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Influence of intramolecular specific interactions on phase behavior of epoxy resin and poly(ε-caprolactone) blends cured with aromatic amines

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Abstract

Two aromatic amines were used as the curing agents to prepare the thermosetting blends of epoxy and poly(ε-caprolactone) (PCL). When cured with 4,4′-methylenebis(2-chloroaniline) (MOCA), the thermosetting blends are miscible in the amorphous state in the entire composition, which was evidenced by the behavior of single, and composition-dependent glass transition temperatures (T_g's) in terms of thermal analysis. Fourier transform infrared spectroscopy (FTIR) showed that there are the intermolecular specific interactions (viz. hydrogen bonding) between the component polymers. However, the 4,4′-diaminodiphenylsulfone (DDS)-cured epoxy forms the immiscible blends with PCL. The blends displayed a typical reaction-induced phase separation morphology. The phase behavior seems to be more than the expected since it was ever proposed that there would be the intermolecular specific interactions between amine-cured epoxy and PCL, which would fulfill the miscibility of the systems. To interpret the phase behavior, we investigated that the miscibility and intermolecular specific interactions in the blends of model compounds and linear homologues of epoxy with PCL. It was observed that in MOCA-cured blends there were much stronger intermolecular specific interactions than in DDS-cured counterparts. The weaker intermolecular specific interactions between DDS-cured epoxy and PCL resulted from the formation of the intramolecular hydrogen bonding interactions within DDS-crosslinked epoxy, which were involved with the sulfonyl groups and the secondary hydroxyls. The intramolecular association could suppress the formation of the strong intermolecular hydrogen bonding interactions between carbonyls and hydroxyls of amine-cured epoxy, which are sufficient to fulfill the homogenization of the system during the in situ polymerization. Therefore, the presence of the intramolecular specific interactions between sulfonyl and hydroxyl groups was taken as the origin of phase-separated morphology for DDS-cured blends of epoxy with PCL.

Keywords: Epoxy; Poly(ε-caprolactone); Blends

1. Introduction

During the past decades, considerable progress has been made to understand the correlation between morphological structures and resulting properties of thermosetting polymer blends [1,2]. This progress is, in part, a consequence of the recognition of the importance of toughening mechanisms in thermosetting blends. The most of the previous studies have been focused on the formation mechanisms of various morphologies in thermosetting blends, to correlate with mechanical properties of materials. Nonetheless, miscibility and intermolecular specific interactions in the thermosetting blends have not been extensively investigated vis-à-vis in linear polymer blends. Compared with linear polymer blends, miscibility and intermolecular specific interactions of thermosetting blends could be much more complicated since the kinetic factors, curing processes and topological structure of thermosetting systems etc. are closely coupled with the thermodynamics of mixing.

Thermodynamically, the formation of crosslinked structure is unfavorable for the entropic contribution (ΔS_m) to the mixing free energy due to the infinitely large molecular weight of crosslinked component and as a consequence phase separation could occur owing to the endothermic enthalpy of mixing. Indeed, the most of thermosetting polymer blends found hitherto are immiscible unless there exist the favorable intermolecular specific interactions (e.g., hydrogen bonding), which affords the exothermic mixing

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(i.e., $\Delta H_m < 0$). It is generally proposed that the decrement of entropic contribution (ΔS_m) caused by the increase of molecular weight is the driving force of polymerization-induced phase separation in thermosetting polymer blends. Nevertheless, the intermolecular interactions could be significantly reduced due to the effect of crosslinking, e.g. steric shielding, the screening effect and chain connectivity resulting from the formation of the three-dimensional crosslinked network [3–6]. This factor can be taken as the effect of topological structure of thermosetting components on free energy of mixing (ΔG_m) since intermolecular interactions can be expressed as the enthalpy of mixing (ΔH_m). In the linear polymer blends, the intermolecular specific interactions (e.g., hydrogen bonding) can be utilized to enhance the miscibility of component polymers [7]. However, in thermosetting blends, the presence of functional groups capable of forming specific interactions unnecessarily means the formation of resulting homogeneous morphology of the blends since the elevated temperature at which curing reaction is carried out could significantly suppress the formation of efficient intermolecular specific interactions. As a result, the decrease in the entropic contribution to mixing free energy dominates the process of phase separation [8–10].

Epoxy resins are a class of important thermosetting polymers and much effort has been made to improve the toughness with rubber and thermoplastics [11–23]. Recently, the blends of epoxy blends with crystalline polymers have been reported [24–36]. For the blends of epoxy with poly(ε-caprolactone) (PCL), the miscibility and phase behavior of the systems were reported by several authors [24–32]. Noshay et al. [24] first reported the miscibility of anhydride-cured blends of epoxy and PCL with various molecular weights and they noted that there was a critical molecular weight for the miscibility. Clark et al. [25] investigated the differences in miscibility for both anhydride- and amine-crosslinked epoxy-PCL blends and the variation in their mechanical properties due to different miscibility. The miscibilization of amine-crosslinked blends has been ascribed to the formation of the intermolecular hydrogen bonding interactions between amine-cured epoxy and PCL. However, Chen and Chang [26] investigated the immiscibility of the blends when an aromatic amine, 4,4′-diaminodiphenylsulfone (DDS) was used as the curing agent. By means of optical and scanning electron microscopy, they found that the mechanisms of phase separation were binodal or spinodal decomposition depending on the PCL concentration in the blends. The phase behavior of DDS-cured blends behavior seems to be more than expected. Since it was proposed that there would be the intermolecular specific interactions in epoxy/PCL blends cured with amine curing agent, which are potential to fulfill the miscibility of the systems [24–32], why are the DDS-cured epoxy/PCL blends heterogeneous? Although a few authors [26,27] have presented some data to report the experimental facts, the lack of knowledge about the origin of the phase behavior leaves a substantial void in understandings the relationships between morphology and specific interactions.

The goal of this work is to evaluate the effect of the intramolecular specific interactions on phase behavior in the thermosetting blends of epoxy and PCL when amines are used as the curing agents. In this work, the thermosetting blends are prepared using two curing agents of aromatic amines, 4,4′-methylenebis(2-chloroaniline) (MOCA) and 4,4′-diaminodiphenylsulfone (DDS) under the identical curing condition. The phase behavior of both systems is compared on the basis of differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and scanning electronic microscopy (SEM). The model compounds and the linear homologue of epoxy polymers are used to investigate the differences in miscibility and intermolecular specific interactions for the two systems.

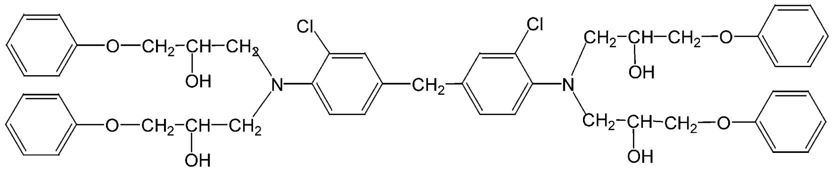
2. Experimental

2.1. Materials and preparation of samples

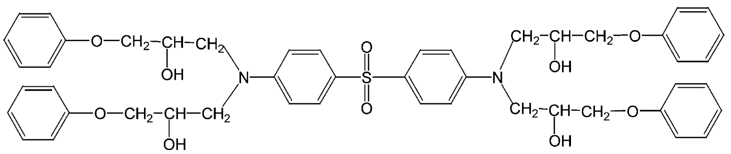
Diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight 185–210 was purchased from Shanghai Resin Co., China. The curing agents were 4,4′-methylenebis (2-chloroaniline) (MOCA) and 4,4′-diaminodiphenylsulfone (DDS), respectively, supplied by Shanghai Reagent Co., China. Poly(ε-caprolactone) (PCL) was obtained from Sigma Aldrich Co., USA. It has a quoted molecular weights of $M_n = 80{,}000$. Phenyl glycidyl ether (PGE) was of analytically pure grade, obtained from Shanghai Regent Co., China.

