The Effect of Curing Cycles on Curing Reactions and Properties of a Ternary System Based on Benzoxazine, Epoxy Resin, and Imidazole

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ABSTRACT: A ternary blend (BEM) of benzoxazine (BA-a), epoxy resin (E44), and imidazole (M) was prepared to study the effect of different curing cycles on curing reactions and properties of cured resins. Reactivity of two binary blends, E44 and BA-a, with the catalyst M, was first investigated based on the curing kinetics. Results suggest that E44/M has lower reaction activation energy than BA-a/M meaning the reaction of E44/M easily proceeds. To further figure out the sequences of the curing reactions of E44, BA-a, and M in BEM, the curing behaviors of three BEM gels at 80, 140, and 180°C (defined as BEM-80g, BEM-140g, and BEM-180g) were studied by DSC and FTIR techniques. For BEM-80g, E44/M cured before BA-a/M. For BEM-180g, both curing reactions occurred simultaneously and the copolymerization of BA-a and E44 was promoted. The crosslinked structures of cured BEM with different initial curing temperatures were strongly influenced by the reaction sequences. The T_gs, flexural properties and thermal stability of the copolymers with different curing cycles were compared. Good performance of this ternary system can be obtained by choosing suitable curing cycles. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polybenzoxazines maintain not only the excellent heat resistance, flame resistance, and mechanical properties of traditional phenolic resins but also good processabilities like low volumetric shrinkage and no release of by-products upon curing.[1–10] However, the crosslinking densities of polybenzoxazines are relatively low due to large numbers of intramolecular and intermolecular hydrogen bonds (OH—N, OH—O) in their crosslinked structures.[11] It has been reported that copolymerization of benzoxazines and epoxy resins may improve the crosslinking densities of polybenzoxazines.[12,13] This is because the phenolic hydroxyl group from the ring-opening reaction of benzoxazine monomers can react with epoxy resins at elevated temperature to generate additional crosslinking points (as seen in Scheme 1). The increase of the crosslinking densities may enhance T_gs and flexural properties of polybenzoxazines. Furthermore, the existence of ether bonds in epoxy resins can improve the toughness of materials. The addition of epoxy resins into benzoxazines is believed to be an effective method to modify the performance of polybenzoxazines.[12,14,15]

Though the curing reactions of both benzoxazines and epoxy resins belong to the ring-opening polymerization, their curing

mechanisms are very different. Benzoxazines can be cured by thermal condition or catalytic ring-opening polymerization with the existence of catalysts. But the ring-opening of epoxy resins can not occur in normally thermal condition without catalysts. Rimdusit[16,17] studied the curing behavior of a binary mixture of benzoxazine and epoxy resin. They found the copolymerization of benzoxazine and epoxy resin occurred after the curing reaction of benzoxazine. This result means the copolymerization can only occur at a high temperature.

Decreasing the curing temperature and shortening the curing time of thermosetting resins are desired for the processing. The addition of some suitable catalysts can exactly meet these requirements. The curing reactions of benzoxazines and epoxy resins belong to a cationic ring-opening mechanism.[18] Imidazole, as an effective catalyst, can catalyze both polymerization reactions because its structure contains the active hydrogen (N—H). So, for a ternary system of benzoxazine/epoxy/imidazole, there are four kinds of reactions including epoxy/imidazole, benzoxazine/imidazole, benzoxazine/epoxy, and independent benzoxazine, respectively. Liu[19] studied the curing reaction of a ternary system of benzoxazines (3,4-dihydro-3-phenyl-6-methyl-1,3-benzoxazine)/
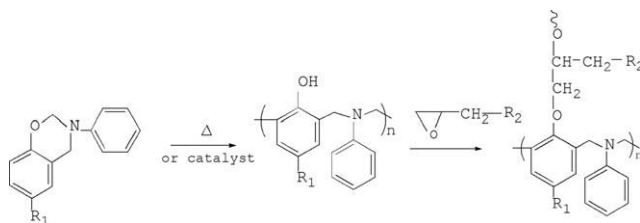
Scheme 1. Copolymerization of benzoxazine and epoxy resin.

