBPE had two compositions, so did CER3000L. The composition with a lower molecular weight might tend to cure faster because of higher diffusion rate,

TABLE II
DMTA Results of Cured Polymers

Sample	$T_{g\text{-DMTA}}$ (°C)	Storage modulus E' (Pa)		Crosslinking density ρ (×10^2 mol m^{-3})
		Glassy region[a]	Rubbery region[b]	
BPE/PX	112	1.53×10^9	6.57×10^6	6.06
BLBPE/PX	124	1.28×10^9	7.50×10^6	6.73
CER3000L/PX	116	1.45×10^9	8.51×10^6	7.77

[a] Storage modulus at 45°C.
[b] Storage modulus at $T_g + 50$°C.

generating precured phases, which then joined later curing of bulk resin system and formed the above structure.

Furthermore, storage modulus (E') in glass region[20] and crosslinking density[21] were reported to influence internal stresses of cured polymers. BLBPE/PX presented comparatively low E' and crosslinking density, and therefore was a hopeful matrix resin to produce low internal stress epoxy cured systems.

TABLE III
TGA and Moisture Absorption Results of Cured Polymers

Sample	$T_{10\%}$ (°C)	Char yield at 750°C (%)	Water absorption (wt %)
BLE/PX	372	22.4	0.95
BPE/PX	418	35.2	2.91
BLBPE/PX	421	28.0	0.63
CER3000L/PX	435	24.5	1.09

Thermal stability

The temperature corresponding to a 10% weight loss ($T_{10\%}$) in TGA was regarded as a crude index of thermal stability.[22] Thus, the cured polymers were compared with $T_{10\%}$ and char yield at 750°C, as shown in Figure 6 and Table III. Iji and Kiuchi[23] reported that restraining the movement of molecular segments could help raise heat resistance. CER3000L/PX had the largest crosslinking density and therefore the least molecular mobility, leading to highest $T_{10\%}$. Among three synthesized systems, BLBPE/PX showed higher $T_{10\%}$, which may result from more restricted movement of molecular segments caused by incorporating two types of rigid and bulky moieties. The char yield of BPE/PX was larger than that of BLBPE/PX presumably because biphenyl groups were more difficult to decompose under heat than binaphthyl groups. With an integration of intermediate crosslinking density and two types of rigid moieties, BLBPE/PX presented generally excellent thermal stability.

Moisture absorption

The moisture absorption of cured polymers was given in Table III. It was reported that water absorption increased with the crosslinking density[24] and content of polar group.[25] Thus, increasing T_g by raising crosslinking density usually enhanced moisture absorption. Although BLBPE/PX had higher crosslinking density and larger functionality than BPE/PX, it showed much lower water absorption. BLE/PX and CER3000L/PX also had relatively low water absorption, which may result from incorporated hydrophobic binaphthyl and biphenyl structures, respectively. And a combination of such two structures, as in BLBPE/PX, led to quite low water absorption. This may signify incorporating binaphthyl and biphenyl structures was able to offset inflation of water absorption derived from increased crosslinking density and polar group content. Thus, it provided an effective way to develop epoxy resins with low water absorption while keeping high T_g.

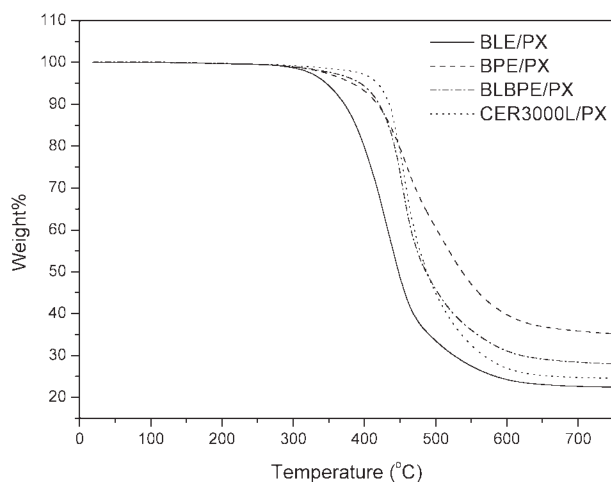


Figure 6 TGA thermograms of cured polymers.

CONCLUSIONS

A novel epoxy resin with both binaphthyl and biphenyl moieties in its skeleton was synthesized and characterized by MS, ^{1}H-NMR, and FTIR. The cured polymer obtained from this new epoxy resin showed remarkably higher T_g and lower moisture absorption, along with comprehensively excellent thermal stability. Compared with that from commercial CER3000L epoxy resin, it presented elevated T_g, char yield, and moisture resistance. Acquired good properties here were considered to depend on the introduction of both binaphthyl and biphenyl moieties in the skeleton as well as enhanced epoxy functionality.

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