

ORIGINAL ARTICLE

Phase separation in benzoxazine/epoxy resin blending systems

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Enlarging dynamic asymmetry *in situ* by controlling the polymerization sequence is known to be a good way to obtain phase separation structures in benzoxazine (BZ)/epoxy resin (ER) blending systems. In this paper, the possible reactions in BZ/ER blends were studied using model components. The results indicated that once phenolic hydroxyl groups (OH) were produced by the polymerization of BZ resin, the copolymerization between BZ and ER resin was unavoidable, which was unfavorable for the phase separation of the BZ/ER system. If ER could polymerize before BZ, the copolymerization between BZ and ER is expected to be suppressed by the lack of phenolic OH, and the dynamic asymmetry between ER and BZ could thus be enlarged, both of which are favorable for phase separation. In the following studies, a series of ER resins having different molecular weights (M_n) were used to study the possibility of phase separation in the BZ/ER systems. The turbidity observation, dynamic mechanical analysis and scanning electron microscope experiments indicated that if the M_n of ER $\geq 4370 \text{ g mol}^{-1}$, phase separation could take place with the polymerization of BZ resin and different morphologies could be observed by varying the ER content.

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INTRODUCTION

In the past few decades, thermosetting (TS) blends have attracted more attention due to their various applications in adhesives, filler-reinforced composite materials, automotive and aircraft components, and coatings for electronic circuits.^{1,2} However, until now, the method for improving the performance of TS blends is still focused on simply varying the compositions, chemical structures, curing conditions, curing agents and so on. Additionally, the research about multiphase structures, which is important to further improve the material properties (such as the impact toughness),^{3,4} has been seldom reported in TS/TS blending systems.

As one of the morphology-developing processes of multi-component polymer systems,⁵ reaction-induced phase separation has been widely used in TS/TP (thermoplastic) blends as the modification of TS resin,^{3,6,7} but its use has been limited in TS/TS blends. For TS/TP blends, for example, epoxy/poly (ether imide) blending systems,⁸ because there are vast differences between TP resins and TS precursors in their thermodynamic properties and initial dynamic asymmetry (for example, molecular weight (M_n), viscosity and glass transition temperature (T_g)), the entropy of mixing, as well as compatibility, can be significantly reduced with the curing reaction of TS resin.⁹ Whereas for TS/TS blends, for example, benzoxazine (BZ)/epoxy resin (ER) blending systems,¹⁰ because the two components are similar in their initial dynamic properties (such as low M_n , low viscosity and T_g), the initial entropy of mixing is very

large. In addition, during the curing process, mutual entanglement of cross-linked networks or copolymerization between the two TS resins leads to the formation of permanently interlocked or copolymer network structures. These two factors make obtaining the phase separation structure difficult in TS/TS blends. Therefore, how to increase the dynamic asymmetry during the curing reaction process and to reduce the mutual entanglement and copolymerization reaction are significant to phase separation in existing TS/TS blending systems.

To solve this problem, one efficient method through sequential polymerization of different components has been reported.^{11–13} The ideal model of sequential polymerization of multi-component blending systems (for example, A/B blending systems) can be described as follows. By controlling curing conditions, component A can polymerize to some extent before monomer B begins to polymerize. Therefore, the difference of M_n (dynamic asymmetry) between the two components is gradually enlarged. Then, the subsequent polymerization of component B can significantly decrease the system entropy of mixing, which will promote the phase separation of polymer A from matrix B. Of course, whether phase separation can occur in the blending system depends on the competitive effects of the kinetics of the thermodynamic driving force for phase separation and cross-linking reaction of the latter polymerization component. Through the sequential polymerization method, Yang *et al.*¹¹ and Dean *et al.*¹² have obtained phase

separation structures in urethane/acrylate resin and ER/methacrylic acid blending systems, respectively. However, it is worth mentioning that in their systems, the thermodynamic compatibilities and polymerization mechanisms between the two components were largely different (for example, photo-initiated and thermal-initiated), and no copolymerization existed between them.

Due to their good processability and excellent thermal and physical mechanical properties, BZ/ER blending systems have attracted much more attention in recent decades.¹⁴ The curing reactions of BZ and ER resin both belong to a ring-opening mechanism,^{15,16} and many studies have indicated that phenolic hydroxyl groups (OH) produced by the ring opening polymerization of BZ can copolymerize with epoxy groups of ER.^{10,17–19} Therefore, no phase separation phenomena have been reported for BZ/ER blends with different compositions, Mns, chemical structures or curing agents.^{10,20–25} Until recently, Grishchuk *et al.*^{26,27} occasionally observed nano-scale (5–150 nm) phase separation structures in a series of ER/BZ/aromatic amine ternary blending systems. However, no systematic investigation about phase separation and its influencing factors was reported.

