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A novel benzoxazine/cyanate ester blend with sea-island phase structures

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Abstract

A novel cardanol-based benzoxazine (C-BOZ)/bisphenol A dicyanate ester (BADCy) blend with sea-island phase structures was successfully prepared via reaction-induced phase separation. The introduction of long-chain alkyl group on the benzene ring significantly enlarged the thermodynamic differences between C-BOZ and BADCy. With the increase of BADCy, the Flory-Huggins interaction parameter (χ) of the blend decreased. By adjusting the ratio of the two components, sea-island phase separations were observed in C-BOZ/BADCy blends during the curing process. The dispersed phase was C-BOZ rich phase while the matrix was the crosslinked network composed of triazine rings and ring-opened C-BOZ. On the DMA curves of 9/1, 8/2 and 7/3 cured blends, there were two distinct T_gs. But with the increase of BADCy, phase separation extent was reduced. When the ratio reached to 5/5, there was only one T_g because the viscosity of the blend was too high to occur phase separation.

Keywords: Benzoxazine; Cyanate ester; Reaction-induced phase separation; sea-island phase structures

1. Introduction

Polybenzoxazine (PBOZ) is a class of high performance polymer possessing superior mechanical properties, high temperature stability and high glass transition temperature (T_g) [1-2]. And cyanate ester (CE) is a well-known thermosetting resin with good thermal properties, low dielectric loss and high T_g [3-6]. Due to their prominent processability and excellent thermal and mechanical properties, cyanate ester modified benzoxazine blending systems have attracted more and more attention in a wide range of application areas [7-10]. However, because of the highly crosslinked structures, BOZ/CE blending systems are brittle materials that show unsatisfied toughness and elongation at break. Therefore, effective toughening strategies are of high interest to enable powerful new applications.

Of various toughing methods, reaction induced phase separation (RIPS), which is designed as the uniform precursor system undergoing a phase separation into a two separated phase structures during the development of the curing process, is the most effective one [11,12]. This method can enhance the fracture toughness of material notably without sacrificing its desirable properties (e.g. glass transition temperatures (T_g) and modulus), therefore has been widely used in the toughening modification of thermosetting (TS) resin with thermoplastic (TP) resin, such as polyether imide or ployether sulfones modified ER, BOZ, cyanate ester, and bismaleimide resins [13-21]. However, the improved toughness resulting from this method is accompanied by a slight decrease in the quality of the thermal properties and a consequent loss in processability due to the poor thermal properties and high molecular weight of TP. Using one type of TS to improve the toughness of another type of TS is a new idea.

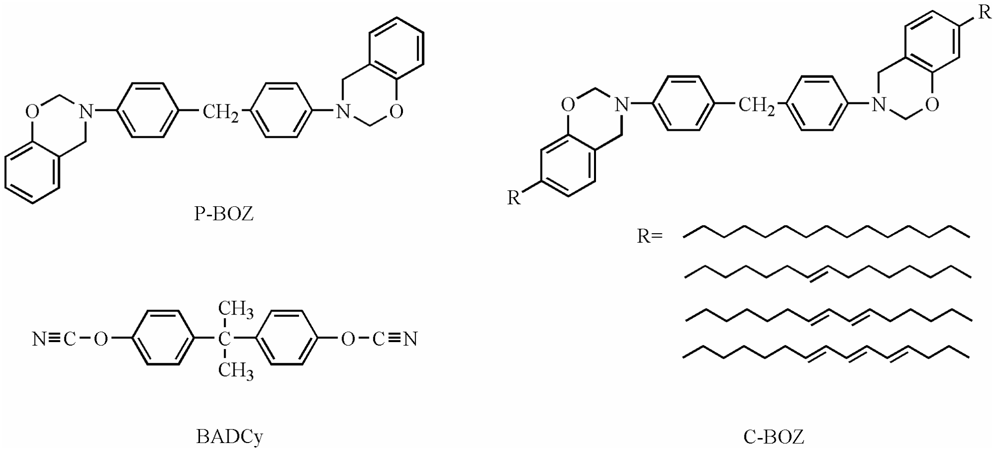
Although the RIPS method is very effective, it is not easy to be realized in TS/TS blending system. According to the Gibbs free energy theory ($\Delta G = \Delta H\text{-}T\Delta S$, where, ΔG represents the free energy of mixing; ΔH represents the enthalpy of mixing which can be characterized by Flory-Huggins interaction parameter χ; and ΔS represents the entropy of mixing) [11, 22], there are at least three factors that make it much more difficult to get phase separation structures in BOZ/CE blends than in the reported RIPS systems [23]. Firstly, the χ value for most of BOZ/CE blends is low estimated according to the Flory-Huggins theory and Hildebrand formula. Secondly, the two components have initially similar low molecular weights, so the contribution of ΔS to ΔG is huge. Thirdly, the copolymerization between the two components always lead to the formation of a crosslinked network composed of triazine rings as part of the polybenzoxazine matrix [7]. Therefore it is still a challenge to obtain micro-sized phase structures in BOZ/CE blends. Until now, there is no report on the phase separation in BOZ/CE blends.