epoxy (butyl glycidyl ether)/imidazole (2-ethyl-4-methyl imidazole) and proposed possible curing mechanisms. First, the imidazole catalyzed the homopolymerization of the epoxy resin at a low temperature, and then the residual epoxy resin copolymerized with the benzoxazine as the increase of the curing temperature. In general, epoxy/imidazole system has a much lower curing temperature (60–120°C) than benzoxazine/imidazole system (150–190°C). This means that the catalytic effect of imidazole on epoxy resins is more significant than that on benzoxazines. Actually, the above four reactions in the curing process of the ternary system have different sensitivity to the temperature. Consequently, the sequences of these reactions can be changed by choosing different curing cycles. The crosslinked structures of resulted polymers may generate corresponding changes. The method of adjusting the curing cycles is meaningful for controlling the polymer structures, but has not been reported before.

The aim of this article is to control the crosslinked structures of polymers by changing the curing cycles. This study used different initial curing temperatures for a ternary system of benzoxazine/epoxy/imidazole, and investigated their effects on the curing reactions, polymer structures as well as thermal and flexural properties of cured resins. The crosslinked structures of the cured resins with different curing cycles were also proposed.

EXPERIMENTAL

Materials

Bisphenol A-aniline benzoxazine monomer (BA-a, mp 113°C) were synthesized and purified according to procedures described earlier.[20] All chemicals were used as received. Biphenol A, aniline, aqueous formaldehyde solution, imidazole (M), toluene, and ethyl alcohol were supplied by Chengdu Kelong Chemical Reagents (China). Diglycidyl ether of bisphenol A (E44, epoxy equivalent 44) were purchased from Lanzhou Bluestar Resin (China).

Preparation of the Ternary System (BEM and BEM Gel)

BA-a was melted in a glass container at 115°C, then E44 was added and stirred for 15 min. The mass ratio of BA-a to E44 is 2 to 1. After that, the temperature of the resin system was decreased to 80°C. M with 1.5 wt % was added and stirred for 3 min. Low temperature and short time were used to avoid possible reactions. This blend (BEM) was poured into a preheated-metal mold. The mold was then pressed under 1 MPa. Three curing cycles were executed as follow: (1) 80°C/4 h, 180°C/2 h; (2) 140°C/2 h, 180°C/2 h; (3) 180°C/4 h. Finally, three groups of cured samples (defined as BEM-80, BEM-140, and BEM-180) with different curing cycles were obtained.

The gels of BEM blend were prepared using a gel time testing instrument. The sample cell of the instrument was first heated

to a required temperature like 80°C. Then, about 1 g of BEM was put on the cell and spread to a disk with a toothpick. The sample was kneaded by pressing it uniformly about every second until the sample was no longer stuck to the spatula. After that, the gel was taken out quickly and stored in a refrigerator for further characterizations. Three BEM gels were obtained at different temperatures, 80, 140, and 180°C, which are defined as BEM-80g, BEM-140g, and BEM-180g, respectively. The gel times of BEM-80g, BEM-140g and BEM-180g were 3200, 260, and 56 s, respectively.

Characterization

Fourier transform infrared (FTIR) spectroscopy was obtained on a Nicolet Magna 650 instrument. The spectral range was 4000 cm^{-1} – 400 cm^{-1} with a resolution of 4 cm^{-1}. The samples were prepared by KBr pellets. Differential scanning calorimetry (DSC) was conducted using a TA Instruments DSC Q20 under nitrogen atmosphere from 40 to 350°C. The heating rates for Figure 1 were 5–20°C min^{-1} and for Figure 4 was 10°C·min^{-1}. The samples with 3–4 mg were used in DSC test. Dynamic mechanical analysis (DMA) was carried out on a TA Instruments DMA Q800. Specimens with the dimension of 35 mm × 12.8 mm × 3.2 mm were tested with a three-point bending mode. Thermogravimetric analysis (TGA) was determined with a TA Instruments high resolution 2950 thermogravimetric analyzer under nitrogen atmosphere from 40 to 800°C at a heating rate of 10°C min^{-1}. The flexural measurements were carried out with a KD-III-5 type computer-controlled electronic universal testing machine according to GB/T 1449-2005. Specimens with the dimension of 80 mm × 13 mm × 3 mm were tested at a rate of 2 mm min^{-1} in a three-point loading. The data presented were an average of five samples.