Currently, our groups are trying to prepare phase separation structures in BZ/ER blending systems by adjusting the polymerization sequence (e.g., growth sequence of the molecular chain) of BZ and ER using specific curing agents. However, from the ideal model of phase separation through sequential polymerization as discussed above, there are still some basic questions that need to be answered, which is the primary purpose of this paper. These questions include the following: (1) which component that polymerizes firstly, that is, BZ or ER, is favorable for the sequential increase of molecular chains? (2) If the dynamic asymmetry (for example, Mn) between BZ and ER is enlarged *in situ*, can phase separation occur in BZ/ER blends from the viewpoint of thermodynamic compatibility?

EXPERIMENTAL PROCEDURE

Materials

BZ resin, based on 4,4'-diaminodiphenyl methane, phenol and paraformaldehyde, was synthesized and characterized as in previous reports²⁸ and was used without further purification. Phenol, 4,4'-diaminodiphenyl methane and paraformaldehyde were purchased commercially from Chengdu Kelong Chemical Reagents Corp. (Chengdu, China) and used as received. The average Mn of BZ resin was $\sim 435 \text{ g mol}^{-1}$. A series of diglycidyl ether of bisphenol-A (DGEBA) ER with different Mn was provided by Shanghai synthetic resin factory (Shanghai, China). The information for the ER with different Mn is shown in Table 1. *N,N*-dimethylaniline (DA) and novolac resin (NR) were used as model compounds to simulate the tertiary amine of Mannich bridge structures and the phenol structures produced by the ring-opening polymerization of BZ resin, respectively. The chemical structures of the materials used are shown in Scheme 1.

Table 1 Information about ER resins used in this study

Type	X_n^a	Mn^b (g mol^{-1})	DP^c
E48	0.48	420	1.3
E41	0.41	492	1.5
E16	0.16	1220	4.1
E11	0.11	1854	6.3
E05	0.05	4370	15.2
E04	0.04	5116	17.8

^aEpoxy value (X_n) measured and calculated as ISO 3001: 1999, IDT standard.

^b $Mn = 2 \times 100/X_n$.

^cAverage degree of polymerization of ER resin.

Preparation of BZ/ER blends

BZ/ER blends were prepared by dissolving BZ and ER resin in acetone, followed by stirring at room temperature until a yellow transparent solution was obtained. After removal of most of the solvent using a rotary evaporator under reduced pressure at 80 °C, the transparent yellow blend was obtained, and it was then poured into a preheated aluminum mold. The curing cycle was set as follows: 130 °C/2 h + 150 °C/10 h + 170 °C/2 h + 200 °C/2 h.

Characterization

Differential scanning calorimetry was conducted using a TA instruments DSC Q20 at a heating rate of 10 °C min⁻¹ from 40 to 350 °C under nitrogen atmosphere (50 ml min⁻¹).

To facilitate the turbidity observation of the blending system, the badge of Sichuan University was placed under the cured samples, and pictures were then taken with a camera.

For scanning electron microscope (SEM) (Philips XL-30 FEG) observations, all of the samples were fractured under liquid nitrogen and etched with acetone at room temperature for 5 h before receiving a gold coating.

Dynamic mechanical thermal analysis (DMA) (TA Q800) was performed with the sample dimension of 30 × 10 × 3 mm³ in a three-point bending mode (span length: 20 mm) from 40 to 270 °C with a heating rate of 5 °C min⁻¹. The maximum strain amplitude was 20 μm, and the oscillating frequency was 1 Hz.