Following these studies, here we designed and prepared a novel BOZ/CE blend with cardanol-based benzoxazine. Based on the theories of RIPS, the phase structures of BOZ/CE blend during the development of the curing process were investigated.

2. Experimental

2.1. Materials

The following chemicals: aqueous formaldehyde solution (13.4 mol/L), 4, 4'-diaminodiphenyl methane, toluene, sodium hydroxide and ethyl alcohol were purchased from the Chengdu Kelong Chemical Reagents Corp. (China). Cardanol was provided by HDSG Beijing Technology Co., Ltd. Phenol-based benzoxazine monomer (P-BOZ) was provided by our laboratory. Bisphenol A dicyanate ester (BADCy) was from Wuqiao resin plant. All reagents were used as received.



Scheme 1. Structures of P-BOZ, BADCy and C-BOZ.

2.2. Synthesis and Characterization of cardanol-based benzoxazine (C-BOZ)

Stoichiometric amounts of 4, 4'-diaminodiphenyl methane (0.2 mol), aqueous formaldehyde solution (0.8 mol), and cardanol (0.4 mol) were dissolved with toluene (50 mL) in a 250 mL three necked flask. The mixture was stirred and refluxed at 80 ^{o}C for 5 h. Then, the product was washed with 1 N sodium hydroxide solution and cooled overnight. The product was filtrated, washed with ethyl alcohol, and dried in vacuum drying oven. A brownish red powder was obtained finally.

Melting point: 95 ^{o}C; IR (KBr): 2921, 2851 (vs, ν_s(-CH$_2$)), 960 (s, oxazine ring).

2.3. Preparation of the samples

The thermosetting blends of C-BOZ and BADCy of different ratios were prepared by melting. The cured samples for DMA experiment were obtained by curing the melted resin in a rectangular mold. The curing schedules of the blends was determined as following: 120 ^{o}C/10h, 140 ^{o}C/2h, 180 ^{o}C/2h and 210 ^{o}C/2h.

2.4. Characterization

Curing behavior was studied by differential scanning calorimetry (DSC) and Fourier transform-infrared spectroscopy (FT-IR), which were performed on TA Instrument DSC-Q20 and Nicolet 5700 FT-IR spectrometer, respectively. The thermal properties of the cured casts were obtained by using TA instruments DMA Q800 dynamic mechanical analyzer (DMA) with sample dimensions of 30 mm ×10 mm × 3 mm in three point bend mode from 40 to 350 ^{o}C with a heating rate of 5 ^{o}C/min and frequency of 1 Hz. The morphologies of the blends of various cure extents were observed by scanning electron microscope (SEM) Philip XL-30 FEG. The samples were fractured under cryogenic conditions using liquid nitrogen. All the fractured surfaces were coated with gold by vapor deposition using avacuum sputterer before examined by SEM.