The low molecular model compounds for DDS (and/or MOCA)-cured epoxy (Scheme 1) were synthesized via the reactions of PGE with DDS (and/or MOCA). Typically, 9.0108 g (0.06 mol) of PGE and 24.8300 g of DDS (0.01 mol) were charged to a 200 ml three-necked flask equipped with a condenser and a mechanical stirrer at room temperature. The reactive system was heated up to 150 °C with vigorously stirring until DDS was fully dissolved. The reaction was allowed to perform at 150 °C for 10 h. The excessive PGE was distilled out under decreased pressure to afford transparent and viscous liquids. The products were subject to infrared and NMR characterization. For MOCA-type model compound, FTIR (cm^{-1}) with cast film onto KBr window: 3500 (O–H); ^{1}H NMR (chloroform-*d*, ppm): 7.28 (m, 8*H*), 7.12–6.90 (m, 12*H*), 6.87 (d, 4*H*), 6.67 (t, 2*H*), 4.07 (m, 8*H*), 3.96 (m, 8*H*), 3.78 (t, 2*H*), 3.47 (m, 4*H*), 3.26 (m, 4*H*). For DDS-type model compound, FTIR (cm^{-1}) with cast film onto KBr window: 3500 (O–H), 1296 (S=O), 1150 (S=O); ^{1}H NMR (chloroform-*d*, ppm): 7.70–7.52 (m, 4*H*), 7.27 (m, 8*H*), 7.02–6.84 (m, 12*H*), 6.75 (tetra, 2*H*), 6.51 (t, 2*H*), 4.30 (m, 8*H*), 3.96 (m, 8*H*), 3.61 (m, 4*H*), 3.30 (m, 4*H*).

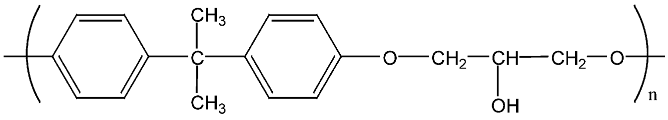
The linear analogous polymer (Scheme 1) of



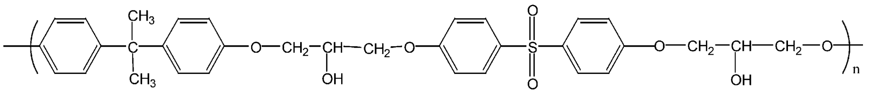
MOCA-type model compound



DDS-type model compound



Poly(hydroxyether of bisphenol A), PH



Poly(HE-*alt*-HES)

Scheme 1. Structures of model compounds and linear analogues of epoxy.

DDS-crosslinked epoxy was synthesized via melt polymerization between diglycidyl ether of bisphenol A (DGEBA) and bisphenol S. The polymer can be taken as the alternated copolymer of hydroxyether (HE) and hydroxyether sulfone (HES). In the general way, an equimolar amount of bisphenol S with respect to DGEBA was added at 150 °C with continuously stirring and degassed to remove bubbles until a homogeneous viscous mixture was obtained. Tetrabutyammonium bromide (1.5 wt%) was used as catalyst and added to the ternary mixture. The mixture was allowed to polymerize in a sealed mould of stainless steel held at 180 °C for 6 h. Under these conditions, the polymerization of equimolar DGEBA and bisphenol S afforded the polymer with $M_n = 2.4 \times 10^4$ and $M_w/M_n = 1.30$ as determined by gel permeation chromatography (GPC), relative to polystyrene standard.

The blends of the model compounds and PCL were prepared by casting from chloroform solution at room temperature. The residual reagent was removed by drying in a vacuum oven for 2 days. The poly(HE-*alt*-HES)/PCL blends were prepared by solution casting from *N*,*N*′-dimethylformamide (DMF) at 50 °C. The total polymer concentration was 5% (w/v). To remove the residual solvent, all the blend films obtained were further desiccated in vacuo at 60 °C for 2 weeks.

To prepare the thermosetting blends, DGEBA and PCL were mixed at 100 °C with continuously stirring for sufficiently long time until PCL were totally dissolved, and then the curing agents were added into the mixture with stirring until the systems became homogenous and transparent. The mixtures were allowed to cure at 80 °C for 2 h plus 150 °C for 3 h to access a complete curing reaction.

2.2. Characterization and measurement

2.2.1. Differential scanning calorimetry (DSC)

A Perkin–Elmer Pyris 1 differential scanning calorimeter (DSC) was used to determine thermal transitions. The instrument was calibrated with standard Indium. A heating rate of 20 °C/min was used in all cases. To remove the thermal history of the samples, a thermal pretreatment was used. All samples (about 10 mg in weight) were heated up to the elevated temperatures and held for 3 min, and then quenched to −70 °C. The DSC curves were recorded at a heating rate of 20 °C/min. The glass transition temperatures were taken as the midpoint of heat capacity change. The crystallization temperatures (T_c) and the melting temperatures (T_m) were taken as the temperatures of the maxima and the minima of both endothermic and exothermic peaks, respectively.

2.2.2. Fourier transform infrared spectroscopy (FTIR)

FTIR measurements were performed on a Perkin–Elmer Paragon 1000 Fourier transform spectrometer. The spectra were obtained at the resolution of 2 cm^{-1} and were averages of 64 scans. The specimens for PCL and the model compounds 1 and 2 together with their blends with PCL were prepared through chloroform solution (2 wt%) casting onto KBr windows at room temperature. The specimens were further dried in vacuo at 60 °C for 2 days to remove residual solvent. The curing blends were granulated and the powder of blends was mixed with KBr and then pressed into small flakes for FTIR measurement. All the specimens used in the study were sufficiently thin to be within a range where the Beer–Lambert law is obeyed. To investigate the intermolecular interactions at the elevated temperatures, the above spectrometer was equipped with a Specac variable temperature cell.

2.2.3. Scanning electronic microscopy (SEM)

The cured epoxy/PCL blends were fractured under cryogenic conditions using liquid nitrogen. The fractured surfaces obtained were immersed in chloroform at room temperature for 30 min. The PCL phase can be preferentially rinsed with the solvent while epoxy phase remains unaffected. The etched specimens were dried to remove the solvents. All specimens were examined with a Hitachi S-2150 scanning electron microscope (SEM) at an activation voltage of 15 kV. The fracture surfaces were coated with thin layers of gold of about 100 Å.

2.2.4. Optical microscopy (OM)

A Leica-DMLP polarized optical microscope (POM) equipped with a hot stage (Linkam TH960, Linkam Scientific Instruments, Ltd.) with a precision of ±0.1 °C was used for morphological observation of samples. The films of poly(HE-*alt*-HES)/PCL blends were sandwiched between two cover glasses and were observed under the polarizing microscope in which the angle between the polarizer and analyzer was 45°. The samples were heated at a rate of 5 °C/min.