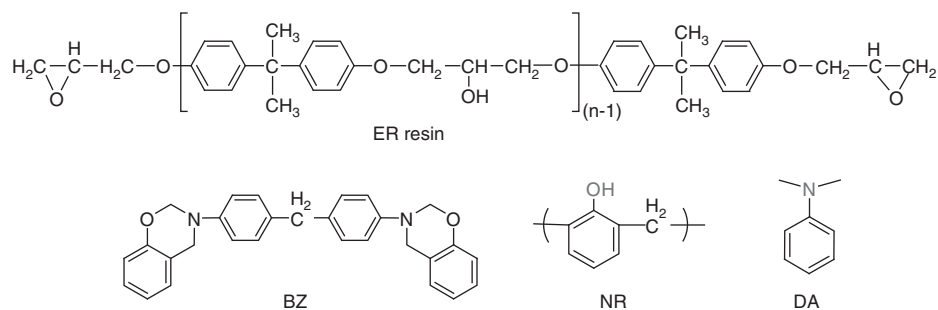
RESULTS AND DISCUSSION

Curing sequence of BZ and ER

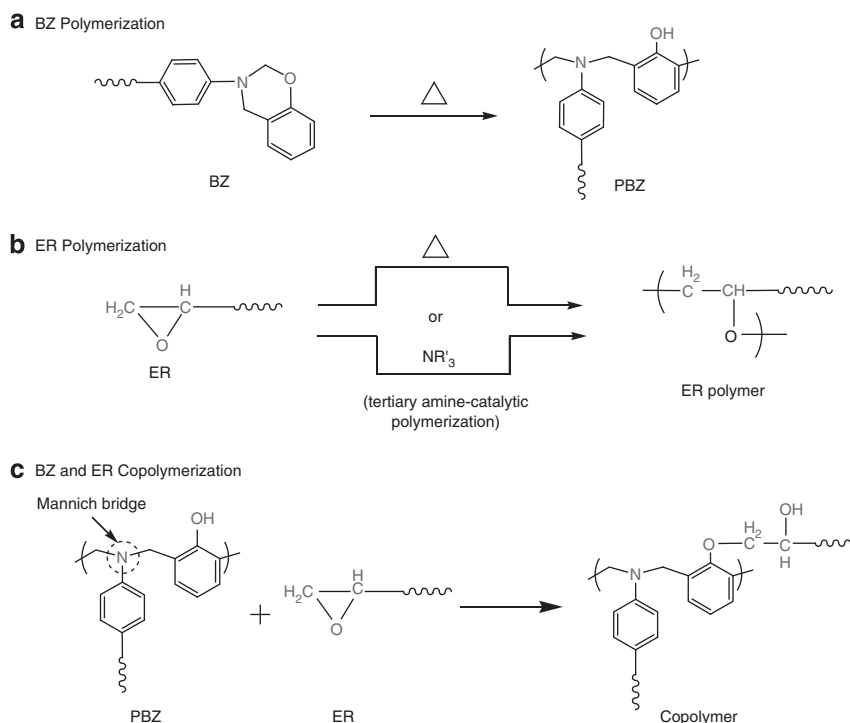
When BZ and ER are considered separately, their polymerizations are relatively simple. However, when they are mixed together, the polymerizations become complex because the tertiary amine of the Mannich bridge and phenolic OH produced by the ring-opening polymerization of BZ resin catalyzes the homopolymerization or copolymerization of ER resin.¹⁰ Therefore, as shown in Scheme 2, at least three types of polymerization reactions might exist in BZ/ER blends: (a) the thermal-induced homopolymerization of BZ resin; (b) the thermal-induced or tertiary amine-catalytic homopolymerization of ER resin (herein, the tertiary amine refers to the Mannich bridge of polybenzoxazine (PBZ)) and (c) the copolymerization between the phenolic OH of PBZ and the epoxy group of ER.

These complex polymerizations made investigation of the curing sequence of the BZ and ER resin much more difficult. To solve this problem, we separately studied the conditions for the above polymerization via two model compounds: DA and NR. These were selected to simulate the tertiary amine-catalytic polymerization of ER (Scheme 2b) and polymerization between epoxy group and phenolic OH (Scheme 2c), respectively.

Because the polymerization of ER or BZ is an exothermic reaction, the exothermic peak in the differential scanning calorimetry curve can be used to investigate temperature conditions for ER or BZ polymerization. As shown in Figure 1, the onset temperature (T_{onset}) for thermal-induced homopolymerization of ER was much higher (a, >250 °C), while after adding an equivalent molar ratio of tertiary amine, T_{onset} shifted to a relatively lower temperature (b, 149 °C). The polymerization between the epoxy group and the phenolic OH of NR occurred at 125 °C (c) but shifted to a lower temperature (76 °C) in the presence of tertiary amine (d). Ishida and Allen¹⁰ claimed that although ER homopolymerization catalyzed by the tertiary amine of the oxazine ring or Mannich bridge structure (Scheme 2b) was possible, it did not appear to be likely, as the phenolic OH reaction with the epoxy group in the presence of tertiary amines (Scheme 2c) had been shown to proceed almost exclusively. Our experimental results highly support this result. Additionally, comparing Figure 1e with Figures 1c and d, both the T_{onset} (209 °C) and peak exothermic temperature (T_{peak} , 244 °C) of the homopolymerization of the BZ



Scheme 1 Chemical structures of materials used in this study.



