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Improvement of thermal properties and flame retardancy of epoxy-amine thermosets by introducing bisphenol containing azomethine moiety

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Abstract. A novel bisphenol 1, 4'-bis{4-[(4-hydroxy) phenyliminomethylidene] phenoxy} benzene (BHPB), which contains azomethine moiety and flexible aromatic ether linkage, was synthesized and introduced into the curing system composed of diglycidyl ether of bisphenol A (DGEBA) and diamine. The curing behavior of DGEBA/diamine changed dramatically due to the introduction of BHPB. The resultant epoxy thermosets containing BHPB had high T_gs (127–160°C), high $T_{d,5\%}$ (≥ 330°C) and high integral procedure decomposition temperature (IPDT) values (662–1230°C) and good flame retardancy because of their high Limiting Oxygen Index (*LOI*) values (above 29.5).

Keywords: *thermosetting resins, thermal stability, flame retardancy, epoxy, bisphenol*

1. Introduction

Diglycidyl ether of biphenyl A (DGEBA) is widely used for its versatile properties and low cost. However, it is thermally unstable and flammable when used in insulation materials. Introducing phosphorus element [1, 2], which is more environmental friendly than halogens, into the main chain of DGEBA via chain extension reaction is a good way to improve the flame retardancy of the resultant thermoset. But the higher the phosphorus content, the lower the thermal stability [2–4]. Nitrogen-containing epoxy thermosets are gradually attracting more attention because they exhibit good flame retardancy, thermal properties, as well as more environmental friendly.

It is well known that bisphenols containing azomethine group (Ar–CH=N–Ar), which is a rigid structure, frequently used as the mesogenic unit for liquid-crystalline epoxy themosets (LCTs) [5–7], can strengthen the thermal stability and increase the char residue when the thermosets containing of them decompose. However, the yield of azomethine-containing epoxy monomers from bisphenols is very low [7], which limited their applications. Furthermore, rigid azomethine moiety may result in brittleness of the resultant thermosets if no flexible structures were introduced. Herein, we synthesized a bisphenol, 1, 4'-bis{4-[(4-hydroxy) phenyliminomethylidene] phenoxy} benzene (BHPB), which contains both the azomethine moiety and flexible aromatic ether linkage, and introduced it directly into the backbone of epoxy-amine thermosets as a 'modifier' to improve the thermal stability and flame retardancy.

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2. Materials and methods

Hydroquinone, *p*-chloronitrobenzene, 4-hydroxybenzaldehyde, hydrazine hydrate (85 wt% water solution), potassium carbonate and Iron (III) chloride ($FeCl_3·6H_2O$) and $ZnCl_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without purification. Ethanol, dimethylformamide (DMF) were purchased from Hangzhou Shuanglin Chemical Reagent Co., Ltd. (Hangzhou, China), ethanol was used as received, and DMF was purified by distillation under reduced pressure over calcium hydride before use. Diglycidyl ether of biphenyl A (DGEBA, NPEL-127E) was granted kindly from Nan Ya plastics of China with an equivalent epoxy molecular weight of 180 g/eq.

Infrared spectra were recorded by using a Vector 22 FTIR spectrophotometer (400–4000 cm^{-1}, KBr pellet). ^1H NMR and ^{13}C NMR were obtained with an Avance DMX500 NMR spectrometer (Bruker, Darmstadt, Germany) at 35°C using d_6-DMSO as a solvent. Elemental analysis was performed on a Flash EA1112 CHN–O–Rapid elemental analyzer using acetanilide as a standard. Curing behavior of BAPB/BHPB/DGEBA system was carried out on a Perkin-Elmer DSC 7 thermal analyzer at a heating rate of 10°C/min at a flow rate of 40 ml/min under N_2. The temperature calculation was regularly made using In and Zn standards at each scanning rate being used. T_g determination was carried out in DSC at a heating rate of 20°C/min under N_2. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer Pyris 1 at a heating rate of 10°C/min from 50°C to 850°C under N_2 atmosphere. *LOI* values were measured on a HC-2 *LOI* tester according to ASTM D-2863-77. The percentage in the O_2–N_2 mixture deemed sufficient to sustain the flame was taken as the *LOI*.

