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Epoxy resin containing poly(ethylene oxide)-*block*-poly(ε-caprolactone) diblock copolymer: Effect of curing agents on nanostructures

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Abstract

An amphiphilic diblock copolymer, poly(ethylene oxide)-*block*-poly(ε-caprolactone) (PEO-*b*-PCL) was synthesized *via* the ring-opening polymerization of ε-caprolactone in the presence of a hydroxyl-terminated poly(ethylene oxide) monomethyl ether. The diblock copolymer was incorporated into epoxy thermosets. It is found that the formation of nanostructures of thermosetting blends is quite dependent on the uses of aromatic amine hardeners. For 4,4′-methylenebis(2-chloroaniline) (MOCA)-cured thermosetting system, the homogeneous morphology was obtained at the compositions investigated. Nonetheless, the nanostructured thermosets were obtained when the blends were cured with 4,4′-diaminodiphenylsulfone (DDS). The differential scanning calorimetry (DSC) showed that the nanostructured thermosets did not displayed any crystallinity although the subchains of the diblock copolymer are crystalline. The nanostructures were evidenced by means of atomic force microscopy (AFM), small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The dependence of morphological structures on the types of aromatic amines for epoxy and PEO-*b*-PCL thermosetting blends were interpreted on the basis of the difference in hydrogen bonding interactions resulting from the structure of curing agents. Considering the complete miscibility of the subchains (*viz*. PEO and PCL) with the precursors of epoxy resin before curing, it is judged that the formation of the nanostructures in the thermosets follows the mechanism of reaction-induced microphase separation, which is in marked contrast to the mechanism of self-assembly, *i.e.*, micelle structures of block copolymers are formed prior to curing, followed by fixing these nanostructures *via* curing.

Keywords: Epoxy; Poly(ethylene oxide)-*block*-poly(ε-caprolactone); Blends

1. Introduction

During the past decade, considerable progress has been made in the studies of morphological structures of thermosetting blends with homopolymers or random copolymers [1,2]. This progress is, in part, a consequence of the recognition of the importance of the effect of morphological structures on mechanical properties. Generally, thermoset blends are prepared starting from the homogeneous solution of a modifier and thermoset precursors. Since these modifiers are some linear homopolymers or random copolymers, reaction-induced phase separation generally occurs on the macroscopic scale with the polymerization proceeding [1]. Recently, it is recognized that the formation of nanostructure in thermosets could further optimize the interactions between thermoset matrix and modifiers and thus endow materials with improved properties [3–20]. Nonetheless, it is still a challenge to control the formation of nanostructures in thermosetting polymer blends.

Bates et al. [3,4] proposed a strategy for creating nanostructures in thermosets using amphiphilic block copolymers. In their approach, precursors of thermosets (*e.g.*, diglycidyl ether of bisphenol A) were used as selective solvents of block copolymers and thus some self-organized micelle structures such as lamellar, bicontinuous, cylindrical, and spherical structures are formed in the mixtures of block copolymer and the precursors

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of thermosets depending on the blend composition before curing reaction. These self-organized structures were further fixed *via* subsequent curing after hardeners are added [3–19]. The requirement for this approach is that block copolymers are self-organized into micelle structures before curing. Nonetheless, this situation does not always occur if all the blocks of block copolymers are miscible with precursors of thermosets. In fact, the more general case is that the modifiers (homopolymers or random copolymers) are miscible with precursors of thermosets. The miscibility (or solubility) is ascribed to the non-negligible entropic contribution (ΔS_m) to free energy of mixing (ΔG_m) in the mixtures since the molecular weights of precursors of thermosets are quite low [1,21]. In addition, the presence of the self-organized microphases formed at lower temperatures does not purport the survival of such structures at elevated temperatures, which are generally required for the curing of high performance thermosets. It has been known that the mixtures of polymers with precursors of thermosets generally displayed upper critical solution temperature (UCST) behaviors [1,21]. In this case, we recently proposed that the nanostructured thermosets can alternatively be obtained *via* the reaction-induced microphase separation [22]. The mechanism of reaction-induced microphase separation could provide ones with tremendous space for maneuver to investigate the formation of nanostructures in thermosets by adjusting some thermodynamic and kinetic factors such as intermolecular specific interactions and competitive kinetics (or dynamics) between microphase separation and polymerization [1,2].

