

Synthesis of a Soluble Azomethine-Containing Bisphenol and the Properties of Its Modified Epoxy Thermosets

Xinghong Zhang,¹ Shang Chen,² Tao Chen,³ XueKe Sun,¹ Fei Liu,¹ Guorong Qi¹

¹Institute of Polymer Science, Zhejiang University, Hangzhou 310027, People's Republic of China

²College of Chemistry and Chemical Engineering, Jishou University, Jishou 416000, People's Republic of China

³Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom

Received 11 December 2006; accepted 1 May 2007

DOI 10.1002/app.26712

Published online 18 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A soluble bisphenol containing azomethine moiety and aromatic ether linkage, 2,2'-bis {4-[4-(hydroxy) phenyliminomethylidene] phenoxyphenyl} propane (BHPP), was synthesized from the reaction of 4-hydroxybenzaldehyde with 2,2'-bis (4-aminophenoxy phenyl) propane (BAPP) and characterized by IR, ¹H NMR, ¹³C NMR, and elemental analysis. To improve the overall properties of epoxy/diamine thermoset, ternary-curing systems combined BAPP/BHPP with diglycidyl ether of biphenyl A (DGEBA) were designed. It was found that the curing behavior and properties of the BAPP/DGEBA system changed dramatically due to the introduction of BHPP. The hybrid-curing

agents BAPP/BHPP exhibited more reactivity toward oxirane group than did BAPP. All the epoxy thermosets had high thermal properties, e.g., glass transition temperatures (T_g s) are between 145 and 170°C, 5% weight loss temperatures over 329°C, integral procedure decomposition temperature (IPDT) varied with 682–1085°C and good flame retardancy for their high limited oxygen index (LOI) values beyond 28.4. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1632–1639, 2007

Key words: epoxy thermosets; flame retardance; resins; crosslinking; bisphenol

INTRODUCTION

Epoxy resins are widely used as functional materials for their superior thermomechanical properties and excellent processability. However, the usage is often limited because of their flammability or brittleness. Although halogen-containing epoxy resins possess excellent nonflammability, they still have some shortcomings of low heat resistance and a series of environmental problems during decomposition or incineration.^{1,2} In the present, many new halogen-free flame retardant epoxy resins/curing agents^{3–26} were developed to meet the environmental protection requirements. For example, covalent incorporation of nitrogen,^{8,19–23} phosphorous,^{3–18} and multiple aromatic structures, or combination of them^{22,24–26} into the backbone of the epoxy polymers could endow the materials with excellent flame retardancy without environmental problems. Especially, nitrogen-containing epoxy thermosets attracted more attentions, not only for their excellent flame retardancy, but also for their superior heat resistance to make “lead-free” electrical/electronic instruments. Whereas they are so brittle due to the introduction of much rigid ring structures and high crosslink density,^{8,19–21} especially for epoxy-amine system. To develop new nitrogen-

containing epoxy thermosets, it is necessary to improve the overall properties synchronously as well as their environmental consistency.

Bisphenols containing double azomethine moieties^{27–41} are kinds of nitrogen-containing monomers and often used to synthesize azomethine-containing epoxide compounds and curing agents, and most of them^{27–33} are usually made liquid crystalline epoxy-based thermosets possessing very high thermal stability, toughness, and low thermal-expansion coefficient. But the yields of azomethine-containing epoxy monomers synthesized from corresponding bisphenols are very low and most of bisphenols are not miscible with epoxy resins and difficult to dissolve into the common solvents for their rigid structure,^{27,28} which limited their applications. In this article, a soluble bisphenol (2,2'-bis {4-[4-(hydroxy) phenyliminomethylidene] phenoxyphenyl} propane, BHPP)⁴¹ was synthesized with high yield from diamine, 2,2'-bis (4-aminophenoxy phenyl) propane (BAPP), and introduced into the backbone of DGEBA/BAPP thermosets in the form of a “modifier” to improve the overall properties.

EXPERIMENTAL

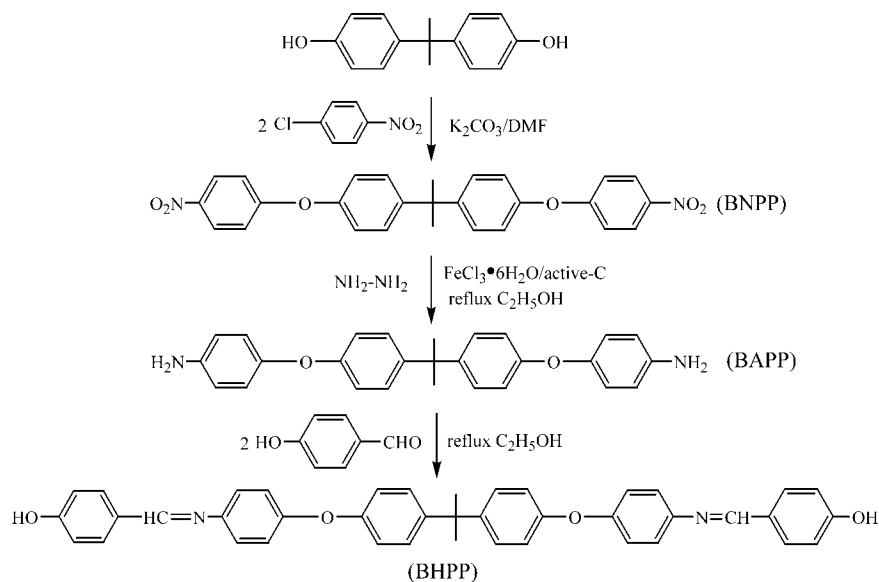
Materials

2,2'-Di (4-hydroxyphenyl) propane, *p*-chloronitrobenzene, 4-hydroxybenzaldehyde, hydrazine hydrate

Correspondence to: G. Qi (qiguorong@zju.edu.cn).