3. Results and discussion

3.1. Miscibility and phase behavior

3.1.1. Epoxy/PCL blends cured with MOCA

The mixtures of DGEBA and PCL are fully miscible in the molten state as rehearsed previously [31]. The thermosetting blends of epoxy and PCL were prepared via in situ polymerization of DGEBA and the curing agents (viz. MOCA and DDS) in the presence of PCL. The thermosetting blends containing PCL up to 90 wt% were obtained. The blends cured with MOCA are transparent at room temperature when the contents of PCL are less than 60 wt%. Owing to the formation of spherulites of PCL, the PCL-rich blends (PCL > 60 wt%) became opaque, which was confirmed by the observation that the opaque samples became clear when heated up to 80 °C. The clarity indicates that all the binary blends cured with MOCA present single, homogeneous, amorphous phase, i.e. phase separation did not occur at least on the scale exceeding the wavelength of visible light. The cured blends were subject to the measurement of thermal analysis and the DSC curves were presented in Fig. 1. It can be seen that each blend displayed a single glass transition temperature (T_g), intermediate between those of the two pure components and changing with the blend composition. In view of the single glass transition behavior, it is concluded that the epoxy/PCL blends cured with MOCA are completely miscible in amorphous state. This result is in a good agreement with that in the blend system containing a lower molecular weight PCL [37].

The T_g-composition dependences of miscible polymer blends can be accounted for with several classic equations [38,39]. Of them, Gordon–Taylor equation [38] has been extensively employed to depict the thermal behavior of miscible polymer blends:

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} \tag{1}$$

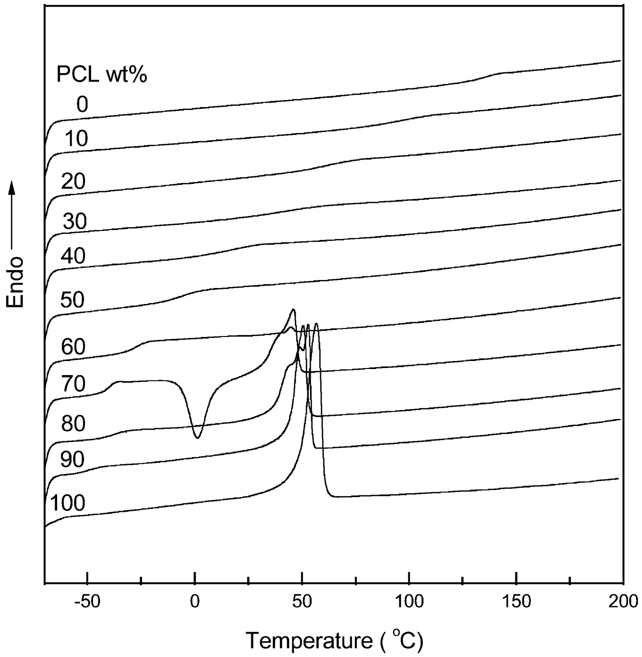


Fig. 1. DSC curves of epoxy/PCL blends cured with MOCA (the second scans after quenching from 180 °C).

where k is an adjusting parameter related to the degree of curvature of the T_g-composition curve. It has been proposed that k can be taken as a semi-quantitative measure of miscibility and strength of intermolecular interactions between components of polymer blends [40–42]. The application of Gordon–Taylor equation to the experimental data yielded the k value of 0.45, fitting the experimental data quite well (Fig. 2).

It should be pointed out that for crystalline polymers-rich samples, the T_g of the blends were not used for the evaluation since there was the enrichment of the amorphous component. From Fig. 2, it was seen that the T_g of blends with PCL more than 70 wt% displayed the obvious positive deviation from the prediction by Gordon–Taylor equation. This observation can be interpreted on the basis of PCL crystallization. On the one hand, PCL crystals could reinforce the amorphous matrix, i.e. restrict the mobility of amorphous component and thus give rise to the increment in T_g. On the other hand, the non-crystallizable component (epoxy) with the higher T_g was enriched in the amorphous region because of the formation of PCL spherulites [43–47].

Returning to Fig. 1, it is seen that for the pure PCL, 10/90 and 20/80 epoxy/PCL blends, no crystallization exothermal transitions were observed in the DSC curves since crystallization was sufficiently rapid and occurred to completion during the quenching. The DSC curves for epoxy/PCL 30/70 blend displayed a cold crystallization transition whereas the blends did not show any crystallinity when the epoxy content is more than 60 wt%, indicating that the crystallization of PCL becomes progressively difficult in epoxy-rich blends. It is seen that the melting temperatures (T_m's) of the crystalline polymers in the blends increasingly depressed with increasing the content of epoxy component. The depression in the melting points could suggest negative intermolecular interaction energy density [48,49]. This is characteristic of miscible blends composed of an amorphous and a crystalline polymer in which the amorphous component possesses the higher glass transition temperature (T_g).

The secondary hydroxyls of amine-crosslinked epoxy resin are potential to form the intermolecular hydrogen bonding interactions with carbonyls of PCL, which are readily to detect with Fourier transform infrared spectroscopy (FTIR). Shown in Fig. 3 are the FTIR spectra of epoxy/PCL blends in the region of 3000–3700 cm^{-1}, recorded at 80 °C. In this region the spectroscopic bands are ascribed to the hydroxyl stretching vibration. For the control epoxy, a broad band centered at 3415 cm^{-1} is attributed to the self-associated hydroxyl groups (i.e., hydrogen-bonded hydroxyl groups) and the width of the band reflects the broad distribution of stretching vibration frequencies for the hydrogen-bonded hydroxyls. The shoulder band centered at 3570 cm^{-1} is assigned to the non-associated, i.e. free hydroxyl groups, the frequency of which remains unvaried at 3570 cm^{-1} but the intensity decreased with increasing PCL concentration. Upon adding PCL to the system, it is seen that a new band appeared at the higher frequency (viz. 3505 cm^{-1}). The appearance of the band suggests that a part of hydroxyl groups were associated with carbonyl groups of PCL via the intermolecular hydrogen bonding interactions. The new band is attributable to the hydroxyls, which are hydrogen-bonded with carbonyls of PCL. With increasing the PCL concentration the

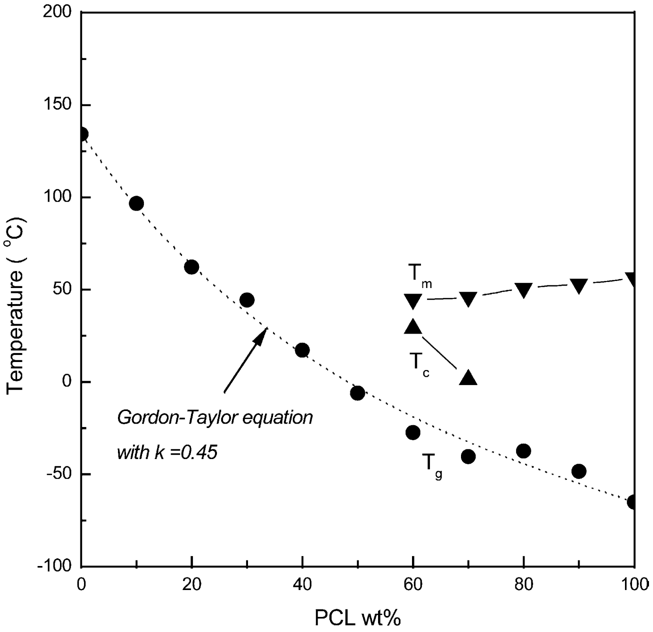


Fig. 2. Thermal transition of epoxy/PCL blends cured with MOCA. The dash line is drawn from the application of Gordon–Taylor equation with $k=0.45$.