3. Experimental

3.1. Synthesis

The synthesis of 1, 4'-bis{4-[(4-hydroxy) phenyliminomethylidene] phenoxy} benzene (BHPB) is shown in Figure 1.

1, 4'-bis(4-nitrophenoxy) benzene, [BNPB, Figure 1, (1)] was synthesized by the reaction of hydroquinone (0.10 mol) and p-chloronitrobenzene (0.22 mol) in DMF (150 ml) in the presence of potassium carbonate (0.22 mol). The mixture was heated to 145–150°C under N_2 atmosphere, and then kept about 8–10 h. After cooled to the room temperature, the mixture was poured into the mixture of water/ethanol (1/1, v/v) and filtered to give solid product and then recrystallized from ethanol. Yield: 92%.

BNPB (0.10 mol), 1.50 g $FeCl_3·6H_2O$, 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 reflux temperature, after the addition was complete, the reaction continued for about 5 h. The mixture was then filtered to remove the catalysts, after cooled to the room temperature; the product [Figure 1, (2)] was precipitated from the filter to obtain 1, 4'-bis(4-aminephenoxy) benzene (BAPB). Yield: 95 %.

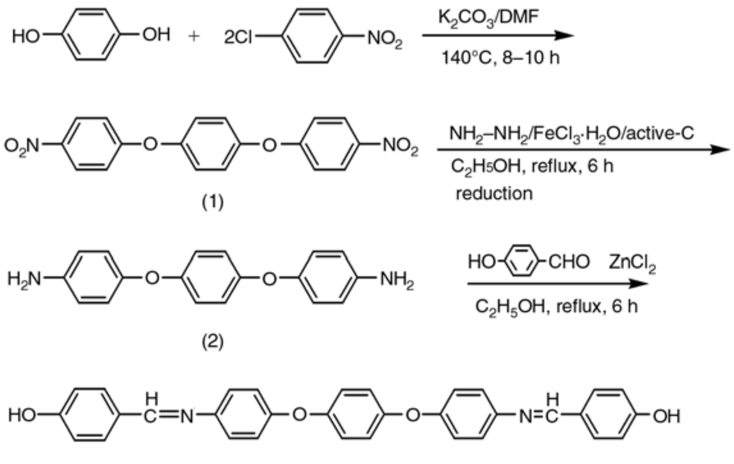

Figure 1. Synthesis routes of bisphenol BHPB. (1) 1, 4'-bis(4-nitrophenoxy)benzene (BNPB); (2) 1, 4'-bis(4-aminephenoxy)benzene (BAPB); (3) 1, 4'-bis{4-[(4-hydroxy)phenyliminomethylidene]phenoxy}benzene BHPB)

BAPB (0.10 mol), 4-hydroxybenzaldehyde (0.20 mol) and a catalytic amount of $ZnCl_2$ were dissolved in 300 ml of dry ethanol. The reaction mixture was stirred at reflux temperature for 6 h, and then was poured into water/ethanol (1/1, v/v). The product [BHPP, Figure 1, (3)] was collected by filtration and washed by deionized water and ethanol thoroughly. Yield: 97%, m.p. 278–280°C.

BHPB: IR (KBr, cm^{-1}): 3368 (Ar–OH), 1605 (HC=N), 1245 (Ar–O–Ar). ^1H NMR (500 MHz, ppm, DMSO-d_6): 10.10 (–OH), 8.47 (CH=N), 7.76, 7.78 (d, 4H), 7.26, 7.27 (d, 4H), 7.01, 7.08 (m 8H), 6.87–6.89 (d, 4H). ^{13}C NMR (500 MHz, ppm, DMSO-d_6): 116.20, 119.38, 110.16, 122.96, 128.08, 130.97, 147.81, 152.92, 155.41, 159.82, 161.06 (C=N). Elemental Analysis: $C_{32}H_{24}N_2O_4$ (500.55): Cal: C, 76.79%; H, 4.86%, N, 5.60%; Found: C, 76.64%; H, 4.98%, N, 5.63%. (The IR, NMR and Elemental Analysis data of BNPA and BAPB were omitted here for the sake of brevity.)