Journal of Applied Polymer Science, Vol. 106, 1632–1639 (2007)
© 2007 Wiley Periodicals, Inc.

 **WILEY**
InterScience®
DISCOVER SOMETHING GREAT



Scheme 1 Synthetic routes of soluble azomethine-containing bisphenol BHPP.

(85 wt % water solution) potassium carbonate, and iron (III) chloride were purchased from Sinopharm Chemical Reagent (Shanghai, China) and used without purification. Ethanol was purchased from Hangzhou Shuanglin Chemical Reagent Co., Ltd. (Hangzhou, China) and used as received dimethylformamide (DMF) was purchased from Hangzhou Shuanglin Chemical Reagent Co., Ltd. (Hangzhou, China) and purified by distillation under reduced pressure over calcium hydride before use. Diglycidyl ether of biphenyl A (DGEBA, NPEL-127E) was granted kindly by Nan Ya Plastics of China with an equivalent epoxy molecular weight of 180 g/eq.

Syntheses of BNPP, BAPP, and BHPP

The syntheses of 2,2'-bis (4-nitrophenoxy phenyl) propane (BNPP), BAPP, and bisphenol (2,2'-bis {4-[4-(hydroxy) phenyliminomethylidene] phenoxy] phenyl} propane, BHPP) are as follows and the synthetic routes of them were shown in Scheme 1.

BNPP was synthesized by the reaction of 2,2'-di (4-hydroxy phenyl) propane (22.8 g, 0.10 mol) and *p*-chloronitrobenzene (34.7 g, 0.22 mol) in DMF (150 mL) in the presence of potassium carbonate (30.4 g, 0.22 mol). The mixture was heated to 145–150°C under N₂ atmosphere and kept for about 8 h. After cooling to the room temperature, the mixture was poured into the water/ethanol (50/50, v/v) solution and filtered to give the yellow powder, and then BNPP was obtained to be recrystallined from ethanol.

Yield: 95%, mp: 120–124°C. IR (KBr, cm⁻¹): 1517, 1344 (–NO₂), 1249 (Ar–O–Ar). ¹H NMR (500 MHz, ppm, CDCl₃): 8.19, 8.20 (d, 4H), 7.30, 7.31 (d, 4H), 7.00–7.03 (m, 8H), 1.74 (s, 6H). Elemental analysis:

C₂₇H₂₂N₂O₆ (470.48): Cal: C, 68.94%; H, 4.68%, N, 5.96%; Found: C, 68.84%; H, 4.74%, N, 6.06%.

BNPP (47.0 g, 0.10 mol), 1.50 g iron (III) chloride, 1.50 g active carbon, and 300-mL ethanol were introduced into a 1000-mL three-necked flask to which hydrazine hydrate (85 wt %, 60 mL) was added dropwise over a period of 1 h at 90°C. After the addition completed, the mixture refluxed for 4 h, and then filtered to remove the catalysts, the white product precipitated from ethanol solution after cooling to obtain BAPP.

Yield: 96%, mp: 128–130°C. IR (KBr, cm⁻¹): 3425, 3404, 3336, 3236 (–NH₂), 1627 (–NH₂), 1222 (Ar–O–Ar). ¹H NMR (500 MHz, ppm, CDCl₃): 7.12, 7.13 (d, 4H), 6.85, 6.87 (d, 4H), 6.81, 6.82 (d, 4H), 6.65, 6.67 (d, 4H), 3.52 (s, –NH₂), 1.63 (s, 6H). Elemental Analysis: C₂₇H₂₆N₂O₂ (410.52): Cal: C, 79.02%; H, 6.34%, N, 6.83%; Found: C, 79.10%; H, 6.27%, N, 6.89%.

BAPP (41.1 g, 0.10 mol), 4-hydroxybenzaldehyde (24.4 g, 0.20 mol), and a catalytic amount of ZnCl₂ were dissolved in 300 mL of dry ethanol. The reaction mixture was stirred at reflux temperature for 8 h, and then poured into water. The precipitate was collected by filtration and washed by deionized water and ethanol thoroughly to obtain BHPP.

Yield: 95%, m.p: 125–127°C. IR (KBr, cm⁻¹): 3415 (Ar–OH), 1604 (CH=N), 1235 (Ar–O–Ar). ¹H NMR (500 MHz, ppm, DMSO-*d*₆): 10.22 (–OH), 8.47 (CH=N), 7.75, 7.77 (d, 4H), 7.24–7.26 (m, 8H), 7.01, 7.02 (d, 4H), 6.77–6.95 (m, 8H), 1.64 (s, 6H). ¹³C NMR (500 MHz, ppm, DMSO-*d*₆): 31.08, 42.05, 116.06, 118.34, 119.86, 122.91, 128.10, 128.47, 131.01, 145.57, 147.85, 154.94, 155.32, 159.74, 161.02 (C=N). Elemental analysis: C₄₁H₃₄N₂O₄ (618.73): Cal: C, 79.59%; H, 5.50%, N, 4.53%; Found: C, 79.04%; H, 5.45%, N, 4.56%.

Preparation of the cured epoxy resins

For binary reaction system, BAPP and BHPP were mixed with DGEBA, respectively, at an equivalent molar ratio of 1 : 1. They are miscible under vigorous stirring at 80°C. Both the samples were preserved in refrigerator (−10°C) for DSC test. The hybrid-curing agents composed of BAPP and BHPP were prepared by mixing BAPP and BHPP with various molar ratios (the molar ratio of BHPP/BAPP is 4, 1.5, 0.3, and 0.125, denoted as A1-A4), and the ternary systems were prepared with equal molar ratio of functionality (Ar—NH₂ and Ar—OH) of curing agents and DGEBA. Desired amounts of A1-A4/DGEBA were dissolved in acetone, and then the mixture was vacuum dried at ambient temperature to obtain the samples.