Scheme 2 The possible reactions that exist in BZ/ER blends: (a) the ring-opening polymerization of the BZ resin, (b) the homopolymerization of the ER resin under the catalysis of the tertiary amine on the Mannich bridge structure of PBZ or elevated temperatures, (c) the polymerization between the phenolic OH of PBZ and the epoxy groups of ER.

resin (Scheme 2a) were higher than those of the polymerization between epoxy groups and phenolic OH (Scheme 2c). Therefore, in BZ/ER binary blends, once the phenolic OH is produced by the ring-opening polymerization of the BZ resin, the polymerization between the BZ and ER resins would take place immediately, which is unfavorable to the sequential growth of molecular chains of BZ and ER.

Although some investigations have indicated that the polymerization temperature of BZ resin can be lowered in the presence of catalysts, such as Lewis acids,²⁹ imidazole,^{30,31} amine^{26,32} and organic acids,^{33,34} etc., these still could not realize the sequential growth of molecular chains of BZ and ER. This is because, until now, no significant polymerization of BZ resin can take place below 100 °C,¹⁵ even with the aid of a catalyst, whereas polymerizations between epoxy groups and phenolic OH can take place at room temperature under the catalysis of tertiary amine (this point has been proved in Supplementary Scheme S1).

In contrast, the polymerization of ER can take place at rather low temperatures (for example, room temperature) with catalysts.^{35,36} Additionally, if ER polymerized preferentially, the copolymerization between ER and BZ could be suppressed as a result of the lack of phenolic OH. Thus, the preferential polymerization of ER is theoretically more beneficial for the sequential growth of molecular chains of ER and BZ.

Phase separation

If ER resin has polymerized to high M_n in the presence of catalyst before the curing reaction of BZ resin, the dynamic asymmetry between BZ and ER should be enlarged. Then, whether phase separation of BZ/ER can take place is dependent on competition between the thermodynamic driving force of phase separation and the cross-linking reaction of the BZ resin. To prove the speculation, a series of DGEBA ER with different M_n were separately blended with BZ resin, and their phase separations were investigated by turbidity

observation, DMA and SEM measurements. Herein, the ER resin was defined according to the epoxy value (X_n). Lower values of X_n correspond to higher values of M_n .

Turbidity

Turbidity measurements are often used as an empirical method to judge phase separation.³⁷ If the phase domain size is larger than the wavelength of visible light, the blend tends to appear opaque; otherwise, the blend tends to be transparent. The transparency of

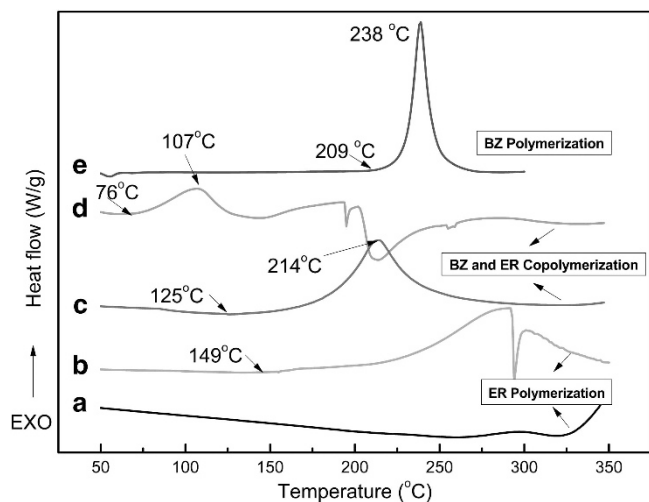


Figure 1 Differential scanning calorimetry exothermic curves of (a) E41, (b) the E41/DA blend (molar ratio: 1/1), (c) the E41/NR blend (molar ratio: 1/1), (d) the E41/NR/DA blend (molar ratio: 1/1/1) and (e) BZ (note: the endothermic peaks in curve b and d correspond to the volatilization of DA). A full color version of this figure is available at *Polymer Journal* online.

cured BZ/ER blends with a different ER content or M_n was investigated, and the results are shown in Figure 2. PBZ/ER blends with a low M_n of ER (E11 is shown here as an example) were transparent over a large range of ER compositions, indicating that homogeneous structures were obtained in PBZ/ER blends if the M_n of ER was low, which might be ascribed to the unavoidable copolymerization between BZ and ER. However, PBZ/ER blends with a higher M_n of ER (E04 and E05) gradually turned opaque when decreasing the ER content from 40 wt% to 10 wt%.

From the above result, we can see that phase separation can take place in PBZ/ER blends if the M_n of ER increases to 4370 g mol^{-1} before the polymerization of the BZ resin. In addition, increasing the M_n of the ER resin ($\geq 4370 \text{ g mol}^{-1}$) and decreasing the content of ER ($\leq 10 \text{ wt\%}$ for BZ/E05 blends and $\leq 30 \text{ wt\%}$ for BZ/E04 blends) is favorable for obtaining phase separation structures in BZ/ER blends.