3. Results and Discussion

3.1. The morphology characteristics of cured blends

P-BOZ/BADCy and C-BOZ/BADCy blends of four ratios, 9/1, 8/2, 7/3 and 5/5, were melted at 120 ^{o}C. Before the curing reaction, all the blends were miscible and presented a transparent yellow color. After the blends were cured at 120 ^{o}C for 10 h, P-BOZ/BADCy blends were still transparent, but C-BOZ/BADCy blends of 9/1, 8/2 and 7/3, except 5/5, became opaque, which meant the occurrence of phase separation in the three systems. Then the fractured surfaces of the three blends were investigated by SEM for the phase structures. As shown in Fig. 1, there were no phase separation in 5/5 blend (a_1, a_2 and a_3), but a typical sea-island phase structure appeared in 8/2 blend and on the surface of island phase, there were some white branched structures (c_2). But the phase morphology of 7/3 and 9/1 blends were not obvious (b_2 and d_2). Then the three blends were etched in acetone for 0.5 h. After etching, the island phases of 8/2 blend changed to holes with the disappearance of the branched structures indicating that the island phases were etched away (c_3). In 9/1 and 7/3 blend, the island-like holes were also observed (b_3 and d_3), which suggested the sea-island phase separation occurred in the two blends as well. Meanwhile, it was easy to find that the phase size of C-BOZ/BADCy blends decreased with the increase of BADCy content.