Characterizations

Infrared spectra were recorded using a Vector 22 FTIR spectrophotometer (400–4000 cm^{−1}, KBr pellet). ¹H NMR and ¹³C NMR were obtained with an Advance DMX500 NMR spectrometer (Bruker, Darmstadt, Germany) at 35°C using *d*₆-DMSO as solvent and tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed on a Flash EA1112 CHN-O-Rapid elemental analyzer using acetanilide as a standard.

About 3.0–5.0 mg of above samples was placed in an aluminum DSC pans and run on a PerkinElmer DSC 7 thermal analyzer. Dynamic scans were conducted at the heating rates of 10, 15, 20, and 25°C/min. Nitrogen was used as carrier gas at a flow of 40 mL/min. Samples for *T*_g and *T*_{d, 5 wt %} determination were cured at 160°C for 1 h and 180°C for 2 h. *T*_g determination was carried out in DSC at a heating rate of 20°C/min under N₂. Thermogravimetric analyses (TGA) were carried out on a PerkinElmer Pyris 1 at a heating rate of 10°C/min from 50 to 850°C under N₂ atmosphere. Specimens for DMA and LOI test were prepared in the procedure of 130–160°C/15 min (heating rate of 2°C/min) + 170°C/90 min in a heat-press (the molar ratio of BHPP/BAPP is 3, 1, and 0.33). And a specimen with 60 mm in length, 12.6 mm in width, and ~ 1.6 mm in thickness was used for DMA test, and performed with a PerkinElmer 7 DMA. The storage modulus *G*' and tan δ were determined while the sample was subjected to temperature scan mode at a programmed heating rate of 3°C/min from room temperature to about 220°C at a frequency of 1 Hz. *T*_g data were obtained from the measurement of the tan δ peak. LOI values were measured on a HC-2 LOI tester. The percentage in the O₂–N₂ mixture deemed sufficient to sustain the flame was taken as the LOI.

RESULTS AND DISCUSSION

Synthesis and characterization of BHPP

Figures 1 and 2 show the ¹H NMR and ¹³C NMR spectra of BHPP, and the chemical shifts of all protons and carbons have been assigned clearly. The proton chemical shift of CH=N is in 8.47 ppm and consistent with the reports.^{27–34,41} The chemical shift of Ar—OH shifts to low field at 10.22 ppm due to its acidity increase for the introduction of azomethine moiety. The characteristic ¹³C NMR chemical shift of CH=N of BHPP is at 161.02 ppm and also consisted with other analogous bisphenols. Figure 3 shows the IR spectrum of BHPP, and exhibits the characteristic azomethine absorption^{27,28} in about 1604 cm^{−1} and hydroxyl absorption in about 2500–3650 cm^{−1}, which are broad peaks. This might result from the intermolecular hydrogen bonding of bisphenols. NMR and IR information combined the result of element analysis of BHPP made us conclude that we synthesized a novel bisphenol successfully.

Unlike other azomethine-containing bisphenols,^{22,27,28} BHPP is easier to be dissolved in epoxy resin DGEBA and some common solvents, such as ethanol or acetone. This is because BHPP has a tetrahedral structure for its *sp*³-hybridized carbon and the existence of two methyl groups in its structure. Good solubility of BHPP is very useful for its application.

Reaction behaviors of BHPP/DGEBA and BAPP/BHPP/DGEBA systems

To investigate the curing behaviors of the BHPP-modified BAPP/DGEBA system, we first studied the reaction of BHPP and DGEBA. FTIR measurement, a direct analysis for curing reaction, which is widely interpretable in terms of chemical structure,⁴² was applied to investigate the reaction of BHPP/DGEBA

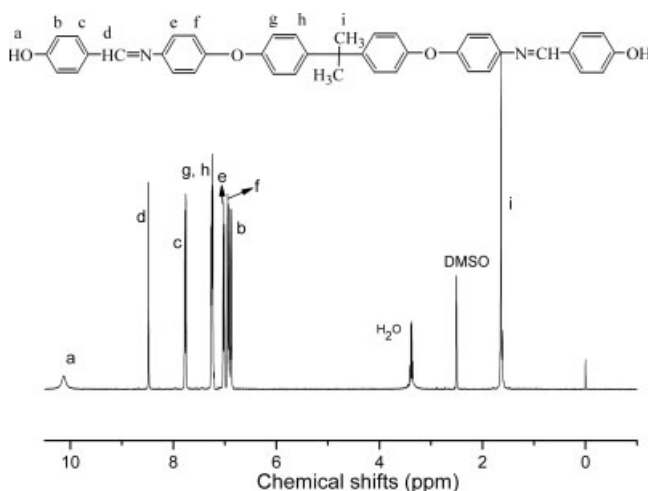


Figure 1 ¹H NMR spectrum of BHPP.