In the present work, we present the studies on the formation of nanostructures in the blends of epoxy thermosets with poly(ethylene oxide)-*b*-poly(ε-caprolactone) diblock copolymer (PEO-*b*-PCL). The blends of epoxy resin with poly(ethylene oxide) (PEO) and/or poly(ε-caprolactone) are among the most investigated thermosetting blends. It is recognized that the miscibility of the two systems are quite dependent on the curing agents used. It was ever reported that phase separation occurred in the blends of epoxy resin with PEO when the blends were cured with tetraethylenepentamine, an aliphatic amine [23]. Nonetheless, subsequent studies showed that the system is miscible when cured with aromatic amines [24]. For the blends of epoxy with PCL, miscibility and phase behavior have been reported by several authors [25–34]. Noshay and Robeson [25] 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. [26] investigated the differences in miscibility for both anhydride- and amine-crosslinked epoxy-PCL blends and the variation in their mechanical properties due to the different miscibility. The miscibility of amine-crosslinked blends has been ascribed to the formation of the intermolecular hydrogen bonding interactions between amine-cured epoxy resin and PCL. However, Chen and Chang [27] investigated the immiscibility of the blends when an aromatic amine, 4,4′-diaminodiphenylsulfone (DDS) was used as the curing agent and they found that the mechanisms of phase separation were binodal or spinodal decomposition depending on the PCL concentration in the blends. The immiscibility of epoxy and PCL blends cured with DDS has been interpreted on the basis of the influence of intra-chain specific interactions on the phase behavior [37]. In views of the previous studies, we proposed that nanostructures could be formed in thermosetting blends of epoxy resin with PEO-*b*-PCL by selecting appropriate curing systems *via* so-called reaction-induced microphase separation mechanism.

The goal of this work is to investigate the effect of curing agent on the formation of nanostructures in thermosetting blends of epoxy resin and PEO-*b*-PCL. To this end, both 4,4′-methylenebis(2-chloroaniline) (MOCA) and 4,4′-diaminodiphenylsulfone (DDS) were, respectively, used as the curing agents by knowing that: (i) the blends of epoxy resin with PEO are miscible when cured with MOCA and DDS [35,36], (ii) the blends of epoxy resin with PCL are miscible when cured with MOCA whereas these blends are immiscible when cured with DDS [27,28,37]. It is expected that we can selectively control the microphase separation of PCL subchains induced by polymerization whereas the PEO subchains remain miscible with the crosslinked epoxy networks while DDS is used as the curing agent. The phase behavior, intermolecular specific interactions and nanostructures were investigated by means of scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), small-angle X-ray scattering (SAXS), atomic force microscopy (AFM) and transmission electron microscopy (TEM).

2. Experimental

2.1. Materials

The epoxy precursor, diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight of 185–210 was supplied by Shanghai Resin Co., China. Both 4,4′-methylenebis(2-chloroaniline) (MOCA) and 4,4′-diaminodiphenylsulfone (DDS) were used as the curing agents, purchased from Shanghai Reagent Co., China. Poly(ethylene oxide) monomethyl ether (MPEO5000) with a quoted molecular weight of $M_n = 5000$ was obtained from Fluka Co., Germany and it was dried by azeotropic distillation with anhydrous toluene prior to use. The monomer, ε-caprolactone (ε-CL) was purchased from Fluka Co., Germany and it was dried over calcium hydride (CaH_2) and distilled under reduced pressure prior to use. Stannous(II) octanoate [$Sn(Oct)_2$] is purchased from Aldrich Co., USA and used as received. The solvents such as tetrahydrofuran (THF), dichloromethane and methanol were of chemical grade, obtained from commercial resources. All other chemicals were of analytical grade and were used without further purification.