RESULTS AND DISCUSSION

Reactivity of E44 and BA-a with M

The catalytic effects of imidazole on epoxy resins and benzoxazines are different. To study the reactivity of BA-a and E44 with the catalyst M, two blends of BA-a/M (BA-a and 1.5 wt % M)
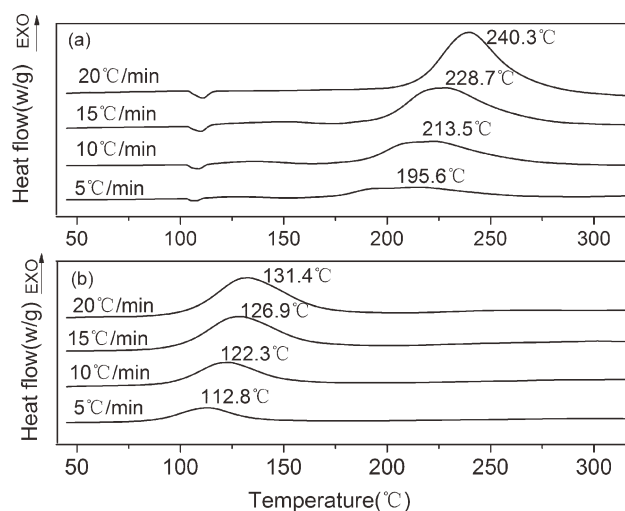
Figure 1. DSC curves of BA-a/M (a) and E44/M (b) at different heating rates (5, 10, 15, and 20°C/min, respectively).

and E44/M (E44 and 1.5 wt % M) were prepared. Their curing kinetics was investigated by dynamic DSC tests. DSC curves of BA-a/M and E44/M at different heating rates are shown in Figure 1. As seen, all exothermic peaks of BA-a/M appeared at higher temperatures (195–240°C) than those of E44/M (110–140°C). The results means that the curing reaction of E44/M can occur at a relatively lower temperature when compared with BA-a/M.

Activation energy (E_a) is the minimum energy necessary for a crosslinking reaction to occur for a thermosetting resin. The lower the activation energy, the more easily the curing reaction can occur. The reaction activation energies of BA-a/M and E44/M were calculated based on Kissinger and Ozawa methods. The Kissinger and Ozawa methods are expressed by eqs. (1) and (2), respectively:

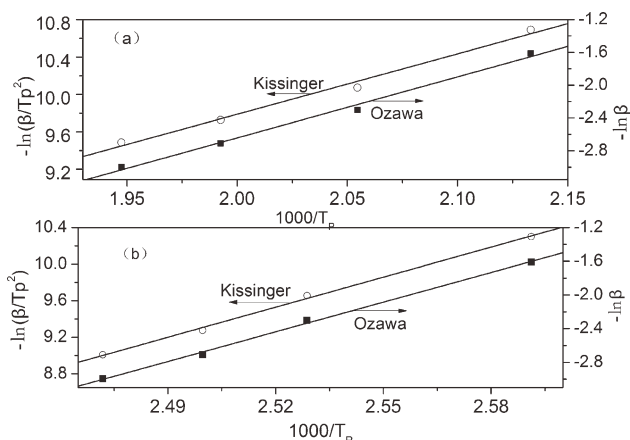$$\ln(\beta/T_p^2) = \ln(AR/E_a) - E_a/RT_p \quad (1)$$

$$\ln \beta = \ln(AE_a/R) - B - 1.052(E_a/RT) \quad (2)$$

where $\beta = dT/dt$ is a constant heating rate and T_P is the temperature of the exothermic peak. By plotting $\ln(\beta/T_p^2)$ and $\ln\beta$ vs. $1/T$ (Figure 2), respectively, the authors obtained their average activation energies; the values were 90.1 and 97.7 kJ mol^{-1} for BA-a/M and 53.7 and 61.8 kJ mol^{-1} for E44/M, respectively. The values suggest that E44/M has lower reaction activation energy than BA-a/M. It is proved that the curing reaction of E44 is more likely catalyzed by imidazole than that of BA-a.
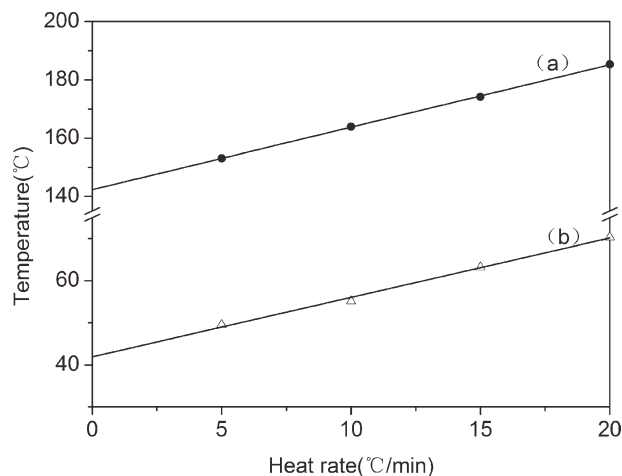
Choice of Curing Cycles