3.2. Preparation of epoxy thermosets

BAPB was mixed with DGEBA at an equivalent molar ratio, as BHPB could not dissolve into DGEBA very well. The hybrid curing agents BHPB/BAPB were prepared in various molar ratios (2, 1.5, 0.3 and 0.125, and denoted as B1, B2, B3 and B4, respectively), and then mixed with DGEBA at an equivalent molar ratio in DMF (weight ratio of sample/DMF is about 1:1) under 60°C, and then the mixture was vacuum dried at ambient temperature to obtain ternary systems. These samples were kept in the refrigerator (–10°C) for DSC test.

For preparing epoxy thermosets containing BHPB for *LOI* test, prepolymerization of samples is necessary. The procedure is as following: the sample was dissolved in a small quantity of DMF (weight ratio of sample/DMF is about 1:1), heated to 120°C under stirring. With the evaporation of DMF, the transparent sample was obtained. The thermosets for TGA measurement were prepared by curing the samples at 160°C for 1 h and 180°C for 2 h. Specimens for *LOI* test were obtained from the prepreg which needs pre-curing process (160°C/10 min), and then heat curing in a heat-press with the procedure of 130–160°C/0.5 h and 180°C/2 h for complete curing of the samples.

4. Results and Discussion

4.1. Synthesis

A novel bisphenol, 1, 4'-bis {4-[(4-hydroxy) phenyliminomethylidene] phenoxy} benzene (BHPB) containing rigid azomethine moiety (Ar–CH=N–Ar) and flexible aromatic ether linkage (Ar–O–Ar), was synthesized by the nucleophilic addition reaction of BAPB [Figure 1, (2)] with 4-hydroxybenzaldehyde in the presence of $ZnCl_2$ respectively. Figure 2 shows the ^1H NMR and ^{13}C NMR spectra of BHPB respectively (The IR and MS spectrum of BHPB is omitted for brevity). The chemical shifts of all protons and carbons have been labeled in Figure 2 clearly. The proton of CH=N in ^1H NMR is at 8.47 ppm, the chemical shift of Ar–OH shifts to lower field and is at 10.10 ppm due to introduction of azomethine moiety, and the carbon of CH=N in ^{13}C NMR is in 161.06 ppm. In the next, BHPB was used as a modifier for the BAPB/DGEBA system for improvement of the heat- and flame-resistance.

4.2. Curing behavior

The curing behavior of the ternary curing system containing BAPB, BHPB and DGEBA was studied by dynamic DSC method. As shown in Figure 3 curve *a*, the temperature at which the maximum conversion rate occurs in the DSC curve (T_p) of the BHPB/DGEBA system is about 213°C and higher than that of BAPB/DGEBA system (curve *f*, 184°C). This indicates that BHPB is difficult to react with oxirane group compared with BAPB. A small endothermic peak at about 275°C in curve *a* is found which is close to the melting point of BHPB. Moreover, curve *b* (the molar ratio of BHPB/BAPB is 2) exhibits no significant change compared with curve *a*. These indicate that more BHPB in the curing system may be not favorable for complete curing. When the molar ratios of BHPB/BAPB are 1.5 and 0.33 (curve *c* and *d*), two obvious exothermal peaks are found in their curves and the area of the first peak increases and their T_ps shift to higher temperature with increasing molar content of BAPB, while the endothermic peak around 275°C becomes smaller gradually, and no endothermic peak is found when the molar ratio of BHPB/BAPB is 0.125 (curve *e*). Although curves *d* and *e* are unsymmetrical, it can be seen that their T_ps are 154°C and 162°C for B3 and B4/DGEBA