In multiphase blending systems, the opaque appearance implies the existence of heterogeneous structure. However, that does not indicate that transparent appearance is homogeneous, as there are other factors that can influence the final transparency. Of these factors, the most important is the degree of phase separation: the larger the degree of phase separation, the more opaque the blend tends to be. For poor phase separation systems, because the refractive index difference between two phases is small, the blend appears much more transparent. In these cases, the turbidity observation was limited to judging phase separation. Therefore, more characterization methods, such as DMA and SEM, were used to further estimate the phase separation of BZ/ER blends.

Relaxation behavior

DMA is another method that is widely used to characterize the phase separation of blending system.^{11,38} The relaxation behaviors of PBZ blends with 10 wt%, 30 wt% and 40 wt% of ER are shown in Figures

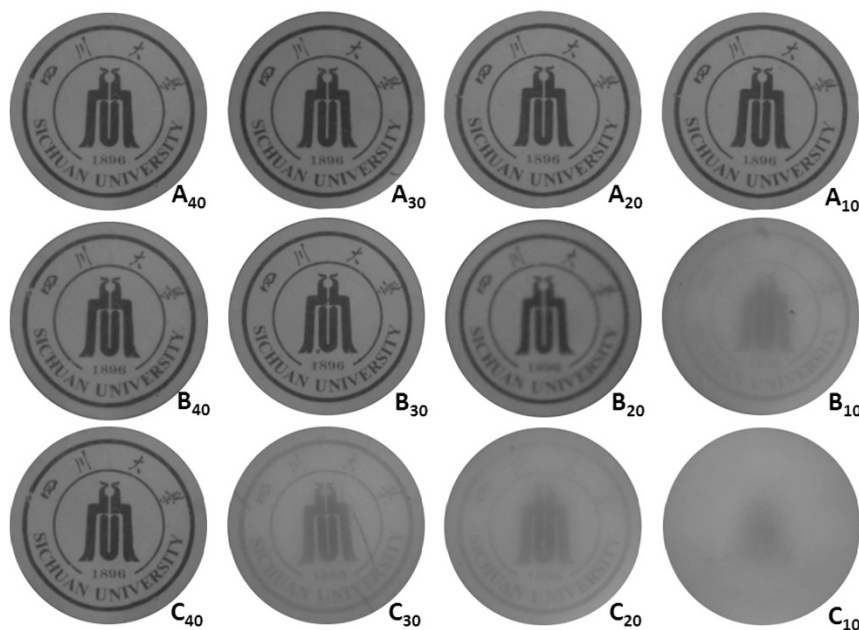


Figure 2 Photographs of the PBZ/ER blends with different contents of E11 (A), E05 (B) or E04 (C) after curing at $130^\circ\text{C}/2 \text{ h} + 150^\circ\text{C}/10 \text{ h}$. (Footnotes 40, 30, 20 and 10 represent the weight fraction of ER in BZ/ER blending systems; the badge printed with 'Sichuan University' was placed at the bottom of the molds to act as the reference for turbidity observations.) A full color version of this figure is available at *Polymer Journal* online.