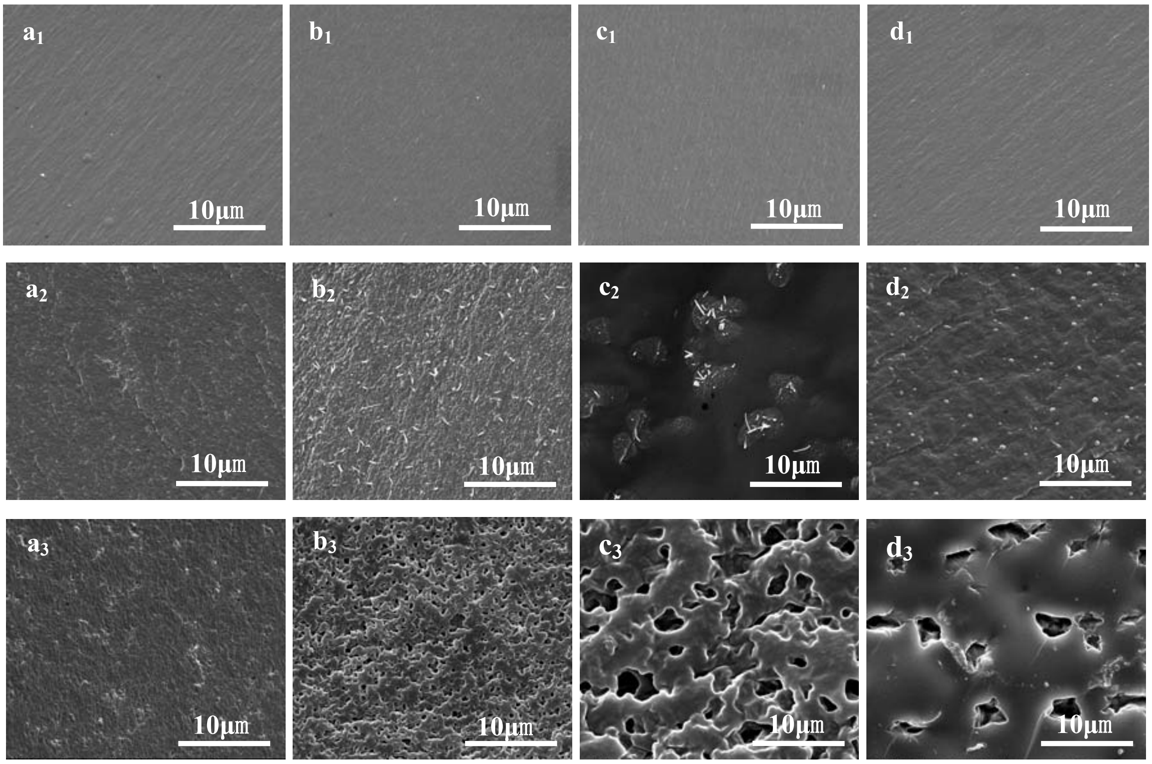


Fig. 1. SEM phase morphology of C-BOZ/BADCy blends: the uncured, cured at 120 °C for 10 h and etched in acetone for 0.5 h of 5/5 blend (a_1, a_2 and a_3), 7/3 blend (b_1, b_2 and b_3), 8/2 blend (c_1, c_2 and c_3) and 9/1 blend (d_1, d_2 and d_3).

3.2. The components of each phase

On the DSC curve of 8/2 blend, there were two obvious exothermic peaks (Fig. 2). According to our previous researches on the benzoxazine/cyanate ester blend [7], the first exothermic peak corresponds to the polymerization of cyanate ester while the second exothermic peak corresponds to the self-polymerization of benzoxazine (Scheme 2). In Fig. 2, the initial reaction temperature of the first peak was about 120 °C, which meant the polymerization of BADCy had catalyzed by the ring-unclosed or ring-opened C-BOZ at this time.

Then the etching solution and the insoluble of 8/2 blend were tested by the infrared spectra respectively (Fig. 3). In the IR spectrum of the etching solution, the peak of oxazine ring at 960 cm^{-1} was observed, but the characteristic peaks of cyano group at 2237 cm^{-1} and 2270 cm^{-1} were not obvious. However, in the IR spectrum of the insoluble, except the peak of oxazine ring, the significant characteristic peaks of triazine ring at 1575 cm^{-1} and 1367 cm^{-1} was also observed.

From the results of DSC and FT-IR tests, it could be concluded that the insoluble should be poly(BADCy) while the etched part corresponded to unpolymerized C-BOZ. Therefore, the dispersed phase was C-BOZ-rich phase, and the matrix was a crosslinked network composed of triazine rings and ring-opened C-BOZ. The branched structures in Fig. 1 b_2 might be due to the re-cooled recrystallization of C-BOZ.