2.2. Synthesis of PEO-b-PCL diblock copolymer

The PEO-*b*-PCL diblock copolymer was synthesized by ring-opening polymerization of ε-CL in the presence of MPEO5000 with $Sn(Oct)_2$ as the catalyst [38]. Typically, MPEO5000 (5 g, 1.0 mmol) and anhydrous toluene (30 ml) were charged to a round-bottomed flask and the toluene was distilled out to eliminate the trace of water in MPEO5000 (*i.e.*, azeotropic distillation). After the toluene was completely removed from the system, ε-CL (5.3 g, 46.5 mmol) and $Sn(Oct)_2$ (0.01 g, 0.025 mmol) were added using syringes. The flask was purged with dry nitrogen and then the purging gas was evacuated. The procedure was repeated for at least three times to eliminate oxygen and then the flask was immersed in an oil bath and the polymerization reaction was allowed to proceed at 120 °C for 24 h. After the reaction was completed, the product was dissolved in dichloromethane and precipitated in a large amount of cold methanol to remove MPEO5000 homopolymers and residual ε-CL monomer. The resulting product was further dried *in vacuo* at 40 °C for 48 h and 9.95 g of polymer was obtained with the yield (or conversion) of 93%. The curve of gel permeation chromatography (GPC, relative polystyrene standard) displayed a unimodal peak and the molecular weight was determined to be $M_n = 14{,}950$ and $M_w/M_n = 1.15$, relative to polystyrene standard.

2.3. Preparation of thermosets containing PEO-*b*-PCL

The binary blends of epoxy resin with PEO (and/or PCL) with the identical molecular weight as in the PEO-*b*-PCL diblock copolymer were prepared as detailed elsewhere [35]. The desired amount of PEO (and/or PCL) was added to DGEBA at ambient temperature with continuous stirring until the diblock copolymer was completely dissolved and then the curing agents (*i.e.*, MOCA or DDS) were added with vigorous stirring until homogeneous blends were obtained. The curing reactions were carried out at a lower temperature such as 140, 150, 160, 170 °C for 2 h plus a higher temperature (*i.e.*, 180 °C) for 2 h to access a complete curing reaction.

The diblock copolymer, PEO-*b*-PCL was added to DGEBA at ambient temperature with continuous stirring until the diblock copolymer was completely dissolved. Then the curing agent, MOCA or DDS was added to the system with vigorous stirring until homogeneous blends were obtained. The ternary mixture was poured into Teflon moulds and cured at 150 °C for 2 h plus 180 °C for 2 h. The thermosetting blends containing PEO-*b*-PCL up to 50 wt% were obtained.

2.4. Measurement and characterization

2.4.1. Fourier transform infrared spectroscopy (FTIR)

A Perkin–Elmer Paragon 1000 Fourier transform infrared spectrometer was used to measure infrared spectra at room temperature (25 °C). To obtain the FTIR spectrum of PCL-*b*-PEO, the diblock copolymer was dissolved in THF and the solution was cast onto a KBr window and the solvent was removed *in vacuo* at 60 °C for 30 min. The samples of thermosets were granulated and the powder was mixed with KBr pellets to press into the small flakes for measurements. All the specimens were sufficiently thin to be within a range where the Beer–Lambert law is obeyed. In all cases 64 scans at a resolution of 2 cm^{-1} were used to record the spectra.

2.4.2. Nuclear magnetic resonance spectroscopy (NMR)

The ^1H NMR measurements were carried out on a Varian Mercury Plus 400 MHz NMR spectrometer at 25 °C. The samples were dissolved in deuterated chloroform and the solutions were measured with tetramethylsilane (TMS) as the internal reference.

2.4.3. Gel permeation chromatography (GPC)

The molecular weights of the polymer were measured on a Perkin–Elmer series 200 permeation chromatography (GPC) instrument with a PL mixed-B10m column. Polystyrene was used as the standard, and THF was used as the eluent at a flow rate of 1 ml/min.

2.4.4. Differential scanning calorimetry (DSC)

The thermal analysis was carried out with a Perkin–Elmer Pyris 1 differential scanning calorimeter in a dry nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. All the samples (about 8.0 mg in weight) were first heated to 180 °C and held at this temperature for 3 min to remove the thermal history, followed by quenching to −60 °C. A heating rate of 20 °C/min was used in all cases. Glass transition temperature (T_g) was taken as the midpoint of the heat capacity change. The crystallization temperature (T_c) and the melting temperatures (T_m) were taken as the temperatures of the minimum and the maximum of both endothermic and exothermic peaks, respectively.