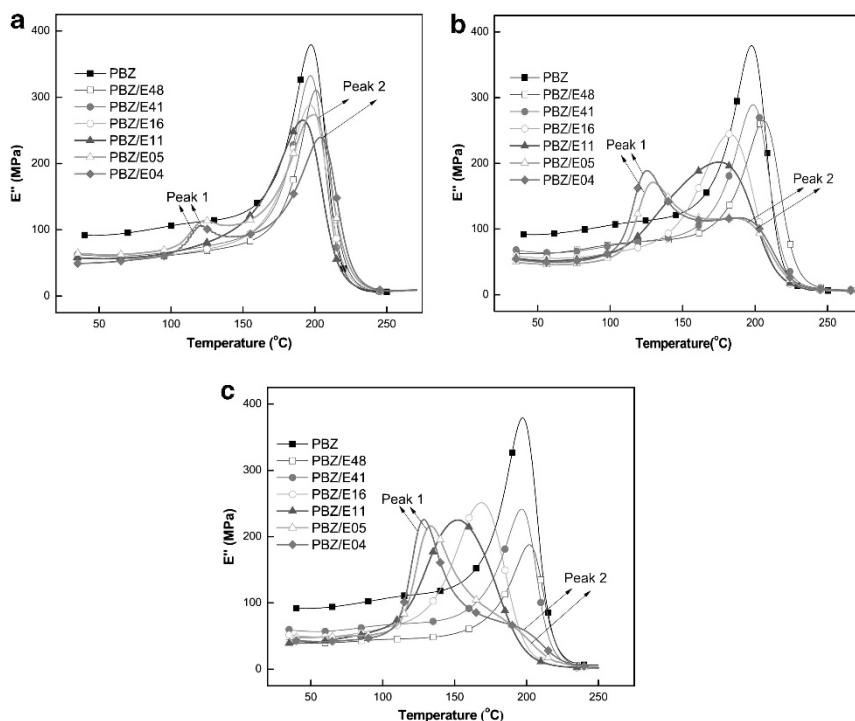


Figure 3 The plots of loss modulus (E'') vs temperature for different PBZ/ER blends with 10 wt% (a), 20 wt% (b) and 40 wt% (c) of ER after curing at 130 °C/2 h + 150 °C/10 h + 170 °C/2 h + 200 °C/2 h. A full color version of this figure is available at *Polymer Journal* online.

Table 2 Thermomechanical properties of PBZ/ER blends

Systems ^a	10 wt% ^b		30 wt% ^b		40 wt% ^b	
	T_g (°C)	$W_{1/2}$ (°C) ^c	T_g (°C)	$W_{1/2}$ (°C) ^c	T_g (°C)	$W_{1/2}$ (°C) ^c
PBZ	197.3	34.4	197.3	34.4	197.3	34.4
PBZ/E48	208.9	27.7	205.9	38.4	202.8	33.8
PBZ/E41	202.4	28.1	198.6	37.0	196.6	35.9
PBZ/E16	196.9	38.4	182.3	50.5	169.0	46.0
PBZ/E11	191.5	47.0	175.8	51.2	125.3	59.0
PBZ/E05	126.1/205.5	—	129.7/190.5	—	133.4/189.7	—
PBZ/E04	122.4/205.9	—	125.4/191.6	—	128.6/190.1	—

Abbreviations: BZ, benzoxazine; DMA, dynamic mechanical analysis; PBZ, polybenzoxazine.

^aThe data were obtained from the DMA experiments.

^bThe weight fraction of ER in BZ/ER blends.

^cHalf-peak breadth of the relaxation peak.

3a–c, respectively. More detailed information about the relaxation behavior of PBZ/ER blends is summarized in Table 2. Over a wide range of temperatures (100–250 °C), only one relaxation peak was observed for PBZ blends with E48, E41, E16 or E11, which corresponded to the glass transition temperature (T_g) of the PBZ/ER copolymer network. With the increase of the Mn of ER, the relative molar content of epoxy groups is reduced, and the Mn between two adjacent crosslinking points is increased. Correspondingly, the cross-linking density of those blends decreased, and the mobility of the segment, as well as the irregular degree of the chain segments, increased. As a result, the T_g of the PBZ/ER blends

decreased and the half-peak width ($W_{1/2}$) increased with the Mn of ER (Table 2). Among the four PBZ/ER blends, a sudden increase of $W_{1/2}$ was observed in the PBZ/E11 and PBZ/E16 systems, especially when the ER content was 40 wt%. Ishida and Lee³⁹ believed that the sudden increase of the $W_{1/2}$ might imply the existence of the phase separation structure. However, in our systems, no apparent phase separation was observed in the PBZ/E16 and PBZ/E11 systems, which was consistent with the result of turbidity measurements and would be confirmed again by the result of morphology.

For BZ/E05 and BZ/E04 blends, two distinct relaxation peaks were observed in all of the three compositions (Figures 3a–c), and the relaxation peak at elevated temperature was independent of the Mn of ER (Table 2), indicating the existence of two phase structures. However, there was a minor discrepancy with the result of turbidity observations, which showed that homogeneous structures were obtained in the BZ/E05 (or BZ/E04) system when the ER content was >20 wt% (or 30 wt%). This disagreement may be caused by the fact that using the turbidity observation method to judge phase separation is limited if the refraction index of each phase is well matched or if the phase domain size is much smaller than the wavelength of visible light.⁴⁰