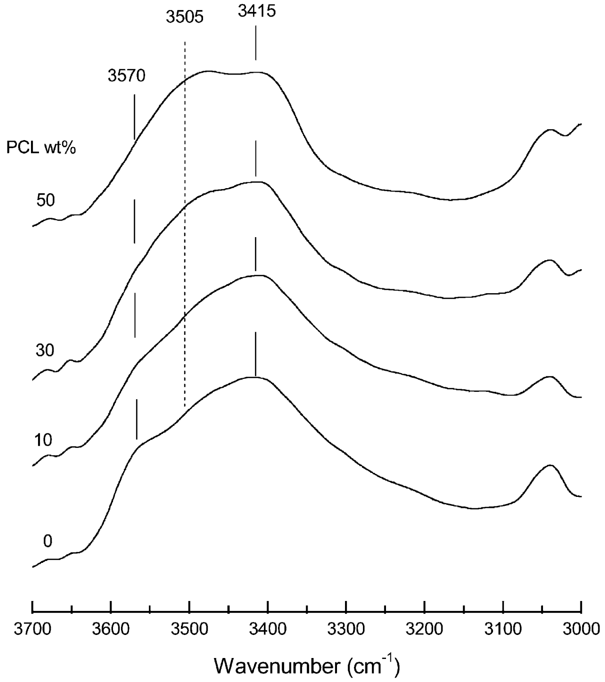


Fig. 3. FTIR spectra in the range of 3100–3700 cm^{-1} for epoxy/PCL blends cured with MOCA, recorded at 80 °C.

intensity of the band increased. It should be pointed out that besides the non- and self-associated hydroxyls there could be the hydroxyls which were associated with ether oxygen atoms in hydroxyl ether structural units and nitrogen atom of tertiary amine moieties. However, these associations are much feeble in comparison with the self-association of hydroxyls, especially in crosslinking systems [50,51].

Fig. 4 shows the FTIR spectra of carbonyl stretching vibration in the region of 1670–1800 cm^{-1} for the epoxy/PCL blends. At 80 °C, the carbonyl stretching vibration of pure PCL occurred at 1735 cm^{-1}, which is characteristic of amorphous chains of PCL. Upon mixing with epoxy, the stretching vibration bands of carbonyls were observed to shift to the lower frequencies. In the meantime, there appeared new shoulder bands at the lower frequency of 1706 cm^{-1}. The observation indicates the formation of the intermolecular hydrogen bonding involving the carbonyl of PCL and the hydroxyl groups of epoxy. The shoulder bands were ascribed to the stretching vibration of the hydrogen-bonded carbonyls.

3.1.2. Epoxy/PCL blends cured with DDS

In marked contrast to the blends cured with MOCA, all the epoxy/PCL blends cured with DDS are cloudy at the ambient temperature. When heated the blends above the melting point of PCL (80 °C), the blends were still not transparent, implying that the phase separation induced by reaction occurred. Shown in Fig. 5 are the DSC curves of the cured blends. The DSC curves of the quenched samples displayed no evidence of crystallization during the heating scans instead of showing the single endothermic peaks almost at constant temperature (55 °C), which correspond to the fusion of PCL before the glass-rubber transitions occurs at ca. 160 °C, suggesting that the blends are phase-separated. In the phase-separated blends, the higher crystallinity of PCL is comparable to that of pure PCL. During the curing process, PCL separated out and thus it is easier for PCL to crystallize from the PCL-rich phase than from miscible blends.

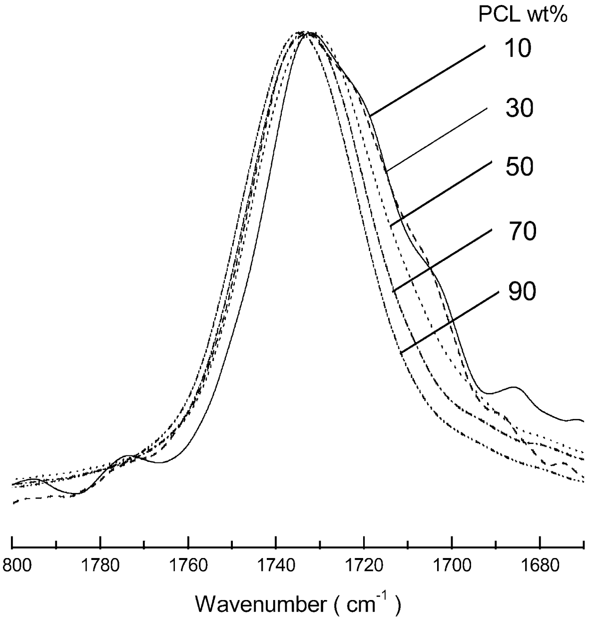


Fig. 4. FTIR spectra in the range of 1670–1800 cm^{-1} for epoxy/PCL blends cured with MOCA, recorded at 80 °C.

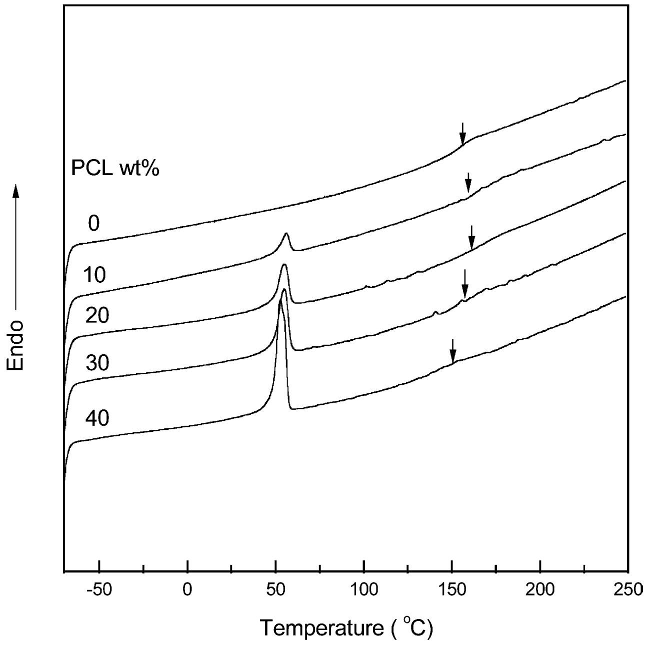


Fig. 5. DSC curves of epoxy/PCL blends cured with DDS (the second scans after quenching from 180 °C).