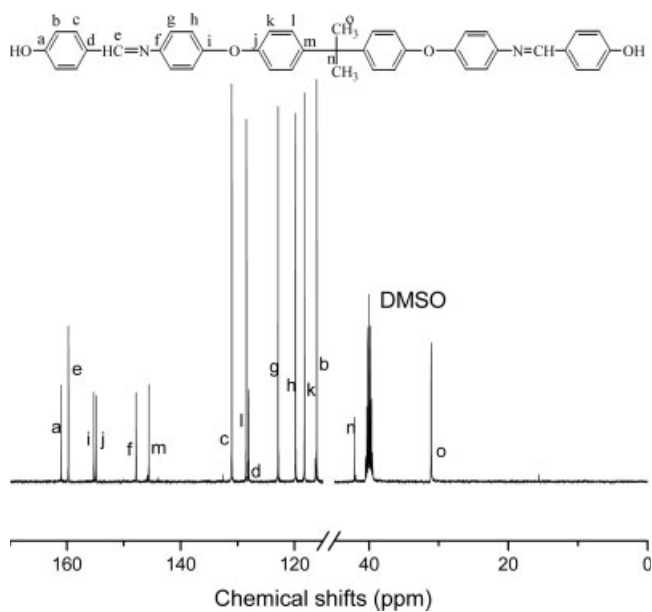


Figure 2 ^{13}C NMR spectrum of BHPP.

system intensively. Figure 4(a) shows the infrared spectra ($800\text{--}1700\text{ cm}^{-1}$) of the BHPP/DGEBA mixture at a heating rate of $20^\circ\text{C}/\text{min}$ (captured one spectrum every 30 s). One can clearly see that the peak intensity of asymmetrical vibration of oxirane ring (915 cm^{-1}) sharply decreased with the increasing curing temperature, and finally disappeared (about 300°C) due to the cleavage of the oxirane ring. Moreover, IR peak at 1285 cm^{-1} , which is another characteristic vibration peak of oxirane ring (often covered partly by the vibration peaks of ether bond), also disappeared correspondingly. Both changes show that oxirane ring reacted completely. From Figure 4(b), one can see the broad peaks in $2500\text{--}3650\text{ cm}^{-1}$ (Ar—OH) of the uncured BHPP/DGEBA system

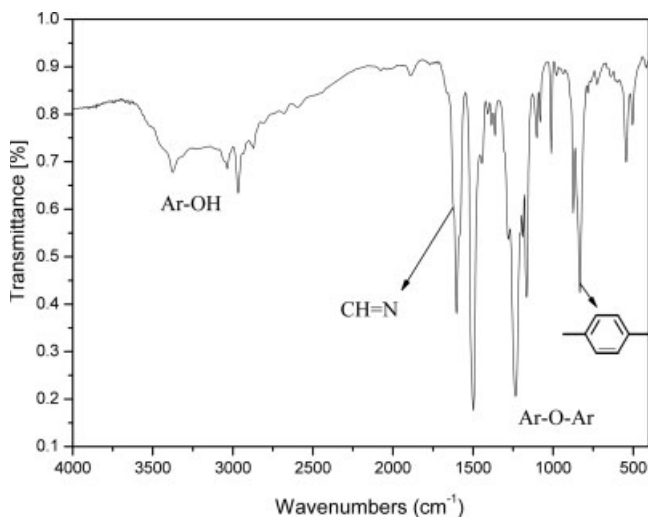


Figure 3 IR spectrum of BHPP.

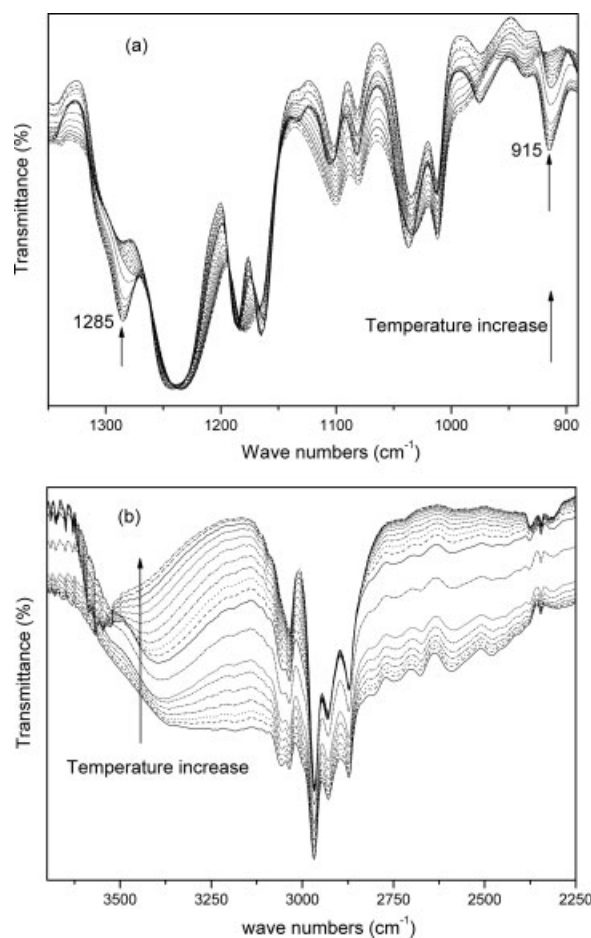


Figure 4 FTIR real time spectra of BHPP/DGEBA curing reaction in a heating rate of $20^\circ\text{C}/\text{min}$ (a) $800\text{--}1700\text{ cm}^{-1}$; (b) $3000\text{--}3650\text{ cm}^{-1}$.

become “thin” and shift to higher wave numbers, this might result from the breakage of hydrogen bonding between BHPP molecules since the reaction of phenolic hydroxyl group and oxirane group. The above IR results suggest that the new chemical bonds formed mainly by the reaction of the phenolic hydroxyl group and oxirane group.