After in-depth observation of the loss modulus curves of BZ/E05 and BZ/E04 systems (Figure 3), we found that the ER content could influence the two relaxation peak positions and their relative heights. To make clear the relationship between those changes and the ER content, the relaxation behaviors of PBZ/E04 blends with different contents of E04 (≤ 40 wt%) were investigated. As shown in Figure 4, two relaxation peaks were observed for all compositions. Compared with the relaxation peak of PBZ shown in Figure 3, the relaxation peak at elevated temperature range (peak 2) should correspond to the T_g of the BZ-rich phase (T_{g2}), and the relaxation peaks at the lower

temperature range (peak 1) should correspond to the T_g of the ER-rich phase (T_{g1}). With the increase of E04 content, the height of peak 1 increased but that of peak 2 decreased; meanwhile, the two peaks shifted inward, implying that the E04-rich phases gradually changed from dispersed phases to continuous phases³⁸ and that the separation degree gradually became small.¹¹ This is because the viscosity of the system and the proportion of copolymerization between the ER and

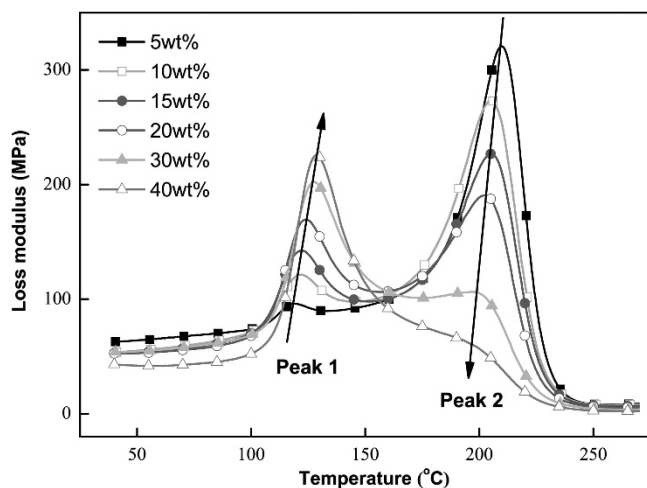


Figure 4 Loss modulus curves of PBZ/E04 systems with different contents of E04. A full color version of this figure is available at *Polymer Journal* online.

BZ resin increased with the increase of E04 content, which prohibited the diffusion of the BZ resin.

Morphology

SEM measurements can directly give information on phase morphology and phase domain size and have thus been widely used to observe the phase separation. The morphologies of the BZ/E04 blends with different E04 contents were studied by SEM. All of the samples were prepared using the same curing procedure: 130 °C/2 h + 150 °C/10 h, under which conditions the phase structure could be fixed as discussed in Supplementary Figure S1. To better investigate the phase structure of the cured blends, the sample surface was etched before SEM observation. Fortunately, with the above curing condition, the PBZ-rich phase gelled and was insoluble in acetone. In the E04-rich phase, because the polymerization between the epoxy group and phenolic OH of the PBZ resin was minimal, owing to the high viscosity and the lower molar content of the epoxy groups of E04, the E04-rich phase was still soluble in acetone.

As shown in Figure 5, when the E04 content was <20 wt%, the sea-island structure with submicron-sized (0.3–0.8 μm) particles (E04-rich phase) evenly dispersed in the PBZ matrix was observed (a and b). When the content of E04 increased to 30 wt%, a ribbon weave-like bicontinuous structure was obtained (c), which was different from the classic bicontinuous morphology of the TP-modified TS resin system.⁴¹ With a continued increase of the E04 content to 40 wt%, a blurry phase-inverse structure, where a continued E04-rich phase enwrapped with a nano-sized (80 nm) BZ-rich phase (that is, spherical ‘nodulus’) was observed (d).