The morphology of the epoxy/PCL blends cured with DDS was investigated by SEM. Fig. 6 presents SEM micrographs of the fracture ends, which were obtained via freezing using liquid nitrogen and subsequent etching with chloroform. The heterogeneous morphology was observed in all the cases, which was in a good agreement with the results of DSC, i.e. the blends were phase separated. For epoxy/PCL 90/10 blend, it can be seen that the spherical particle was uniformly dispersed in the continuous matrix after PCL phase was rinsed by chloroform and the size of spherical particles is ca. 0.5 μm in diameter (Fig. 6(A)). The spherical phase was attributed to PCL-rich phase whereas the continuous was ascribed to the epoxy matrix. With increasing PCL, the blends displayed remarkably different morphologies. For epoxy/PCL 80/20 blend, it is seen that PCL domains began to inter-connect and exhibited irregular shapes. At the same time, there appear the spherical particles on the surface of the etched blends with broad distribution of size, which are responsible for epoxy phase since PCL-rich phase was dissolved by chloroform. Therefore, this is a combined morphology, i.e. the phase inversion began to appear; the totally phase-inverted morphology was observed for blends with PCL content more than 20 wt% (Fig. 6(B)). For epoxy/PCL 70/30 blend, the epoxy spherical epoxy particles with uniform size were observed after PCL-rich phase was etched (Fig. 6(C)). Similar observations can

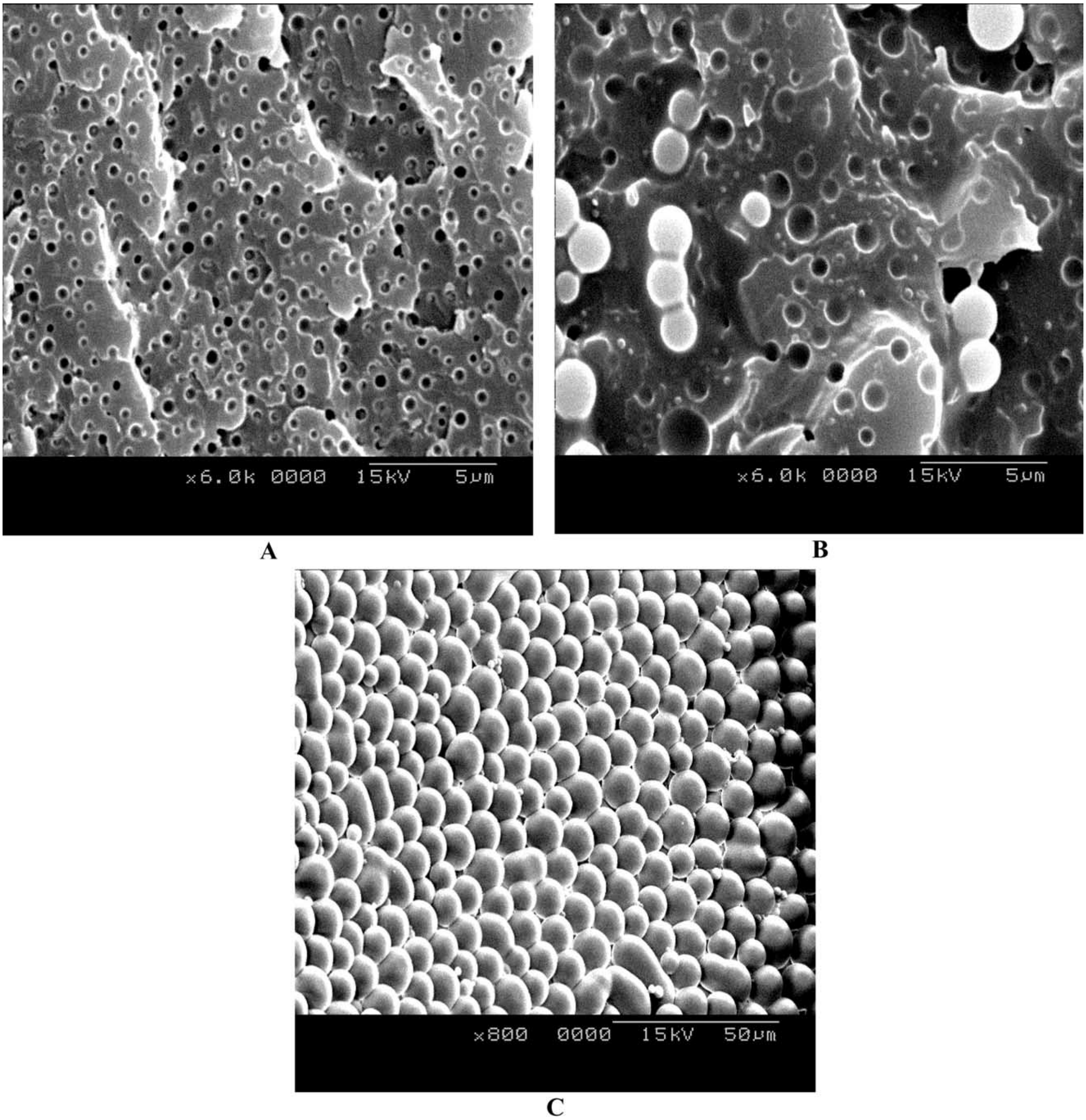


Fig. 6. SEM micrographs of epoxy/PCL blends cured with DDS: (A) 90/10; (B) 80/20; (C) 70/30.

be found in some thermoplastics-modified epoxy systems [52–54].

3.2. Interpretation of phase behavior

The intermolecular specific interactions (e.g., hydrogen bonding) between PCL and amine-cured epoxy have been taken as the driving force for miscibility of the polymer blends [24–34]. Nonetheless, it is worth noticing that the utilization of amines as curing agents does not always afford miscible blends. In the present work, the epoxy/PCL blends cured with MOCA were miscible in the entire composition, which can be ascribed to the formation of the intermolecular hydrogen bonding interactions between the secondary hydroxyls of amine-cured epoxy and the carbonyls of PCL. The intermolecular specific interactions were evidenced by Fourier transform infrared spectroscopy (FTIR). However, the phase behavior of DDS-cured blends behavior seems to be more than the expected although the blends were also cured with a structurally similar aromatic amine, DDS. How do we evaluate the role that the intermolecular specific interactions played in the two systems? To this end, it is necessary to use the model compounds to investigate the intermolecular specific interactions due to the insolubility of the thermosetting blends. Herewith, we synthesized the two compounds (see Scheme 1), which can be taken as the model homologues of repeat units for MOCA- and DDS-crosslinked epoxy, respectively. The model compounds were employed to blend with PCL to investigate the miscibility and intermolecular specific interactions, especially to examine the difference in the intermolecular specific interactions for the two systems under the standard curing condition.

3.2.1. Blends of PCL with model compounds

All the blends of the model compounds with PCL are transparent at the temperature above the melting point of PCL (80 °C), implying that the two blend systems are homogeneous in the amorphous state. Differential scanning calorimetry shows that each blend displayed a single glass transition temperature (T_g), which was intermediate between those of the two pure components and changed with the blend composition. In view of the single glass transition behavior, it is concluded that the blends of the model compounds with PCL are completely miscible in the amorphous state. Shown in Figs. 7 and 8 are the plots of thermal transition of the blends as functions of concentration of PCL in the blends. Considering that there could be the intermolecular specific interactions between the model compounds and PCL, Kwei equation [55,56] was employed to account for the T_g-composition relationships:

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2 \qquad (2)$$

The first term on the right hand side of Eq. (2) is identical to Gordon–Taylor equation, which represents the mixing term derived from the additive rule of entropy and/or of the volume of the blends. The quadratic term (qW_1W_2) was introduced to compensate for the binary interaction between the segments of the component polymers. The physical meaning of the parameter q, which is related to the change in energy associated with the formation of a contact pair between different segments in the mixture, has been discussed by Kwei et al. [57] and was given by the following equation:

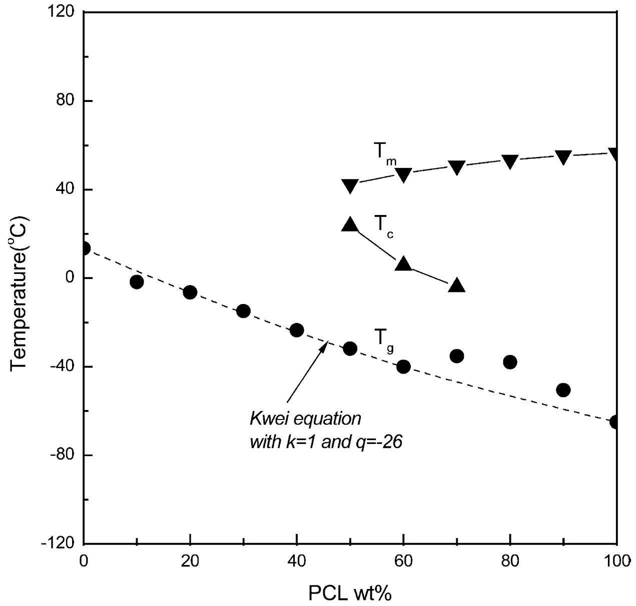


Fig. 7. Thermal transition of the blends of MOCA-type model compound and PCL. The dash line is drawn from the application of Kwei equation with $k=1$ and $q=-26$.

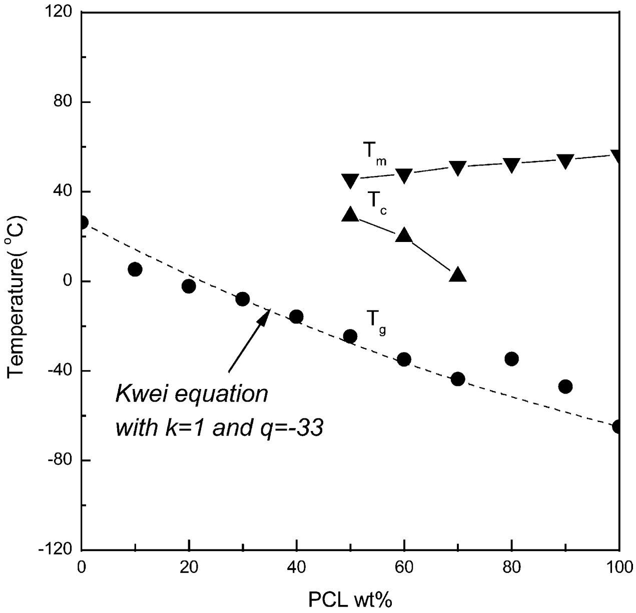


Fig. 8. Thermal transition of the blends of DDS-type model compound and PCL. The dash line is drawn from the application of Kwei equation with $k=1$ and $q=-33$.

$$q = \frac{2f}{3k_B}\left[E_{12} - \frac{1}{2}(E_{11} + E_{22})\right] \qquad (3)$$

where f is the dispersion factor related to the completeness of the intermixing process of the two polymers, k_B is the Boltzman constant, and E_{11}, E_{22} and E_{12} represent the contact energy of the segments of polymers 1 and 2. Therefore, q can account for intermolecular specific interactions in the mixture. The application of Kwei equation to the experimental data, yielded $k=1$, $q=-26$ and $k=1$, $q=-33$ for MOCA- and DDS-type model compound blend systems as shown in Figs. 7 and 8, respectively. It is worth noticing that with the same k values, the absolute q value for the blends of MOCA-type model compound with PCL is significantly higher than that of DDS-type counterpart, implying that the intermolecular hydrogen bonding interactions in the former system are much stronger than those in the latter. The result will be substantiated by Fourier transform infrared spectroscopy (FTIR) (see infra).

The intermolecular hydrogen bonding interactions between the model compounds and PCL can be readily to detect by means of Fourier transform infrared spectroscopy

(FTIR). Shown in Fig. 9 (curve A) are the FTIR spectra of MOCA (and/or DSS)-type model compound and its blends containing 50 wt% of PCL in the range of 3000–3800 cm^{-1}, recorded at 80 °C. The spectroscopic bands are ascribed to hydroxyl stretching vibration and the very broad bands reflect the wide distribution of hydrogen-bonded hydroxyl stretching frequencies. The shoulder bands centered at 3570 cm^{-1} are ascribed to the free hydroxyls. Upon adding PCL to the system, it is noted that at the higher frequency, there appeared a new band at ca. 3502 cm^{-1} whereas the intensity of the initial band at 3570 cm^{-1} significantly decreased. The new band is ascribed to the hydroxyls, which were H-bonded with carbonyls of PCL; the band of free hydroxyls became indiscernible up adding PCL to the system. The fact that the new hydroxyl stretching vibration occurred at the higher frequency indicates that the MOCA-type model compound-PCL specific interactions are much weaker than those of self-association of the hydroxyls. The similar results were also found in the blends of DDS-type model compound with PCL as shown in Fig. 9 (curve B). Nonetheless, it is noted that the intensity of free hydroxyls for DDS-type model compound is much weaker than that of the counterpart of MOCA. More importantly, the relative intensity of the initial band at 3502 cm^{-1} is much higher than that in the blend of MOCA-type model compound with PCL, implying that there are fewer hydroxyls which were associated with PCL in the blend of DDS-type model compound than in that of MOCA-type model compound. This result could be due to the formation of the intramolecular specific interaction within DDS-type model compound. For the blends of DDS-type model compound with PCL, the specific interactions could be additionally involved with the intermolecular hydrogen bonding interactions between the sulfonyl groups and the secondary hydroxyl groups of the model compound, which could be evidenced by the comparison of several equilibrium association constants reported in the literature, which were measured with the model compounds in the dilute solution. According to the Painter-Coleman association model [58,59], the three subscripts 2, B and S are used to denote the equilibrium constants, K_2, K_B and K_S of dimers, multimers of hydroxyl moiety and the trans-association between hydroxyl and sulfonyl groups, respectively. Using 1,3-diphenoxy-2-propanol (DPP) as the model compound of the structural unit of hydroxyl ether in poly(hydroxyether of bisphenol A), Coleman et al. [51] and Iruin et al. [60] have separately obtained $K_2=12.9$ (dimensionless unit), $K_B=21.3$ (dimensionless unit) and $K_2=14.4$ (dimensionless unit), $K_B=25.6$ (dimensionless unit) for the self-association of DPP in the dilute solution of toluene, derived by infrared spectroscopic data. According to the same method, we previously measured the K_S to be 15.6 (dimensionless unit) when we selected 1,4-diphenyl sulfone (DPS) as the model compound of diphenyl sulfonyl moiety in poly(hydroxyether of sulfone) [60–62]. In order to quantitatively investigate the association strength between the secondary hydroxyls and the carbonyls of PCL, Coleman et al. [51] determined the inter-association equilibrium constant, K_A, between hydroxyl ether structural units and aliphatic ester type functionalities from a least squares fitting of the stoichiometric equations to fraction of free carbonyls, $f_F^{C=O}$ data as a function of volume fraction of poly(hydroxyether of bisphenol A) in the blends. The value of K_A was obtained to be 7.9 (dimensionless unit) at 25 °C. It is noted that the K_S value is much lower than the values of $K_B=21.3$ (dimensionless unit) and/or $K_B=25.6$ (dimensionless unit) but significantly higher than the value of $K_A=7.9$ (dimensionless unit). The comparison of the several association equilibrium constants indicates that the hydrogen bonding interactions between hydroxyl and sulfonyl groups is weaker than that between hydroxyl and hydroxyl groups but stronger than that between the hydroxyls and carbonyls of PCL. Therefore, ones can understand the reason that there are fewer hydroxyls that were associated with PCL in the blend of DDS-type model compound than in that of MOCA-type model compound owing to the formation of OH···O=S hydrogen bonding interactions in DDS-type model compound in place of –OH···O=C< hydrogen bonding.