Figure 5 shows the dynamic DSC thermograms for the reaction of BHPP/DGEBA (1 : 1, molar ratio) at the heating rates of 10, 15, 20, and $25^\circ\text{C}/\text{min}$. Two unsymmetrical exothermal peaks were found in each DSC thermograms of BHPP/DGEBA at different heating rates, and it seems that two different mechanisms in whole reaction process existed. The first exothermal peak is mainly ascribed to the additional reaction of phenolic hydroxyl group on oxirane group, while the second exothermal peak might result mainly from the reaction of the unreacted oxirane group with the unreacted hydroxyl group and the generated secondary hydroxyl group. The onset temperature of the first exothermal peak of BHPP/DGEBA in Figure 5 is quite low comparing with other phenol-epoxide reaction, e.g., formaldehyde phenol

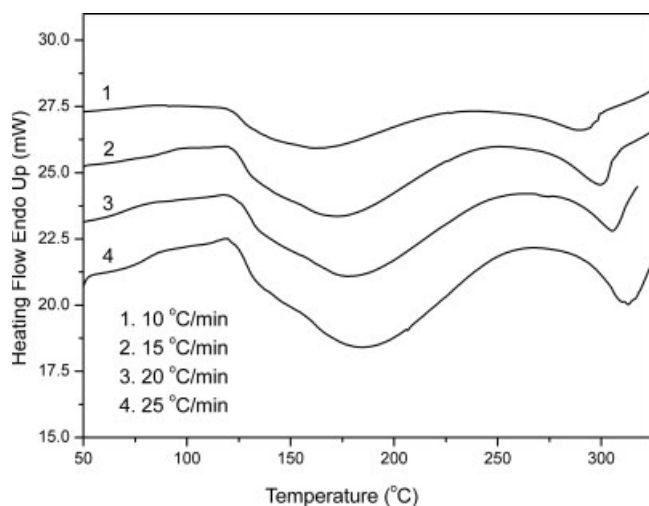


Figure 5 The DSC curves of BHPP/DGEBA at different heating rate of 10, 15, 20, and 25 °C/min.

novolac-epoxide reaction.⁴³ This might result from the strong acidity of the phenolic hydroxyl group of BHPP because of the introduction of azomethine moiety, which proved by the chemical shift of phenolic hydroxyl group in ¹H NMR spectrum. Like another bisphenol/DGEBA system,²² the BHPP/DGEBA polymer also has very low crosslinking density. Thus, the main structure of the BHPP/DGEBA polymer led us to introduce BHPP into the BAPP/DGEBA system to change the properties of the resulting thermoset.

Figure 6 shows the DSC exothermic curves of the BAPP/BHPP/DGEBA with various molar ratios. From curves a to c, the first peak of each DSC curves shift to lower temperature and the second peaks disappear grad-

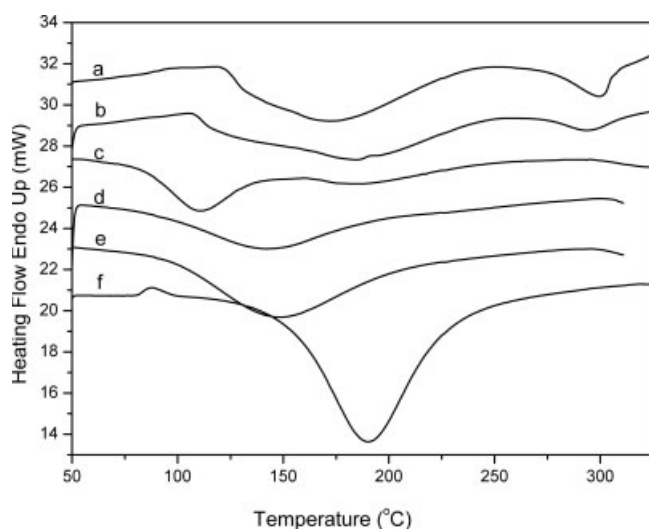


Figure 6 The DSC thermograms of DGEBA cured with (a) BHPP; (b) A1 (BHPP/BAPP = 4); (c) A2 (BHPP/BAPP = 1.5), (d) A3 (BHPP/BAPP = 0.33), (e) A4 (BHPP/BAPP = 0.125), and (f) BAPP under N₂ at a heating rate of 15 °C/min.

ually with increasing molar content of BAPP. This suggests that the hybrid-curing agents BHPP/BAPP is easier to react with oxirane group than BHPP. From curves d to f, only one exothermic peak is found in their DSC curves, and the peak shifts to higher temperature with increasing molar content of BAPP. Curve f is a typical exothermal curve of diamine/DGEBA system. This means that the hybrid-curing agents BHPP/BAPP are also easier to react with oxirane group than BAPP. Furthermore, it is obvious that the onset reaction temperatures of ternary-curing systems are lower than those of BAPP/DGEBA and BHPP/DGEBA systems. Thus, the introduction of BHPP into the BAPP/DGEBA system made the curing reaction of BAPP and DGEBA easier to occur.

Structure and properties of the thermosets

Glass transition temperatures

The glass transition temperatures (T_g s) of all epoxy thermosets were measured from a second heating trace with DSC at a heating rate of 20 °C/min (Fig. 7) at N₂ atmosphere. These thermosets exhibit high T_g in the range of 145–170 °C. The obvious difference on T_g value of BAPP/DGEBA thermoset and BHPP/DGEBA thermoset could be attributed to the reaction nature of amino and phenolic hydroxyl group toward oxirane group. T_g s of the ternary thermosets (A1–A4/DGEBA thermosets, 145–156 °C) are close to the T_g of the BHPP/DGEBA thermoset (154 °C). That is, T_g s of these ternary-epoxy thermosets do not distribute evenly in the range of T_g s of BAPP/DGEBA and BHPP/DGEBA thermosets as our original expectation. This nonsensitive relationship of T_g s toward the