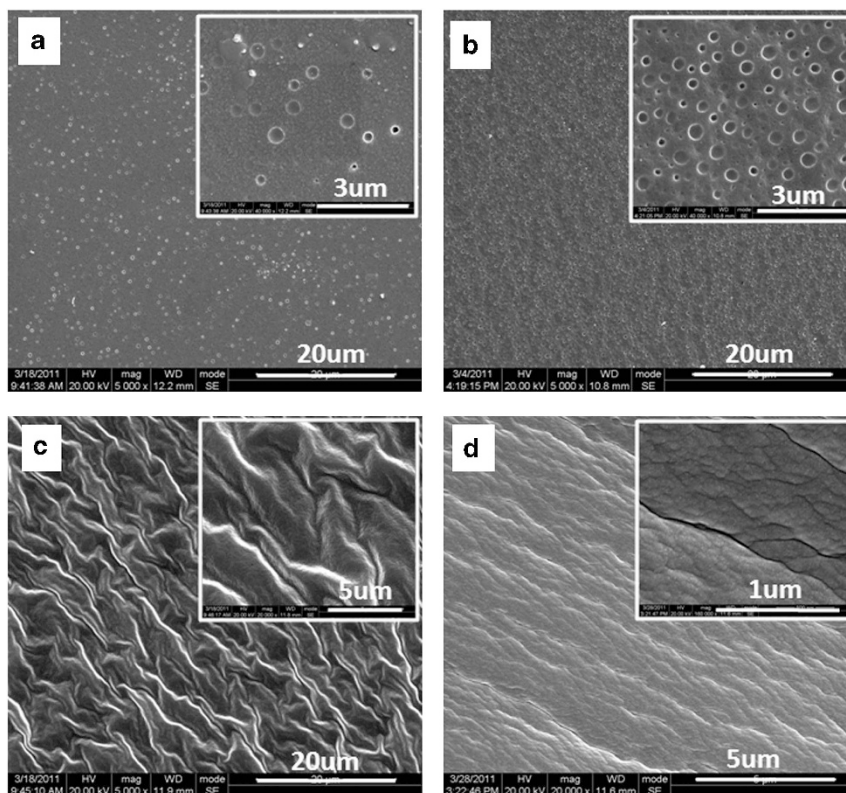


Figure 5 SEM morphologies of the BZ/E04 blend with 10wt% (a), 20 wt% (b), 30 wt% (c) and 40 wt% (d) of E04 after curing at 130 °C/2 h + 150 °C/10 h. (The sample surface was etched with acetone for 5 h before observation.)

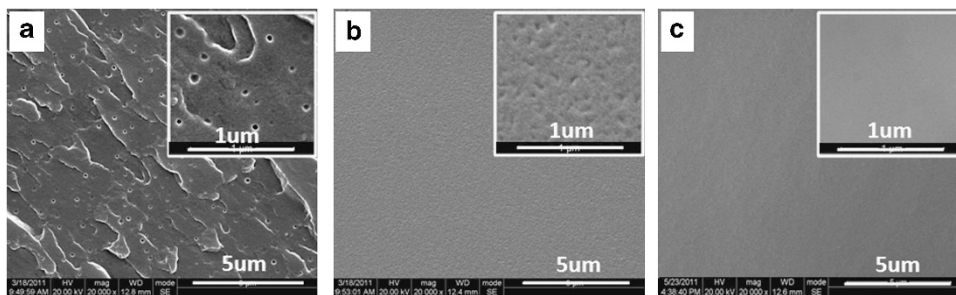


Figure 6 SEM morphologies of PBZ/E05 (a, b) and PBZ/E11 (c) blends after curing at 130 °C/2 h + 150 °C/4 h; a and c: 10 wt% ER; b: 20 wt% ER. (The sample surface was etched with acetone for 5 h before observation.)

As for PBZ/E05 blends (Figure 6a), when the content of E05 was 10 wt%, sea-island structure with the dispersed size of 0.1–0.2 μm could be observed. With an increase of the E05 content to 20 wt%, only tiny (70 nm) and anomalous etched marks were observed in a partial enlargement of the micrograph (Figure 6b). For systems of PBZ blending with E48, E41, E16 or E11, no phase separation was observed by SEM, even when the ER content was as low as 10 wt% (BZ/E11 is shown in Figure 6c as an example).

From the above SEM observations, we can see that the difference of the Mn (dynamic asymmetry) between BZ and ER has an important role in the phase separation of BZ/ER blending systems and that the relative content of ER has an important influence on the phase morphology and phase domain size. By increasing the ER content in the blend, the ER-rich phase gradually transformed from a dispersed phase to a continuous phase. If the dispersed phase was an ER-rich phase, the phase domain size increased with the increasing ER content, whereas if the dispersed phase was PBZ-rich, the phase domain size decreased sharply.

CONCLUSION

In BZ/ER blends, if BZ can polymerize before ER, the phenolic OH produced by the ring-opening polymerization of the BZ resin can copolymerize with the epoxy group of the ER resin immediately, which is unfavorable for the sequential growth of molecular chains of BZ and ER. Instead, if ER can polymerize preferentially, the copolymerization between BZ and ER is suppressed as a consequence of the lack of a phenolic OH, and the dynamic asymmetry between ER and BZ could thus be enlarged, both of which are theoretically favorable for phase separation. The influences of the Mn of ER, as well as the ER content, on the phase separation of BZ/ER blends were studied using turbidity observations and DMA and SEM measurements. The results indicate that if the Mn of ER can exceed 4370 g mol⁻¹ before the BZ resin starts to polymerize, phase separation could take place, and the degree of phase separation could be enlarged by increasing the Mn of ER or reducing the relative content of ER. By varying the ER content, different morphologies, such as sea-island structure, ribbon weave-like bicontinuous structure and inverted-phase structure, could be observed. This research is expected to provide guidance for phase separation in BZ/ER blending systems.

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