According to above DSC results about the exothermic peaks and reaction activation energies, the reaction between E44 and imidazole requires lower temperature than BA-a and imidazole. So, the initial curing temperature in the curing cycle is vital for the sequences of these reactions. When the initial curing temperature is lower than that needed for the reaction of BA-a/M, the curing reaction of E44/M takes up a dominant part while the reaction of BA-a/M can not proceed. Otherwise, the reactions of BA-a/M and E44/M occur simultaneously.

The initial-reaction temperature of BA-a/M and E44/M can be determined by the extrapolation of the characteristic tempera-
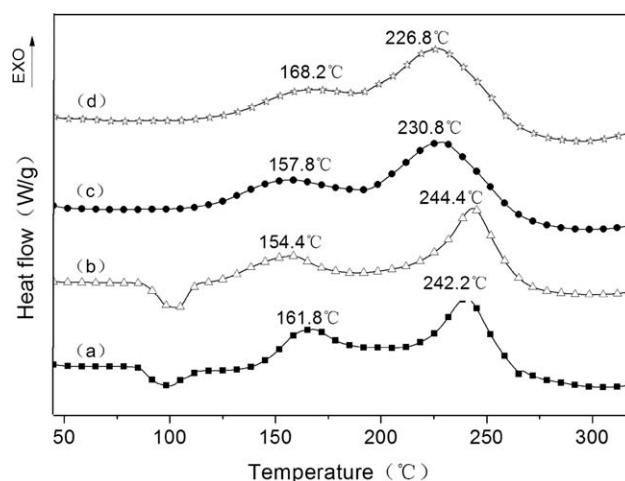
Figure 3. Plots of initial curing temperatures of BA-a/M (a) and E44/M (b) to heating rates.

tures in the dynamic DSC curves. A fitting line can be obtained by plotting the initial curing temperatures vs. the heating rates (Figure 3). When the heating rate is closed to 0, the corresponding temperature can be supposed to be the actual initial reaction temperature.[21] Based on this method, the initial curing temperatures of BA-a/M and E44/M were obtained and the values were 140 and 42°C, respectively. This means that the curing reaction of E44/M can occur above 42°C, but the curing reaction of BA-a/M can not occur until the temperature reach 140°C. So, the sequences of these different curing reactions can be controlled by adjusting the initial curing temperature. Based on the above results, 80, 140, and 180°C were chosen as different initial curing temperatures to compare their effects. In addition, to get the similar cure extents, all samples were postcured at 180°C.

Curing Reactions of the Ternary System

The curing reactions between different components in BEM were studied by comparing the DSC curves (Figure 4) of BEM

Figure 2. Kissinger and Ozawa methods plots for average activation energies of BA-a/M (a) and E44/M (b).

Figure 4. DSC curves of BEM blend (a), BEM-80g (b), BEM-140g (c), and BEM-180g (d).