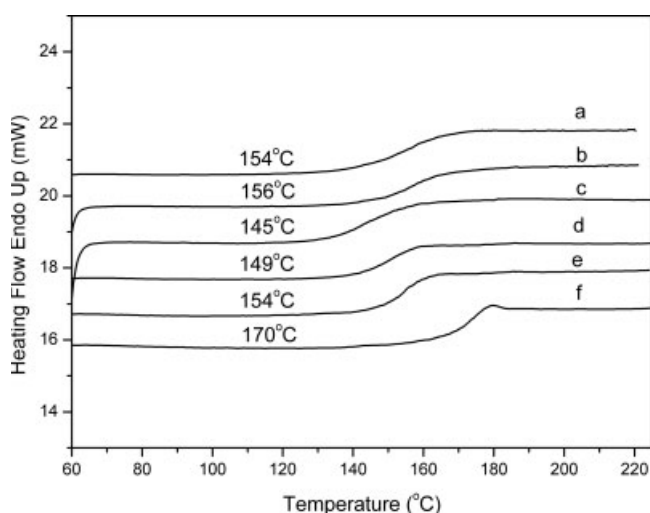


Figure 7 The glass transition temperature (T_g) of the epoxy thermosets DGEBA cured with (a) BHPP; (b) A1 (BHPP/BAPP = 4); (c) A2 (BHPP/BAPP = 1.5), (d) A3 (BHPP/BAPP = 0.33) (e) A4 (BHPP/BAPP = 0.125), and (f) BAPP.

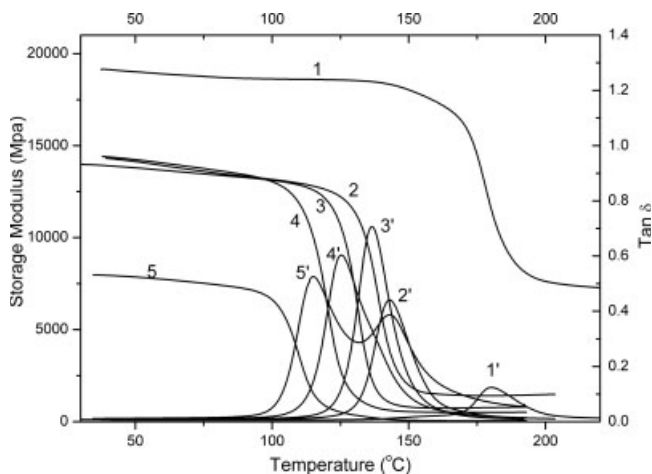


Figure 8 Dynamic mechanical analyses of the BHPP/BAPP/DGEBA thermosets with a heating rate of 3°C/min. 1,1': BAPP; 2,2': BAPP/BHPP = 3; 3, 3': BAPP/BHPP = 1; 4, 4': BAPP/BHPP = 0.33, and 5,5': BHPP.

networking structure of these ternary thermosets was also found in other bisphenol/DGEBA system.²² This reveals that BHPP with longer molecular length may have more impacts on the chain structures of the thermoset. Moreover, imperfect curing technique may be responsible for this result because all samples were cured in the same conditions, which may not be the optimum conditions for the embodiment of the effect they should play.

Although above ternary-curing systems contain BHPP that can decrease the crosslink density of the resultant thermosets, they still exhibit relatively high T_g s. Therefore, these epoxy thermosets containing azomethine moiety were potentially useful as advanced composite matrices because of high T_g s, excellent thermomechanical properties as well as excellent thermal stabilities.

Dynamic mechanical analysis

DMA can provide information about the microstructure and thermomechanical properties of the cured epoxy resins. Samples for DMA measurement were made in hot-press in the curing procedure of 130–160°C/15min (heating rate of 2°C/min) + 170°C/90

min. Figure 8 shows the dynamic mechanical behaviors of the BAPP/BHPP/DGEBA thermosets with a heating rate of 3°C/min from room temperature to about 220°C at a frequency of 1 Hz. One can see that the storage modulus (G') of the BAPP/DGEBA thermoset is higher than those of the epoxy thermosets containing BHPP before α -relaxation transition, after α -relaxation transition, G' of the BAPP/DGEBA thermoset is still high and is a typical DMA curve of a thermosetting resin, while the BHPP/DGEBA thermoset has lowest initial G' , and its G' decrease to about 100 MPa after α -relaxation transition, just as a typical DMA curve of a thermoplastic resin due to the flexible aromatic ether linkage and its lower crosslink density. For ternary-epoxy thermosets, their initial G' is about equal, but their G' in $T_g + 40^\circ\text{C}$ decrease with increasing the content of BHPP.

According to the rubber-elastic theory,⁴⁴ the crosslink density of a thermosetting resin is proportional to the G' in $T_g + 40^\circ\text{C}$, so that the ratio of the crosslink density of the BAPP, BAPP/BHPP (=3), BAPP/BHPP (=1), BAPP/BHPP (=0.33), and BHPP/DGEBA thermosets are about 72.7: 14.5: 7.8: 5.7: 1 (as shown in Table I). Correspondingly, the T_g value of these epoxy thermosets decrease obviously with the increasing BHPP content. T_g s of the ternary thermosets from DMA determination are lower than those from DSC method. This may result from different curing technique. Actually, the resulting thermoset has suitable thermomechanical properties (Table I) when the molar ratio of BAPP/BHPP is three. It is interesting that the BHPP/DGEBA thermoset has two $\tan \delta$ peaks (113 and 143°C), which might result in the formation of heterogeneous networks.

From the earlier discussion, it is concluded that the introduction of BHPP can toughen the BAPP/DGEBA thermoset without obvious decrease of thermal stabilities (esp. when the molar ratio of BAPP/BHPP is three), and this also supported by the following TGA.