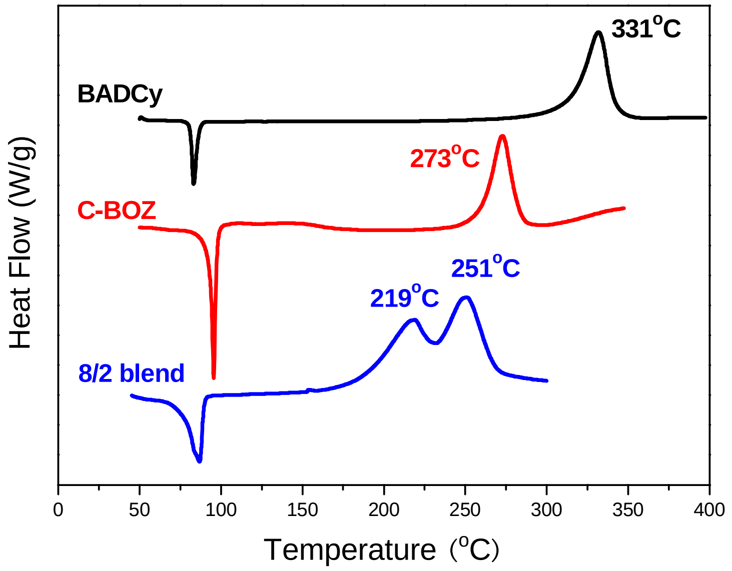
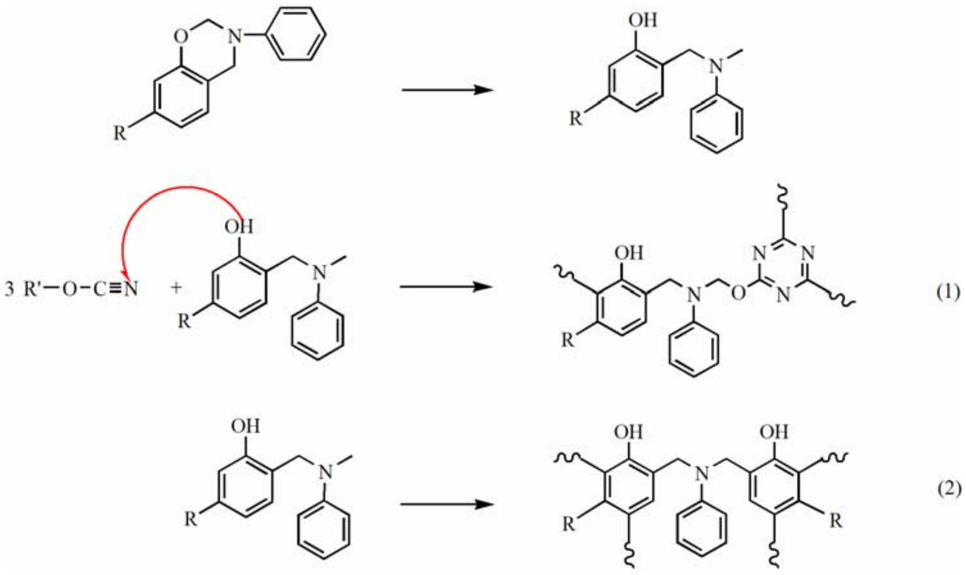


Fig. 2. DSC curves of BADCy, C-BOZ and 8/2 blend.



Scheme 2. The reactions of copolymerization of C-BOZ and BADCy: (1) the polymerization of cyanate ester catalyzed by the ring-opened benzoxazine; (2) the self-polymerization of benzoxazine.

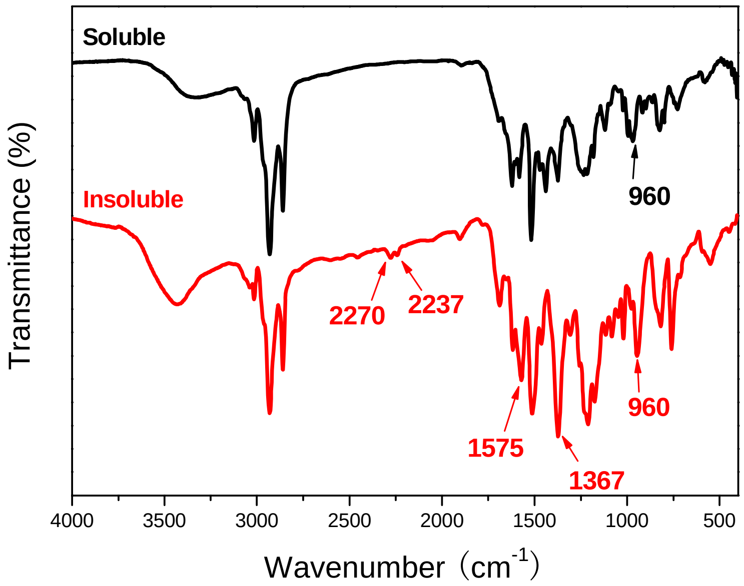


Fig. 3. FT-IR spectrum of the acetone soluble and the insoluble of 8/2 blend.

3.4. Dynamic mechanical properties of samples

After cured at 120 °C for 12 h, the phase separated blends were further cured at 140°C, 180°C and 210 °C. In Fig. 4, BADCy had completely polymerized with no characteristic peaks of cyano group at 2237 cm^{-1} and 2270 cm^{-1} after cured at 140 °C for 2h. At 180°C, the peak of oxazine ring at 960 cm^{-1} disappeared, which suggested C-BOZ had self-polymerized. Finally, there was almost no change in the infrared spectrum at 210 °C with the final formation of a stable crosslinking network.