blend and three BEM gels. The BEM gels were prepared at 80, 140, and 180°C, respectively. The reaction extent of the BEM gels increased with the increase of preparation temperature. All the DSC curves showed two overlapped-exothermic peaks in a wide range. For uncured BEM blend, two exothermic peaks at 162 and 242°C were observed. According to above analysis about the reactivity of E44/M and BA-a/M, the first-exothermic peak had to belong to the curing reaction of E44/M, and the second peak was mainly attributed to the curing reactions of benzoxazine including BA-a/M and BA-a/E44 as well as the homopolymerization of BA-a.
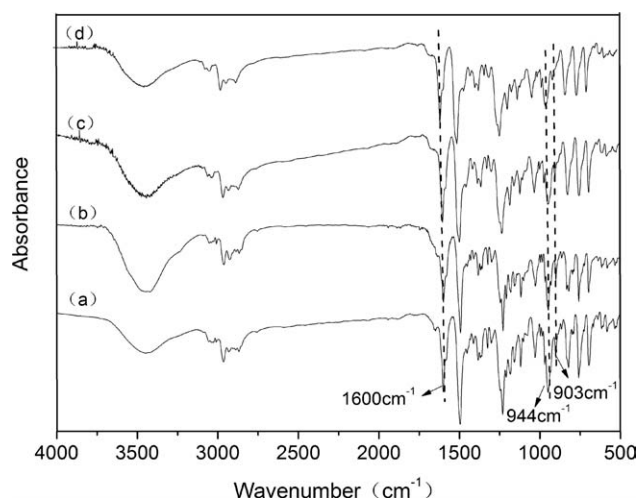
For BEM-80g, the first-exothermic peak turned to a low temperature of 154°C. According to a cationic ring-opening mechanism, the active hydrogen of imidazole can catalyze the ring-opening reaction of E44. During the preparation of the gel, the curing reaction of E44/M has been already started and some active centers for polymerization have been generated. When the gel was heated in DSC test, these active centers played a role of catalyzing the polymerization of E44, which made the exothermic-peak shift to low temperature. At the same time, the second-exothermic peak attributed to the curing reactions of BA-a showed few changes, meaning the curing reaction of BA-a has not occurred during the preparation of the gel.

When the gel was prepared at 140°C, a retardation of the peak temperature for the first peak when compared with BEM-80g can be seen. This is because that the increase of reaction extent of E44/M made the network segmental mobility restricted. The curing reaction of BA-a/M started to proceed according to the study of the initial-reaction temperature. This means that some benzoxazine may undergo the ring-opening reaction and generate the phenolic hydroxyl group, which can further catalyze the curing reaction of the benzoxazine. So, the second-exothermic peak shifted to a low temperature of 231°C. For BEM-180g, two exothermic peaks showed similar change trend.

In general, the change of the enthalpy in a DSC curve can be used to characterize the reaction extent of a thermosetting resin. The overlapped-exothermic peaks in Figure 4 were detached by a peak separation soft and their respective enthalpies were obtained. The results are listed in the Table I. ΔH_1 and ΔH_2 represent the enthalpies of the first- and second-exothermic peaks, respectively. As seen in Table I, when compared with BEM blend, ΔH_1 of BEM-80g turned to decrease and its ΔH_2 has no change meaning only the reaction of E44/M occurred for BEM-80g. Both ΔH_1 and ΔH_2 of BEM-140g started to reduce suggesting the curing reactions of E44 and BA-a occurred simultaneously at 140°C. When the gelation temperature increased to 180°C, the reaction extents of these samples further enhanced.