Thermal stabilities and flame retardancy

Thermal stabilities of these epoxy thermosets were assessed by TGA with the following parameters: 5 wt

TABLE I
DMA Analyses of the Epoxy Thermosets

DGEBA cured with	T_g (°C, DMA)	Height of $\tan \delta$	Modulus 50°C (MPa)	Modulus $T_g + 40^\circ\text{C}$ (MPa)
BAPP	181	0.125	19023	7274
BAPP/BHPP = 3	143	0.440	14111	1450
BAPP/BHPP = 1	137	0.707	13808	776
BAPP/BHPP = 0.33	125	0.603	14280	573
BHPP	115/143	0.526/0.387	7848	~ 100

TABLE II
Thermal Stability Parameters for the Epoxy Thermosets

The cured epoxy resin	T_g (°C)	$T_{d, 5\%}$ (°C)	$Y_c\%$ (850°C)	A^*	K^*	IPDT (°C)
BAPP/DGEBA	170	370	13.36	0.593	1.456	682
A4/DGEBA	154	354	17.52	0.580	1.379	732
A3/DGEBA	149	342	22.54	0.612	1.574	811
A2/DGEBA	145	329	26.18	0.630	1.680	883
A1/DGEBA	156	337	31.53	0.657	1.911	1041
BHPP/DGEBA	154	333	32.56	0.664	1.972	1085

IPDT can be calculated by Doyle method⁴⁵ from TGA curves; A^* is the area ratio of total experimental curve divided by total TGA thermogram, K^* is the coefficient of A^* .

% decomposition temperature ($T_{d, 5\%}$), and integral procedure decomposition temperature (IPDT). $T_{d, 5\%}$ indicates the apparent thermal stability of the epoxy thermosets. IPDT proposed earlier by Doyle⁴⁵ can be discussed in a quantitative thermal analysis containing the char residue of the resulting thermosets at high temperature.

From the TGA results, the IPDT is calculated by the following equation:⁴⁶

$$\text{IPDT}(\text{°C}) = A^*K^*(T_f - T_i) + T_i \quad (1)$$

where A^* is the area ratio of total experimental curve divided by total TGA thermogram, K^* is the coefficient of A^* , T_i and T_f are the initial and final experimental temperature, respectively.

The thermal parameters ($T_{d, 5\%}$ and IPDT) of these thermosets are listed in Table II. For binary epoxy thermosets, $T_{d, 5\%}$ value of the BAPP/DGEBA thermoset is 370°C and higher than that of the BHPP/DGEBA thermoset (333°C). However, the char yield ($Y_c\%$) of the BHPP/DGEBA thermoset (32.56%) is higher than that of the BAPP/DGEBA thermoset

(13.36%) because BHPP has azomethine moiety, which facilitate the formation of char residue during decomposition.^{47,48} The same case happens for the IPDT value, which indicates that the introduction of azomethine moiety can improve the inherent thermal stability of the epoxy thermosets dramatically. For ternary-epoxy thermosets, one can see that the $T_{d, 5\%}$ values of these epoxy thermosets are all above 329°C, indicates that they all have excellent thermal stability. The char yields and IPDT values of these ternary-epoxy thermosets increase with the increasing molar content of BHPP, and are higher than those of 4, 4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenyl ether (DDE), and 4,4'-diaminodiphenyl sulphone (DDS)/DGEBA epoxy thermosets.²² Herein, we found that char yields of these thermosets were related to their composition. The relationships of char yield and weight percent of azomethine (W_A , the weight percentage of azomethine in a sample) in the binary and ternary-epoxy thermosets are shown in Figure 9 line a. It can be seen that Y_c increase with the increasing W_A and exhibit good linearity. Thus, we concluded that the thermal stabilities of these epoxy thermosets could be adjusted by changing the molar ratio of BHPP/BAPP.

Limited oxygen index (LOI) can be used as an indicator to evaluate the flame retardancy of epoxy thermosets, LOI is defined as the minimum fraction of oxygen in an oxygen–nitrogen mixture that is just sufficient to sustain combustion of the specimen after ignition. Herein, we found that LOI values (28.4–34.0) of these thermosets are higher than that of the common epoxy resins (LOI is about 19.8) and increase linearly with increasing the content of azomethine moiety (Figure 9, line b). This shows that the resulting epoxy thermosets are endowed with flame retardancy due to the introduction of azomethine structure.

CONCLUSIONS

A soluble bisphenol BHPP containing rigid azomethine moiety and flexible aromatic ether bond was synthesized and used as a modifier to BAPP/DGEBA curing system. Introduction of BHPP can change the

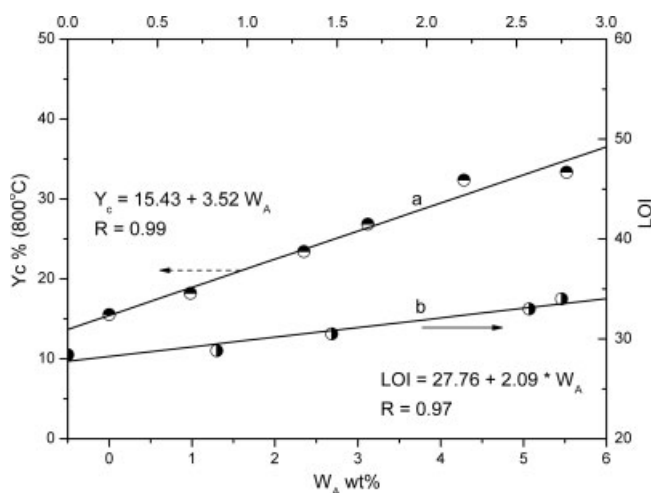


Figure 9 The relationships of char yield (Y_c) and LOI vs. content of azomethine (W_A) in the BHPP/BAPP/DGEBA thermosets. Line a: Y_c vs. W_A ; Line b: LOI vs. W_A .

reaction behaviors and the properties of the resulting thermoset. The epoxy thermosets containing BHPP exhibited high glass transition temperature, high initial decomposition temperatures, good flame retardancy, and good thermomechanical properties. Furthermore, char yield and LOI have linear relationships with the content of azomethine structure respectively were found in the epoxy thermosets.