2.4.5. Scanning electron microscope (SEM)

In order to observe the phase structure of epoxy blends, the samples were fractured under cryogenic condition using liquid nitrogen. The fractured surfaces so obtained were immersed in dichloromethane at room temperature for 30 min. The PCL phases could be preferentially etched by the solvent while epoxy matrix phase remains unaffected. The etched specimens were dried to remove the solvents. The fractured surfaces were coated with thin layers of gold of about 100 Å. All specimens were examined with a Hitachi S210 scanning electron microscope (SEM) at an activation voltage of 15 kV.

2.4.6. Small-angle X-ray scattering (SAXS)

The SAXS measurements were taken on a Bruker Nanostar small-angle X-ray scattering system. Two-dimensional diffraction patterns were recorded using an image intensified CCD detector. The experiments were carried out at room temperature (25 °C) or elevated temperature using Cu Kα radiation ($\lambda = 1.54$ Å, wavelength) operating at 40 kV, 35 mA. The intensity profiles were output as the plot of I^*q^2 *versus* scattering vector, $q = (4\pi/\lambda)\sin(\theta/2)$ (θ = scattering angle).

2.4.7. Atomic force microscopy (AFM)

The thermoset samples were trimmed using a microtome machine and the specimen sections (*ca.* 70 nm in thickness) were used for AFM observations. The AFM experiments were performed with a Nanoscope IIIa scanning probe microscope (Digital Instruments, Santa Barbara, CA, USA). Tapping mode was employed in air using a tip fabricated from silicon

(125 μm in length with *ca.* 500 kHz resonant frequency). Typical scan speeds during recording were 0.3–1 line × s^{-1} using scan heads with a maximum range of 2 × 2 μm.

2.4.8. Transmission electron microscopy (TEM)

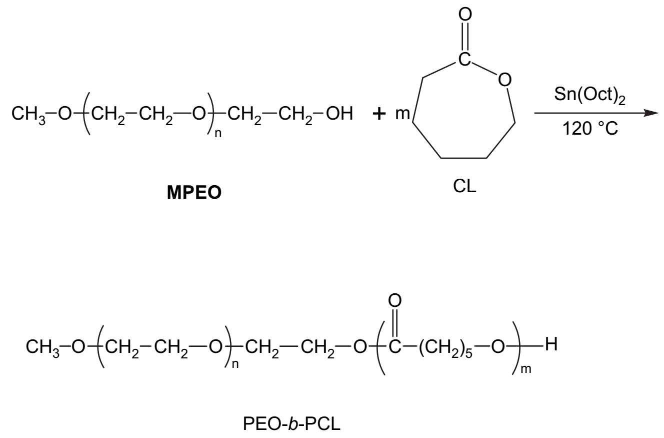
Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 high-resolution transmission electron microscope at an acceleration voltage of 120 kV. The samples were trimmed using a microtome machine and the sectioned samples were stained with OsO_4 to increase the contrast. The stained specimen sections (*ca.* 70 nm in thickness) were placed in 200 mesh copper grids for observations.

3. Results and discussion

3.1. Synthesis of PEO-b-PCL diblock copolymers

The PEO-*b*-PCL diblock copolymer was synthesized by the ring-opening polymerization of ε-CL in the presence of MPEO5000 which acts as a macroinitiator and stannous(II) octanoate [$Sn(Oct)_2$] was used as the catalyst (see Scheme 1). The ^1H NMR spectrum of the polymer together with the assignments of resonance signals is presented in Fig. 1. The sharp single resonance centered at 3.62 ppm is attributed to methylene protons of PEO and the resonance signals at 4.03, 2.28, 1.61 and 1.36 are assigned to methylene protons of PCL block. The signal assignable to the protons of terminal methoxy group of MPEO5000 appeared at 3.38 ppm. In terms of the ratios of integration intensity of methylene protons of PEO to those of PCL, the caprolactone/ethylene oxide molar ratio ([CL]/[EO]) of the product was estimated to be 82/114, which is very close to the feed ratio, and thus the molecular weight of PEO-*b*-PCL diblock copolymer was thus estimated to be $M_n = 14{,}300$, which is in good agreement with the results of GPC. The above results indicate that ring-opening polymerization of ε-CL was carried out in a living fashion.