Figure 5. FTIR spectra of BEM mixture (a), BEM-80g (b), BEM-140g (c), and BEM-180g (d).
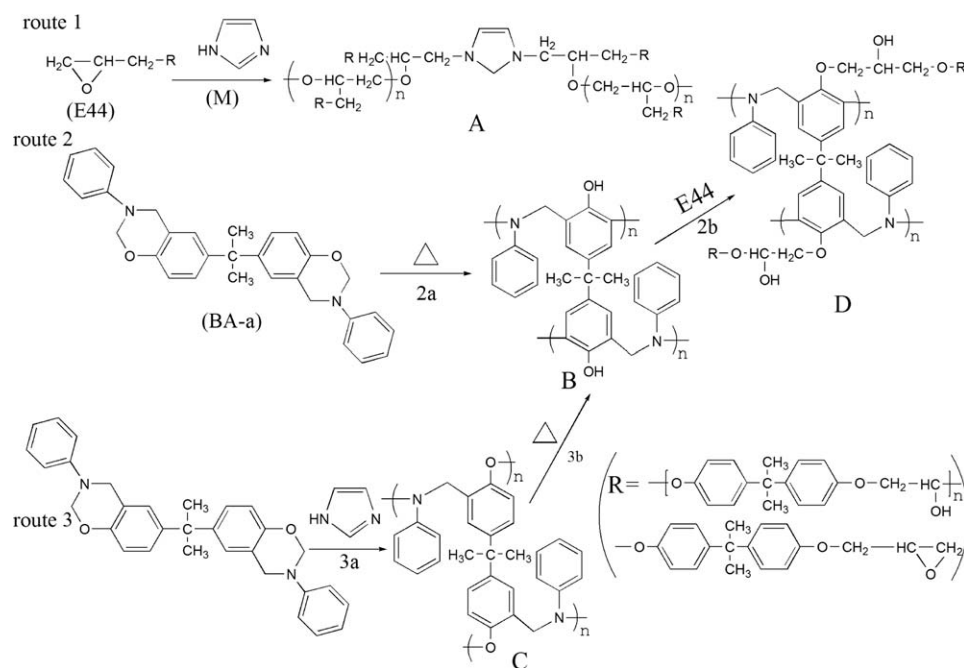
The difference of the curing reactions occurred at different initial curing temperatures can also be observed in FTIR spectra (Figure 5). The bands at 903 and 944 cm^{-1} were attributed to the characteristic bands of E44 and BA-a, respectively. Their band areas are defined as A_1 and A_2, respectively. The band at 1600 cm^{-1} attributed to monosubstitute benzene ring was used as an internal standard and its area was A_0. The reaction extents of BA-a and E44 can be compared by the area ratios of A_1 and A_2 to A_0. The values are also listed in Table I. For BEM-80g, the value of A_1/A_0 decreased from 0.119 to 0.089 and the value of A_2/A_0 has no change. The value of A_2/A_0 turned to decrease for BEM-140g meaning the occurrence of the reaction of BA-a. These results agree well with the above DSC results indicating that the curing reactions of BA-a and E44 in BEM can be controlled by choosing different initial curing temperatures.

Crosslinked Structures of Cured BEM

Different curing reactions generate different crosslinked structures for same resin system. For BEM, different initial curing temperatures led to different curing reaction sequences, which directly affected the resulted polymer structures. For BEM-80, the homopolymerization of E44 was first catalyzed by M at 80°C and formed the crosslinked structure A in Scheme 2. After cure at 80°C, the curing reaction of E44 had to complete but BA-a still existed as a monomer. When the curing temperature was elevated to 180°C, the curing reaction of BA-a occurred under thermal conditions and resulted in Mannich base phenolic-type structures (structure B). It had to be noted that the ring-opening reaction of E44 may completed at 80°C, which can not make the copolymerization of E44 and BA-a occur. So, the main crosslinked structures in BEM-80 are the structures A and B.

For BEM-140, the curing reactions of E44 and BA-a were simultaneously catalyzed by M at 140°C. Among them, cured E44 formed the structure A. BA-a catalyzed by M mainly formed Mannich base phenoxy-type structure C.[19,22] The copolymerization of E44 and BA-a still can't occur because no phenolic hydroxyl group exists in the structure C. After further cure at

Table I. Results of DSC Curves and FTIR Spectra

Sample	ΔH_1 (J/g)	ΔH_2 (J/g)	A_1/A_0	A_2/A_0
BEM	175.2	202.6	0.119	0.652
BEM-80g	134.2	204.2	0.089	0.646
BEM-140g	95.9	191.3	0.061	0.596
BEM-180g	91.4	168.6	0.055	0.510

Scheme 2. Crosslinked structures of cured BEM.

180°C, the structure C underwent a rearrangement reaction of hydrogen at the *ortho* position of benzene ring and changed to the structure B.[22–24] Although the structure B contains phenolic hydroxyl groups, the epoxy groups have completely reacted at 140°C. So, the crosslinked structures of BEM-140 mainly contain the structures A and B. Actually, because of the complexity of curing reactions of benzoxazines and epoxy resins, some copolymers may exist in BEM-140.

When the initial curing temperature of BEM was 180°C, except the reactions of E44 and BA-a simultaneously catalyzed by M, BA-a was thermally cured and directly formed the structure B at a high temperature. The copolymerization of E44 and BA-a can occur at this time due to the existence of both phenolic hydroxyl groups in the structure B and the epoxy groups in E44. The copolymerized crosslinked structure D was shown in Scheme 2. So, the crosslinked structures of BEM-180 contained the structures A, B, and D.