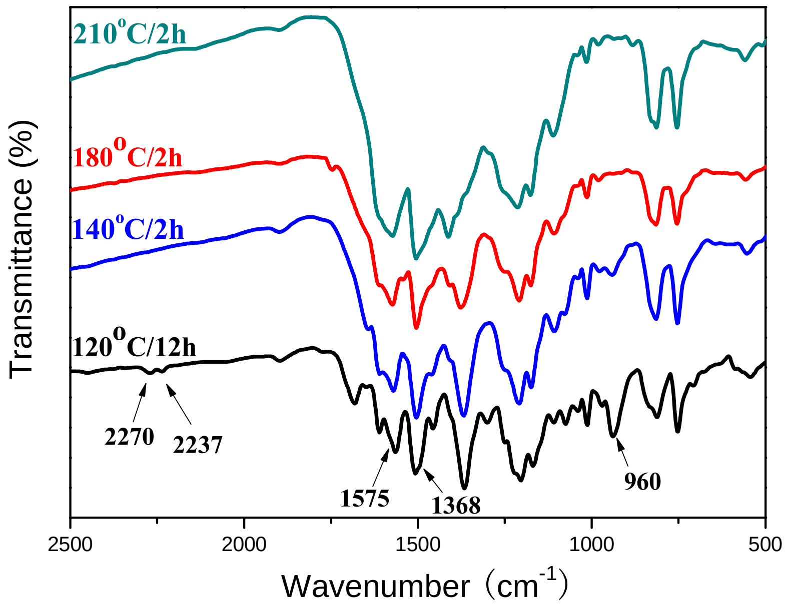


Fig. 4. FT-IR spectrum of the 8/2 blend cured at 120°C, 140°C, 180°C and 210 °C.

A dynamic mechanical analyzer (DMA) can not only be used to investigate the mechanical properties, but it is also sensitive to the phase separation of blends. In order to further confirm the phase separation of cured samples, a DMA was used. The glass transition temperature (T_g) is defined as the peak temperature on a tan δ curve. The peak numbers, peak height and the half peak width can reflect the degree of phase separation, crosslink density and amount of movable chain segments. DMA results of the completely cured samples were shown in Fig. 5. Both poly (C-BOZ) and poly (BADCy) have only one relaxation peak of glass transition at 100 °C and 324 °C, respectively. Different with them, most of poly(C-BOZ/BADCy) blends have two distinct relaxation peaks (Table 1). Compared with the relaxation peak of poly(C-BOZ) and poly (BADCy), the peak at lower temperature corresponded to the T_g of poly(C-BOZ)-rich phase while the peak at higher temperature corresponded to the T_g of poly(BADCy)-rich phase.

In Fig. 1, the phase size of 9/1 blend was largest, indicating the highest degree of phase separation. So, the T_gs of the two phases neared to the ones of each homopolymer. With the increase of BADCy, the phase size of 8/2 blend became smaller with the decrease of the degree of phase separation, which led the T_gs of the two phases got close to each other. In 7/3 blend, the degree of phase separation further reduced so that the T_g of poly(BADCy)-rich phase was not obvious. When the ratio reached to 5/5, there was only one T_g on the DMA curve because the phase separation could not occur.