References

1. Derouet, D.; Morvan, F.; Bross, J. C. *J Appl Polym Sci* 1996, 62, 1885.
2. Camino, G.; Costa, L.; Martinasso, G. *Polym Degrad Stab* 1989, 23, 359.
3. Shau, M. D.; Wang, T. S. *J Polym Sci Part A: Polym Chem* 1996, 34, 387.
4. Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S. *J Polym Sci Part A: Polym Chem* 1997, 35, 565.
5. Wang, C. S.; Lin, C. H. *Polymer* 1999, 40, 747.
6. Wang, C. S.; Lin, C. H. *J Polym Sci Part A: Polym Chem* 1999, 37, 3903.
7. Lin, C. H.; Wang, C. S. *J Polym Sci Part A: Polym Chem* 2000, 38, 2260.
8. Shieh, J. Y.; Wang, C. S. *Polymer* 2001, 42, 7617.
9. Lin, C. H.; Wang, C. S. *Polymer* 2001, 42, 1869.
10. Liu, Y. L. *J Polym Sci Part A: Polym Chem* 2002, 40, 359.
11. Liu, Y. L.; Tsai, S. H. *Polymer* 2002, 43, 5757.
12. Wu, C. S.; Liu, Y. L.; Chiu, Y. S. *Polymer* 2002, 43, 1773.
13. Liu, Y. L.; Wu, C. S.; Hsu, K. Y.; Chang, T. C. *J Polym Sci Part A: Polym Chem* 2002, 40, 2329.
14. Lu, S. Y.; Hamerton, I. *Prog Polym Sci* 2002, 27, 1661.
15. Liu, Y. L.; Wu, C. S.; Chiu, Y. S.; Ho, W. S. *J Polym Sci Part A: Polym Chem* 2003, 41, 235.
16. Espinosa, M. A.; Galia, M.; Cadiz, V. *J Polym Sci Part A: Polym Chem* 2004, 42, 3516.
17. Lin, C. H. *Polymer* 2004, 45, 7911.
18. Liu, Y. L.; Chen, Y. J. *Polymer* 2004, 45, 1797.
19. Von, G. W.; Huber, J.; Kapitza, H.; Rogler, W. *J Vinyl Addit Technol* 1997, 3, 175.
20. Wu, C. S.; Liu, Y. L. *J Polym Sci Part A: Polym Chem* 2004, 42, 1868.
21. Zhang, X. H.; Wan, H. M.; Min, Y. Q.; Qi, G. R. *J Appl Polym Sci* 2005, 96, 723.
22. Zhang, X. H.; Chen, S.; Min, Y. Q.; Qi, G. R. *Polymer* 2006, 47, 1785.
23. Tarek, A.; Hajime, T.; Tsutomu, T. *Polymer* 2004, 45, 7903.
24. Sergei, V. L.; Edward, D. W. *Polym Int* 2004, 53, 1901.
25. Chen, C. S.; Bulkin, B. J.; Pearce, E. M. *J Appl Polym Sci* 1982, 27, 1177.
26. Iji, M.; Kiuchi, Y. *J Mater Sci Mater Electron* 2001, 12, 715.
27. Mormann, W.; Bröcher, M.; Schwarz, P. *Macromol Chem Phys* 1997, 198, 3615.
28. Mormann, W.; Bröcher, M. *Macromol Chem Phys* 1998, 199, 1935.
29. Pere, C.; Angels, S.; Marina, G.; Marta, G.; Cossimo, C. *J Polym Sci Part A: Polym Chem* 2003, 41, 1.
30. David, R.; Angels, S.; Mantecón, A. *J Polym Sci Part A: Polym Chem* 2003, 41, 1465.
31. Ribera, D.; Mantecón, A.; Serra, A. *J Polym Sci Part A: Polym Chem* 2002, 40, 3916.
32. Choi, E. J.; Ahn, H. K.; Lee, J. K.; Jin, J. I. *Polymer* 2000, 41, 7617.
33. Mormann, W.; Bröcher, M. *Polymer* 1998, 40, 193.
34. Chattha, M. S.; Cassatta, J. C.; Siegl, W. O. *J Appl Polym Sci* 1987, 33, 1829.
35. Mikroyannidis, J. A. *Makromol Chem* 1989, 90, 1867.
36. Mikroyannidis, J. A. *Polym Int* 1991, 25, 91.
37. Mija, A.; Cascaval, C. N.; Stoica, G. H.; Rosu, D.; et al. *Eur Polym J* 1996, 32, 779.
38. Mititelu, A.; Cascaval, C. N.; Stoica, G.; Mustata, F. *J Polym Eng* 1998, 18, 397.
39. Su, W. F. *Thermochim Acta* 2002, 392, 93.
40. Choi, E. J.; Seo, J. C.; Bae, H. K.; Lee, J. K. *Eur Polym J* 2004, 40, 259.
41. Keiichiro, W.; San, M.; Patrick, E. C.; William, S. H. U.S. Pat. 5,066,765 (1991).
42. Elias, H. G. *An Introduction to Polymer Science*; VCH Publication: New York, 1997.
43. Ren, S. P.; Lan, Y. X.; Zhen, Y. Q.; et al. *Thermochim Acta* 2006, 440, 60.
44. Tobolsky, A. V. *Properties and Structure of Polymers*. Wiley: New York, 1960.
45. Doyle, C. D. *Anal Chem* 1961, 33, 77.
46. Park, S. J.; Cho, M. S. *J Mater Sci* 2000, 35, 3525.
47. Mikroyannidis, J. A. *J Appl Polym Sci* 1990, 41, 2613.
48. Palaninathan, K.; Singaravelu, R.; Pachagounder, S. *Polymer* 2004, 45, 7895.