Viscoelastic Analysis of Copolymers
The dynamic-mechanical spectrum shows the characteristic features of crosslinked thermosetting materials. DMA spectra of BEM-80, BEM-140, and BEM-180 are shown in Figure 6 and the results are listed in Table II. As seen, BEM-80 has the highest $E'_{initial}$ (5119 MPa) while BEM-140 has the highest T_g (152.3°C). To explain this phenomenon, the authors calculated the crosslinking densities of three copolymers based on their DMA spectra.

The crosslinking densities of thermosetting resins can be estimated from the plateau of the elastic modulus in the rubbery state using eq. (3) from the statistical theory of rubbery elasticity.[11] This equation is applicable to the polymer network that has a rubbery plateau region.[5,25–27]

$$\rho = E'/3\varphi RT \qquad (3)$$

where φ is the front factor and equal to 1, which is unity for ideal rubbers, R the gas constant, T the absolute temperature, and E' is the storage modulus of the sample at temperature T. To assure that each sample was in its rubbery region, the ρ values were calculated at the T_g plus 40°C according to this equation to compare the crosslinking density of each sample.[12] The values of their crosslinking densities are listed in Table II. The crosslinking densities of the copolymers increased from 2.29 × 10^3 to 3.89 × 10^{-3} mol m^{-3} with the raising of the initial curing temperature. According to above analyses of their curing reactions, the main curing reactions were the homopolymerization of the epoxy resin and benzoxazine to form the crosslinked
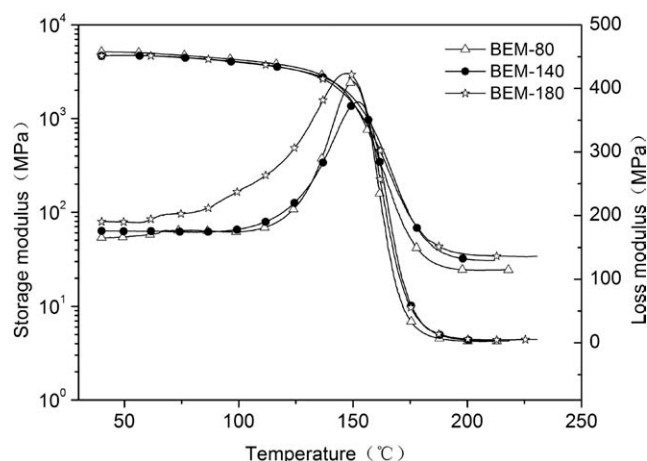

Figure 6. DMA spectra of sample BEM-80, BEM-140, and BEM-180.

Table II. Characteristics of Cured Systems

Sample	$E'_{initial}$ (MPa)	$T_{E''max}$ (°C)	Crosslink density (mol/m^3)	Flexural strength (MPa)	Deflection (mm)
BEM-80	5119	149.8	2.29×10^3	92.2 ± 7	1.93 ± 0.2
BEM-140	4719	152.3	3.02×10^3	140.7 ± 11	3.68 ± 0.3
BEM-180	4707	146.8	3.89×10^3	170.3 ± 14	4.10 ± 0.2

structures A and B when the curing cycle proceeded at a low temperature (like 80°C). When the initial curing temperatures were more than 140°C, the copolymerization of the epoxy resin and benzoxazine occurred and crosslinked structure D appeared. As the further increase of the initial curing temperature, more copolymerization reactions occurred, which led to the substantial increase of the crosslinking density.

However, high crosslinking density may not result in high T_g. Though BEM-180 has the highest crosslinking density, its T_g was the lowest. On one hand, intermolecular and intramolecular hydrogen bonds generated during the curing process of benzoxazine may restrict the mobility of chain segments and lead to increased rigidity, which probably results in high T_g. On the other hand, the existence of lots of hydrogen bonds retards the formation of crosslinked structures and leads to a low crosslinking density, which is the reason why polybenzoxazines have low crosslinking density.[28,29] Among the crosslinked structures A, B, C, and D, the hydrogen bonds more easily exist in structure B due to lots of the phenolic hydrogen groups. For BEM-180, the copolymerization of epoxy resin and benzoxazine consumed the phenolic hydroxyl groups (—OH) from the ring-opening reaction of benzoxazine, and made the amount of the hydrogen bonds decrease, which led to low T_g and high crosslinking density.