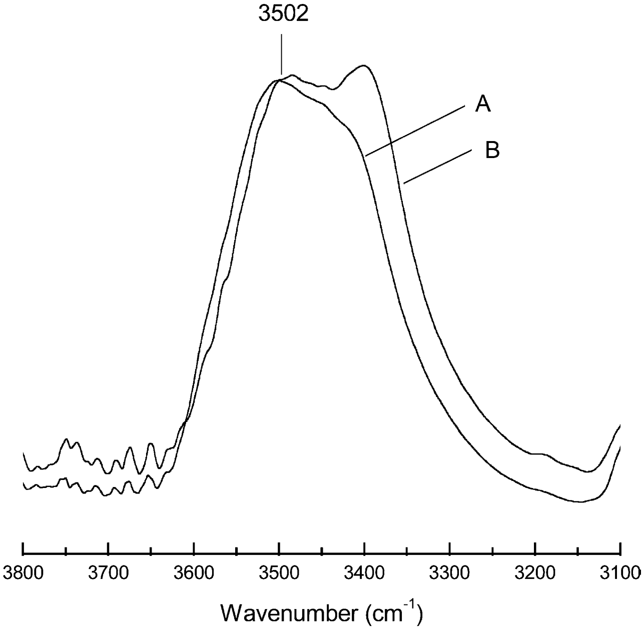


Fig. 9. FTIR spectra in the range of 3100–3800 cm^{-1} for the blends of model compounds containing 50 wt% of PCL, recorded at 80 °C: (A) MOCA-type blend, (B) DDS-type blend.

The above results can be further confirmed with the investigation of the association degree of PCL carbonyls in the blends. Shown in Fig. 10 are the FTIR spectra of the blends of the model compounds with PCL (50/50 wt) in the range of 1640–1840 cm^{-1}, recorded at 80 °C. For the blends, it is seen that the bands became quite broad and asymmetrical. There appeared shoulder bands at the lower frequencies at 1706 cm^{-1}. The shoulder band could be ascribed to the stretching vibration of hydrogen-bonded

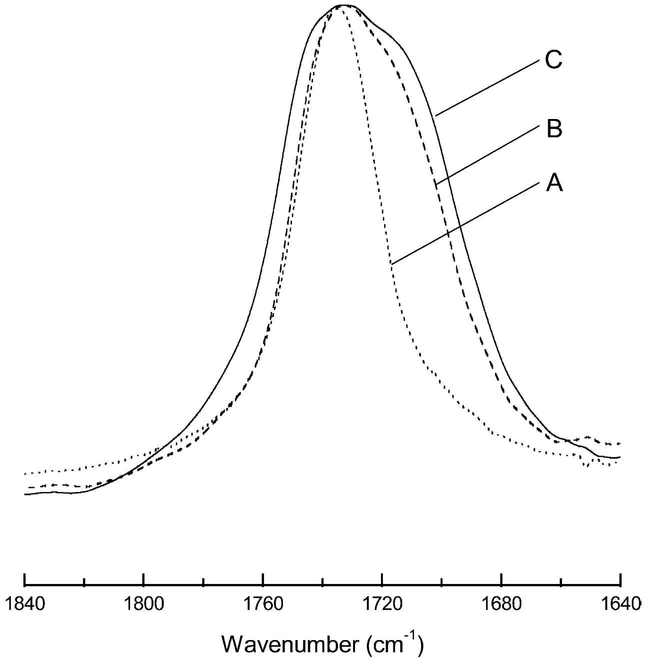


Fig. 10. FTIR spectra in the range of 1640–1860 cm^{-1} for PCL and the blends of model compounds containing 50 wt% of PCL, recorded at 80 °C: (A) PCL, (B) DDS-type blend, (C) MOCA-type blend.

carbonyls. By comparison, it is seen that the carbonyl band for MOCA-type model compound blend is obviously broader than that of DDS-type counterpart. This observation indicates that the degree of carbonyl association with the hydroxyls in the former system is significantly higher than that in the latter, which is in a good agreement with the observation of FTIR spectra in the hydroxyl stretching vibration region. In fact, the results well accord with T_g-composition behavior expressed as Kwei equation. It is possible to resolve the non-associated and the associated carbonyl bands using spectral curve fitting method. The Gaussian line shape function was used in this fitting procedure and the good fitting was carried out for the blends. The F_{co}^{f} is the fraction of the non-associated carbonyl bands, calculated from the values of absorbency for the associated and the non-associated band contributions:

$$F_{co}^{f} = \frac{A_f}{A_f + (\varepsilon_f/\varepsilon_a)A_a} \quad (4)$$

where ε_i is the molar absorption coefficient. The subscripts, f and a stand for free and associated carbonyl groups, respectively. To carry out this calculation, we require the knowledge of the molar absorption coefficients (ε_f and ε_a) or their ratio ($\varepsilon_f/\varepsilon_a$) for the non-associated and associated carbonyl bands. Using the $\varepsilon_f/\varepsilon_a$ value of 1.3 for the inter-association of ester type carbonyls with the hydroxyls of poly(hydroxyether of bisphenol A) blends determined by Coleman et al. [59,63], we calculated the fraction of non-associated carbonyl bands. The variation of F_{co}^{f} as a function of temperature is shown in Fig. 11. It is seen that at 80 °C the fractions of association of carbonyls were 44.3 and 38.6 mol% for the blends of MOCA- and DDS-type model compounds with PCL (PCL 50 wt%), respectively. The fractions of carbonyl association decreased with increasing the temperature. When the samples were heated up to 150 °C, at which all epoxy/PCL blends were cured, the fractions of association of carbonyls were reduced to 42.9 and 35.3 mol% for the blends of MOCA- and DDS-type model compounds with PCL, respectively. It is seen that the difference in the degree of carbonyl association almost maintained invariant until the temperature of the systems were enhanced up to 150 °C, at which the epoxy/PCL blends were cured. This result indicates that there are always much stronger intermolecular specific interactions in the MOCA-moiety containing blends than in DDS moiety containing blends, even at the curing temperature (i.e., 150 °C). It is plausible to propose that the presence of intramolecular hydrogen bonding interactions between the sulfonyl and secondary hydroxyl groups in DDS-cured epoxy suppress the formation of the intermolecular hydrogen bonding interactions between carbonyls and hydroxyls of amine-cured epoxy.