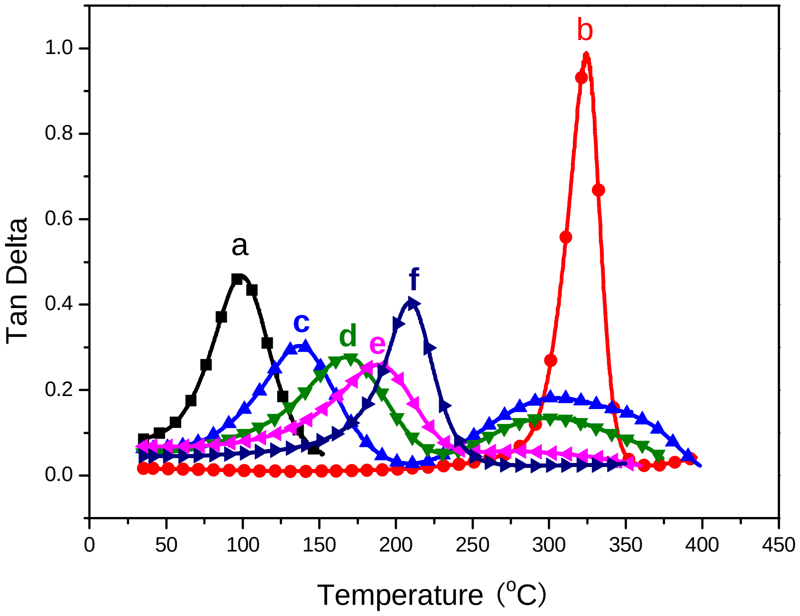


Fig. 5. Tan δ curves of the cured samples. (a) Poly(C-BOZ); (b) Poly(BADCy); (c) 9/1 blend; (d) 8/2 blend; (e) 7/3 blend; (f) 5/5 blend.

Table 1. T_gs of the cured samples.

	Poly(C-BOZ)	Poly(BADCy)	9/1 blend	8/2 blend	7/3 blend	5/5 blend
T_g (°C)	100	324	137/305	167/301	189/275	209

3.4. Theoretical analysis of forming phase separation

Due to the excellent designability of benzoxazine, we introduced a long-chain alkyl group into its structures to synthesize cardanol-based benzoxazine. Based on the Flory-Huggins theory, which is a well-known thermodynamic equation for mixing and phase separation, the change in the free enthalpy of mixing was defined as below.

$$\Delta F_M = -RT\left(n_a \ln\phi_a + n_b \ln\phi_b + \chi_1\phi_a\phi_b\right) \quad (1)$$

Where *R* and *T* are the gas constant and temperature respectively. n_i and ϕ_i are the number of moles and volume fractions of components a and b, and χ_1 is the Flory-Huggins interaction parameter. The Flory-Huggins interaction parameter, χ_1, can be estimated by the method developed by Hilderbrand and Scott in Eq. (2), which is applicable at room temperature.

$$\chi_1 = \frac{V_{\mathrm{ref}}}{RT}\left(\delta_{\mathrm{i}} - \delta_j\right)^2 \tag{2}$$

Where R is the gas constant, T is the absolute temperature, δ_i is the solubility parameter and V_{ref} is the reference volume. The solubility parameters δ_i and δ_j are determined by using group contribution methods that involve the summation of individual functional group contributions for different components of structural groups. The reference volume V_{ref} is calculated as the mean value of the molar volume of repeating units for different polymers, as follows in Eq. (3).

$$V_{ref} = M_a\phi_a/\rho_a + M_b\phi_b/\rho_b \tag{3}$$

Where M_a and M_b are the molar masses of the different components; ρ_a and ρ_b are the densities of the different components, which are measured following GBT15223-2008.

In practice, the interaction parameter, χ, is expected to decrease with increasing temperature [24], through a relationship of the type χ = A + B/T, which means that the value of χ at 120 ^{o}C is lower than the value at room temperature.

The second derivative of the free energy gives the spinodal and consequently the critical interaction parameter for phase separation, which is expressed as Eq. (4).

$$\chi_{1c} = \frac{1}{2}\left(\frac{1}{x_{\mathrm{a}}^{\frac{1}{2}}} + \frac{1}{x_{\mathrm{b}}^{\frac{1}{2}}}\right) \tag{4}$$

Where x_a and x_b represent the degree of polymerization (actual number of repeating units) of a and b. Notice that the value of χ_1 decreases with increasing molecular weight. The blends are miscible if $\chi_1 < \chi_{1c}$. If χ_1 is considerably greater than the critical value, then blends are immiscible. If the value of χ_1 is slightly greater than the critical value, then the blends are partially miscible. So long as the measured χ and the corresponding critical values are calculated based on the same reference volume, comparing the measured χ_1 with the critical value would provide a good indication of the degree of blend miscibility.