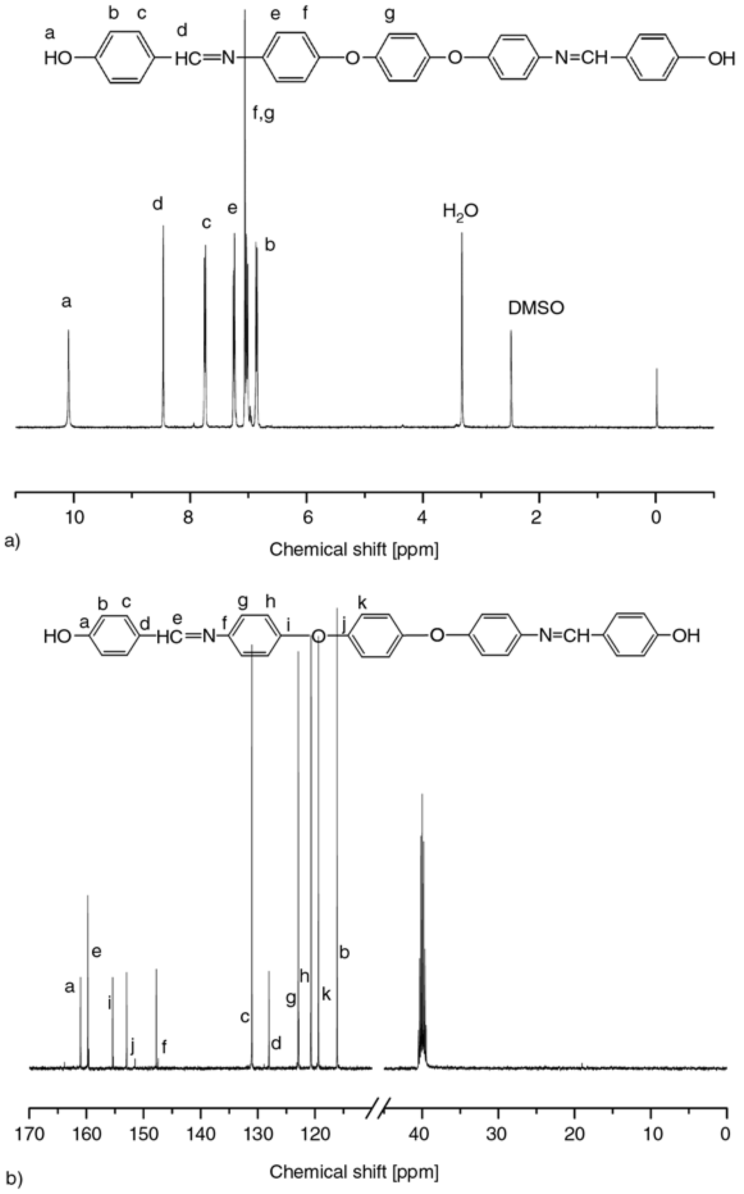

Figure 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of BHPB

system respectively, which are obviously lower than those of BHPB/DGEBA system (213°C) and BAPB/DGEBA system (184°C). Thus, introduction of the suitable amounts of BHPB (BHPB/BAPB is about less than 0.33) into the BAPB/DGEBA system made the curing reaction of BAPB and DGEBA easier to occur.

4.3. Thermal stability and flame retardancy

The glass transition temperatures (T_gs) of all epoxy thermosets were measured by a second heating trace with DSC (Figure 4). These thermosets exhibit high T_gs in the range of 127°C to 160°C. The difference on T_g of the BAPB/DGEBA thermoset (160°C) and the BHPB/DGEBA thermoset (132°C) could be attributed to the reaction nature of amino and phenolic hydroxyl group towards oxirane group and molecular size of BHPB and BAPB [8, 9]. On the other hand, the chain segment between the crosslink points of the BHPB/DGEBA thermoset is longer on the average than those of the BAPB/DGEBA thermoset.

For the ternary thermosets (B1-B4/DGEBA), T_gs are in the range of 127–147°C and close to the T_g of the BHPB/DGEBA thermoset (132°C). Moreover, T_gs of these ternary thermosets are not all in the range of T_g of the BAPB/DGEBA thermoset and the BHPB/DGEBA thermoset as our original expectation. This reveals that BHPB with longer molecules may have more impact on the chain structure of the thermoset. Moreover, the non-sensitive relationship of T_gs towards the networking structure of these thermosets might stem from the imperfect curing technique because all samples were cured under the same conditions, which may not be the optimum condition for the realization of their potential effect.