The strong hydrogen bonds easily increase material rigidity. The high E at the initial temperature ($E'_{initial}$) of BEM-80 in DMA curve was attributed to the existence of lots of hydrogen bonds in structure B. The decrease of $E'_{initial}$ for BEM-180 also supported the above conclusion that the amount of hydrogen bonds decreased when the main crosslinked structures were A and D.

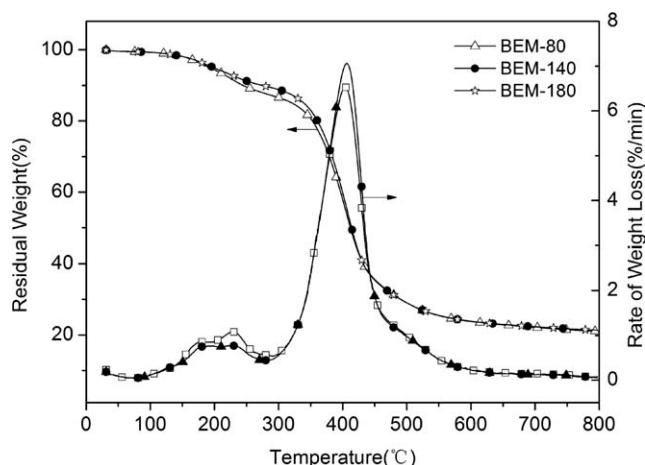**Flexural Properties of Copolymers**

The flexural properties of three copolymers were determined and the results are also listed in Table II. As the increase of the initial curing temperature, flexural strength of the samples showed increase from 92 to 170 MPa. The flexural strength of a thermosetting resin is influenced by a number of interrelated parameters. Among them, crosslinking density is a main factor. The high crosslinking density from the copolymerization of E44 and BA-a in BEM-180 created its high flexural strength. As seen in Table II, BEM-180 showed a high deflection of 4.10 mm. Combining with its high flexural, it is believed that the toughness of BEM-180 is higher than other two systems. In the main crosslinked structure D of BEM-180, lots of ether bonds were introduced into the main chain by the copolymerization of E44 and BA-a. These flexible structures may give the good toughness of BEM-180.

Thermal Stability of Copolymers

The thermal stability of three samples was studied by TGA (Figure 7). The values of decomposition temperatures $T_{5\%}$ and $T_{10\%}$ (temperatures at which the 5 and 10% weight loss is measured, respectively) and char yields are listed in Table III. The maximum weight loss for all three copolymers occurred at 300–500°C and there was no difference. As the increase of the initial curing temperature, the $T_{5\%}$ and $T_{10\%}$ increased. Especially for BEM-180, its $T_{10\%}$ reached to 275°C, which was a great increase for BEM-80. It is believed that the high crosslinking density of BEM-180 may directly result in good-thermal stability. In addition, the char yields of three copolymers were almost same meaning the different crosslinked structures of the copolymers of epoxy resin and benzoxazine have no effect on resulted char yields.

CONCLUSION

The effect of curing cycles on curing reactions of BEM and their mechanical and thermal properties were studied. Different

Table III. Results of Thermogravimetric Analysis

Samples	$T_{5\%}$ (°C)[a]	$T_{10\%}$ (°C)[a]	Char yield (800°C) %
BEM-80	192	243	21.1
BEM-140	198	274	21.4
BEM-180	199	275	21.4

[a]Temperatures at which the 5 and 10% weight loss is measured, respectively.

Figure 7. TGA spectra of BEM-80, BEM-140, and BEM-180.

initial curing temperatures can change the sequences of the curing reactions of BA-a and E44 and affect their properties. For BEM-80, the curing reaction of E44 with M occurred before that of BA-a with M. Its crosslinked structure mainly contains structures A and B. For BEM-140, the ring-opening reactions of E44 and BA-a with catalyst M occurred simultaneously. The structure formations of polybenzoxazine changed from the phenoxy-type structure (C) to the phenolic-type structure (B). The copolymerization reaction of BA-a and E44 occurred for BEM-180 due to the reaction of phenolic hydroxyl groups and epoxy groups. The crosslinked structures D resulted in high crosslinking density and flexural strength of 170 MPa. The initial curing temperature has no effect on the thermal stability of cured BEM. According to these results, one can control the curing reactions of benzoxazine and epoxy resins and get desired crosslinked structures by adding the catalysts and adjusting the curing cycles.

ACKNOWLEDGMENTS

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