In this paper, the thermoset monomers can be simplified as a component or a solvent at the early stage of phase separation, so before phase separation x_a and x_b are equal to 1. After the reaction of the components reaches high conversion, the degree of polymerization becomes approximately unlimited. So the value of χ_{1c} is limited at (0, 1).

The Flory-Huggins interaction parameter (χ) of different blends were showed in Table 1. It is can be seen that, the calculated χ value of C-BOZ/BADCy at room temperature was much higher than that of P-BOZ/BADCy. In general, the interaction parameter (χ) of the two components is higher, they are easier to phase separate. However, P-BOZ has the same structures with C-BOZ except the long-chain alkyl group. So, it can be deduced that the introduction of long-chain alkyl group significantly enlarged the thermodynamic differences between the two components. And with the decrease of BADCy, the χ of the blend increased, which indicated the greater possibility of phase separation.

Table 1. The Flory-Huggins interaction parameter (χ) of different blends.

	χ(P-BOZ/BADCy)	χ(C-BOZ/BADCy)
9/1	0.54	13.39
8/2	0.52	12.31
7/3	0.5	11.23
5/5	0.46	9.07

3.4. Formation progress of sea-island phase structures

In addition to the thermodynamic factors, due to the complexity of the binary blending system, phase separation and phase morphology may be influenced by a lot of other factors, such as the composition ratios, temperatures, the competition between the kinetics of phase separation and crosslink chemical reaction, *et al*. According to the Gibbs free energy theory and our present results, the formation of sea-island phase structures in the C-BOZ/CE blend can be explained as follows: at the early stage of curing, firstly partial oxazine rings of C-BOZ opened to copolymerize with BADCy and catalyze the self-polymerization of BADCy, and then a crosslinked network composed of triazine rings formed gradually while only a small amount of C-BOZ was polymerized, and the rest of them were still in the state of low molecular weight. Hence the preferential polymerization of BADCy increased the dynamic asymmetry (difference of molecular weight, viscosity, etc.) between BADCy and C-BOZ. Then the compatibility of poly(BADCy) with the surrounding C-BOZ resins decreased. Theoretically, the increase of molecular weight owing to the polymerization of BADCy resulted in the significant decrease of ΔS, which pushed the increase of ΔG (during this process, the ΔH mainly associated with chemical structures was almost unchanged). When $\Delta G > 0$, phase separation occurred. Then due to the viscoelastic property of polymer, the crosslinked network tended to shrink to exclude the entrapped C-BOZ, which led to the formation of micro-sized sea-island structures. With the increase of BADCy, the viscosity of the blend increased so quickly that the separation of C-BOZ from the crosslinked network became difficult, so the degree of phase separation decreased.

When the ratio of the two components was equal, the viscosity was too high to occur phase separation. As the curing reaction going on, phase separation was gradually suppressed and the phase morphology was fixed due to the vitrification or chemical gelation.

4. Conclusion

The introduction of long-chain alkyl group on the benzene ring significantly enlarged the thermodynamic differences between C-BOZ and BADCy. With the increase of BADCy, the Flory-Huggins interaction parameter (χ) of the blend decreased. By adjusting the ratio of the two components, sea-island phase separations were observed in C-BOZ/BADCy blends during the curing process. The dispersed phase was C-BOZ rich phase while the matrix was the crosslinked network composed of triazine rings and ring-opened C-BOZ. On the DMA curves of 9/1, 8/2 and 7/3 cured blends, there were two distinct T_gs. But with the increase of BADCy, phase separation extent was reduced. When the ratio reached to 5/5, there was only one T_g because the viscosity of the blend was too high to occur phase separation.

Acknowledgements

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