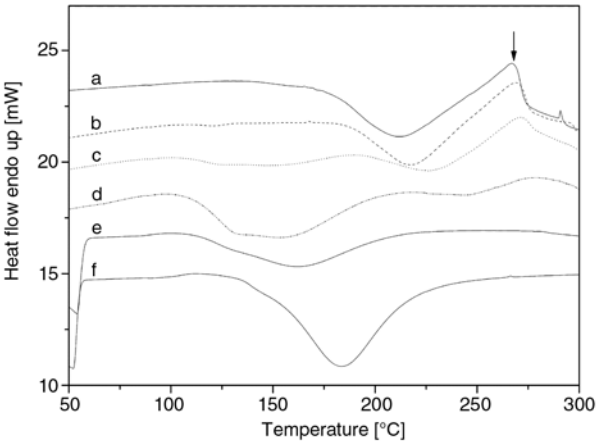

Figure 3. The DSC thermograms of DGEBA cured with a) BHPB; b) B1 (BHPB/BAPB = 2); c) B2 (BHPB/BAPB = 1.5), d) B3 (BHPB/BAPB = 0.33); e) B4 (BHPB/BAPB = 0.125) and f) BAPB under N_2 at a heating rate of 10°C/min

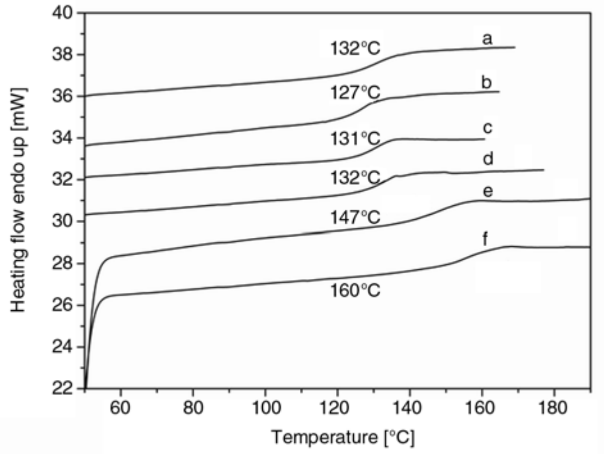

Figure 4. The T_g of BHPB/BAPB/DGEBA thermosets from a second DSC trace under N_2 at a heating rate of 20°C/min. a) BHPB/DGEBA; b) B1/DGEBA; c) B2/DGEBA; d) B3/DGEBA; e) B4/DGEBA and f) BAPB/DGEBA

Although BAPB and BHPB contain flexible aromatic ether bond, they still exhibit relatively high T_gs. So these epoxy thermosets containing azomethine moiety were potentially useful as advanced composite matrices because of high T_g as well as excellent thermal stability, which will be discussed in detail in the following.

Figure 5 shows the TGA thermograms of the BHPB/BAPB/DGEBA thermosets. The thermal parameters ($T_{d,5\%}$, and *IPDT*) of these ternary thermosets are listed in Table 1. It can be seen that the $T_{d,5\%}$ of these thermosets are all above 330°C and higher than that of DGEBA/dicyandiamide thermoset (about 290°C from our experiment). This

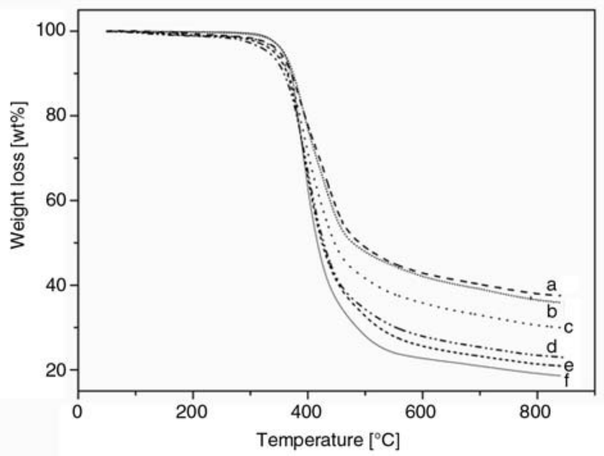

Figure 5. TGA thermograms of the ternary cured polymers, in N_2, 10°C/min. a) BHPB/DGEBA; b) B1/DGEBA; c) B2/DGEBA; d) B3/DGEBA; e) B4/DGEBA and f) BAPB/DGEBA