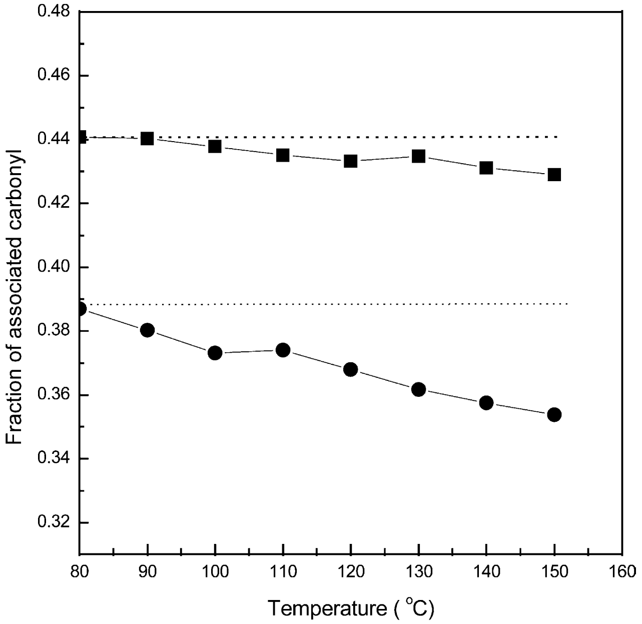


Fig. 11. Fraction of associated carbonyl groups of PCL as a function of temperature or the blends of model compounds containing 50 wt% of PCL. (■) MOCA-type model compound-PCL blend; (●) DDS-type model compound-PCL blend.

3.2.2. Blends of poly(HE-alt-HES) and PCL

The investigations via the model compounds have shown that there are much stronger intermolecular specific interactions in the MOCA moiety containing blends than in DDS moiety containing blends, even at the curing temperature (i.e., 150 °C). It is noted that even in DDS moiety containing blends, there were still considerable amount of hydrogen-bonding association between carbonyls and hydroxyls. The purpose that we investigated the intermolecular hydrogen bonding interactions in the mixture of the model compounds and PCL is to simulate the difference in the specific interactions between PCL and the repeat units of the crosslinked epoxy. Obviously, the cases of the blends of low molecular weight compounds with PCL are unable to represent the case of crosslinked epoxy/PCL blends. It is proposed that there is considerable overestimation of the intermolecular hydrogen bonding interactions, which results from the screening effect and the restriction of chain connectivity due to polymerization and crosslinking of polymer monomers [3–6]. As pointed out by Coleman et al., such factors directly affect the fraction of intermolecular hydrogen-bonded groups and effectively reduce the contribution of mixing enthalpy (ΔH_{m}) to the free energy of mixing (ΔG_{m}) vis-à-vis analogous low-molecular-weight analogues [3–6]. Therefore, it is necessary to examine the miscibility and intermolecular specific interactions of PCL and linear analogous polymers of high molecular weight for the epoxy resins. In this work, both poly(hydroxyether of bisphenol A) (PH) and poly(HE-*alt*-HES) were considered as the linear analogues of MOCA- and DDS-cured epoxy resins. As well known, PH is fully miscible with PCL even at the elevated temperature (e.g., 150 °C) and there were the intermolecular hydrogen bonding interactions between the two component polymers [64]. In marked contrast to PH/PCL blends, all the blends of poly(HE-*alt*-HES) with PCL blends were cloudy, even at the temperature above the melting point of PCL (e.g., at 120 °C), suggesting that the blends are immiscible. Optical miscopy shows that the blends displayed typical phase-separated morphology as shown in Fig. 12. Although the FTIR spectroscopy showed that in the blends of DDS-type model compound with PCL the hydroxyl groups are capable of forming the intermolecular hydrogen bonding interactions with carbonyl group, the relatively weaker intermolecular specific interactions were significantly reduced due to the screening effect and the restriction of chain connectivity in the blends of the high-molecular-weigh polymers, which in turn gives rise to the immiscibility. This observation is important for ones to understand the formation of the phase-separated morphology for DDS-cured epoxy/PCL blends, i.e. the introduction of sulfonyl moiety in place of isopropyl or methylene moiety in crosslinked epoxy result in the reduced intermolecular specific interactions resulting from the formation of the intramolecular specific interactions between sulfonyl and the hydroxyl groups. The decreased intermolecular specific interactions were further weakened with proceeding of polymerization and the formation of the crosslinked networks.

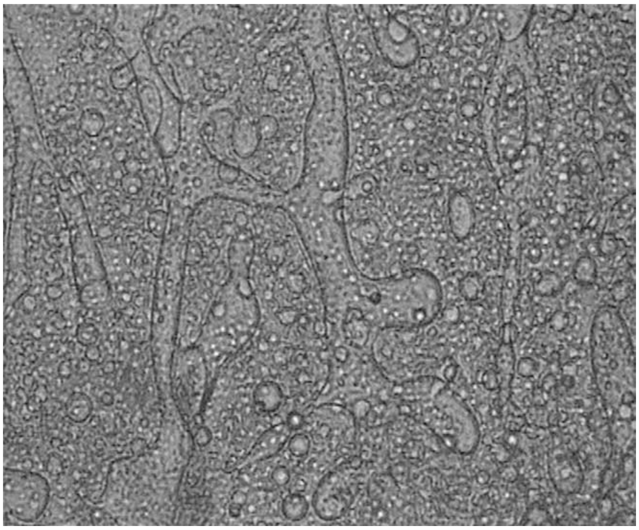


Fig. 12. Phase contrast micrograph of poly(HE-*alt*-HES)/PCL 50/50 blend, recorded at 120 °C.

4. Conclusions

The thermosetting blends of epoxy and poly(ε-caprolactone) (PCL) were prepared via in situ curing reaction of epoxy monomer and the curing agents in the presence of PCL. The curing agents used in this work are 4,4′-methylenebis (2-chloroaniline) (MOCA) and 4,4′-diaminodiphenylsulfone (DDS), respectively. In the case that MOCA was employed, the blends are miscible in the amorphous state in the entire composition, which was evidenced by the behavior of single, and composition-dependent glass transition temperatures (T_{g}’s). FTIR showed that there are the intermolecular specific interactions (viz. hydrogen bonding) between MOCA-crosslinked epoxy and PCL. In contrast, the epoxy-PCL blends cured with DDS displayed a typical reaction-induced morphology, which was revealed by scanning electronic microscopy (SEM). The converse phase behavior motivates us to investigate the role that the specific interactions play in the formation of the resulting blends. The investigation by means of thermal analysis and infrared spectroscopy via model compounds indicates that in the DDS-crosslinked epoxy/PCL blends, there are much weaker intermolecular specific interactions than in MOCA-cured blends. The decreased intermolecular specific interactions between DDS-cured epoxy and PCL result from the formation of the intramolecular hydrogen bonding interactions within DDS-crosslinked epoxy, which are involved with the sulfonyls of DDS moiety and the hydroxyls of epoxy. This result was further confirmed by the immiscibility of PCL blends with poly(HE-*alt*-HES), which can be taken as the linear homologue of high molecular weight. The intramolecular hydrogen bonding interactions are weaker than the self-association of hydroxyls but much stronger than the interassociation between hydroxyls of epoxy and carbonyls of PCL. The intramolecular association could suppress the formation of the intermolecular hydrogen bonding interactions between carbonyls and hydroxyls of amine-cured epoxy, which are sufficient to fulfill the homogenization of the system during the in situ polymerization. Therefore, the presence of the intramolecular specific interactions between sulfonyl and secondary was taken as the origin of phase-separated morphology for DDS-cured blends of epoxy with PCL.

Acknowledgements

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