Table 1. Thermal stability parameters and *LOI* values of the epoxy thermosets

The epoxy thermosets	T_g [°C]	$T_{d,5\%}$[1] [°C]	Y_c% (850°C)	A^*	K^*	IPDT [°C][2]	LOI[3]
BAPB/DGEBA	160	357	18.61	0.574	1.347	662	26.0
B4/DGEBA	146	331	22.94	0.595	1.466	743	29.5
B3/DGEBA	130	350	27.70	0.634	1.734	919	31.0
B2/DGEBA	131	347	29.82	0.638	1.759	948	32.9
B1/DGEBA	127	357	35.90	0.681	2.138	1202	–
BHPB/DGEBA	132	350	37.54	0.686	2.181	1230	–

[1] 5 wt% decomposition temperature ($T_{d,5\%}$), indicates the apparent thermal stability of the epoxy thermosets;

[2] Integral procedure decomposition temperature (*IPDT*), proposed earlier by Doyle [13] 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: $IPDT(°C) = A^*K^*(T_f - T_i) + T_i$, 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;

[3] the B1/DGEBA and BHPB/DGEBA thermosets were not cured to that extent that the *LOI* measurement could be carried out.

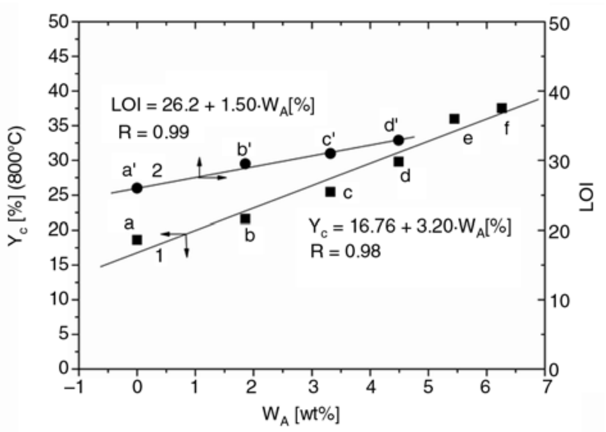

Figure 6. The relationship of char yield (Y_c) and content of azomethine in the BAPB/BHPB/DGEBA thermosets. Diamine: bisphenol = (a, a') 0:1; (b, b') 2; (c, c') 1.5; (d, d') 0.33; (e) 0.125 and (f) 1:0

indicates that they all have excellent thermal stability and can meet the requirement of 'lead-free' copper clad laminate ($T_{d,5\%} \geq 330°C$). The char yields (Y_c, wt%) of these thermosets increase with increasing molar content of BHPB for the introduction of azomethine moiety which had been proved to facilitate formation of char residue during decomposition [10, 11]. As shown in Figure 6, Y_c increases with increasing W_A (W_A, the weight percentage of azomethine in a sample) and exhibits good linearity ($R = 0.98$). According to Van Krevelen's theory [12], increase of the char formation will depress the flammability of the materials. Thus, it is rational to assess flame retardancy of these thermosets via char residue. The integral procedure decomposition temperatures (*IPDT*) of these thermosets increase dramatically with increasing molar content of BHPB from Table 1. This means that the inherent thermal stability of these thermosets was improved due to the introduction of azomethine moiety, which may be useful for improving the flame retardancy.

Limited oxygen index (*LOI*) measures the minimum oxygen concentration (in a flowing mixture of oxygen-nitrogen gas) required to support candle-like downward flame combustion [2]. A material with *LOI* of 26 or higher is rated as a flame-retardant material. It is strongly dependent on the char residue for halogen-free polymers [12] and is suitable as a semi-qualitative indicator of the effectiveness of the flame retardants in the laboratory. Herein, we found that *LOI* values (26.0–32.9) of these thermosets are beyond 26 and higher than that of the common epoxy thermoset (*LOI* of DGEBA/dicyandiamide thermoset is about 19.8) and increase linearly with increasing the content of azomethine moiety (Figure 6, line 2). This shows that the resultant thermosets were endowed with flame retardancy due to the introduction of azomethine moiety.

5. Conclusions

In summary, a novel bisphenol BHPB, which contains azomethine moiety and flexible aromatic ether linkage, was synthesized and introduced into the curing system composed of diglycidyl ether of biphenyl A (DGEBA) and diamine. The resultant epoxy thermosets containing BHPB had high thermal stability and good flame retardancy, and can be potentially applied in the electrical/electronic industries, especially can be used as the environment friendly 'green' materials.

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