Fig. 2 shows the FTIR spectrum of PEO-*b*-PCL diblock copolymer. The strong absorption appears at 1725 cm^{-1}, indicating the presence of the stretching vibration band of carbonyl groups in PCL block. The bands at the 1115 and 1242 cm^{-1} are due to the stretching vibrations of C–O–C and C–O bonds. These absorptions indicate the existence of ester structural units in the copolymer. The band at 2943 cm^{-1} is assigned to the C–H stretching vibrations of CH_2 in PCL block, whereas the band at 2865 cm^{-1} corresponds to the C–H stretching vibration of PEO. In addition, the weak absorption band at 3446 cm^{-1} was attributed to be the terminal hydroxyl groups in the block copolymer.



Scheme 1. Synthesis of PEO-*b*-PCL.

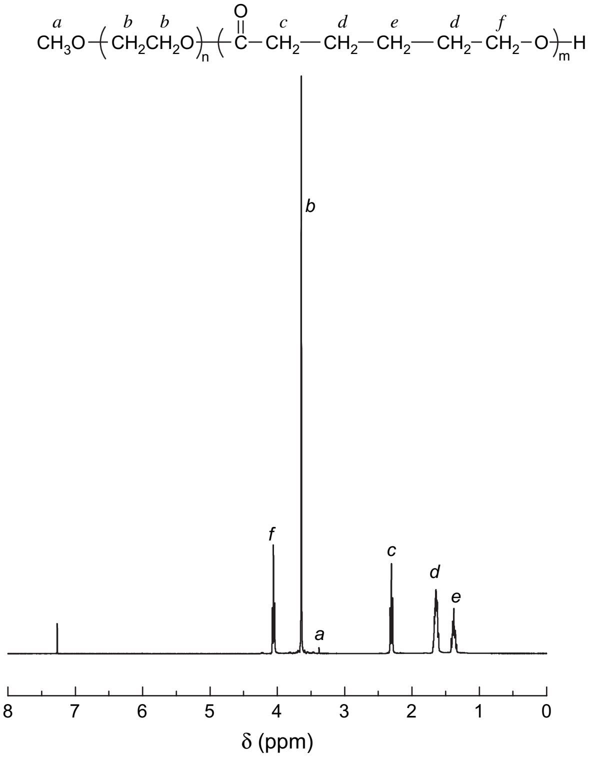


Fig. 1. The ^1H NMR spectrum of PEO-*b*-PCL diblock copolymer.

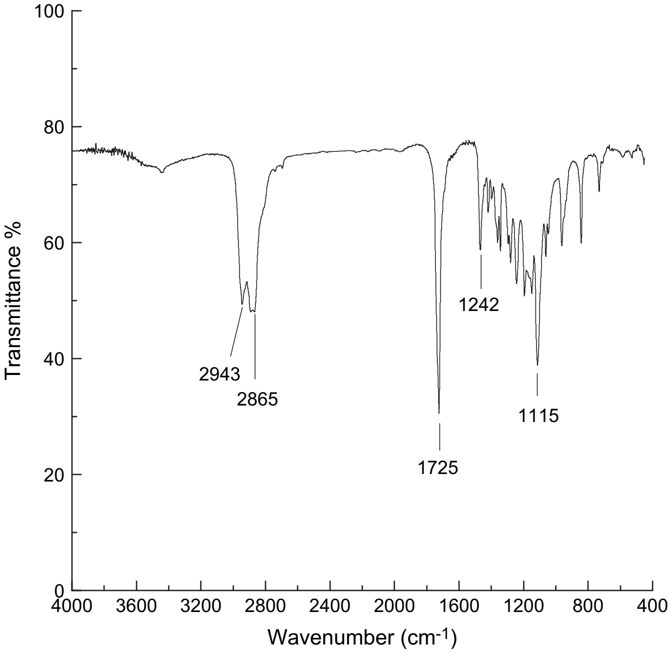


Fig. 2. The FTIR spectrum of PEO-*b*-PCL diblock copolymer.

3.2. Binary thermosetting blends of epoxy with PEO (and/or PCL)

It is necessary to know the miscibility and phase behavior of binary blends of epoxy with PEO (and/or PCL) (*viz*. the subchains of the diblock copolymer) after and before curing in order to understand the formation mechanism of the morphological structures in the thermosetting blends of epoxy with PCL-*b*-PEO diblock copolymer. Before curing, all the mixtures of epoxy precursors (*viz*. DGEBA and the curing agents) and PEO (and/or PCL) are fully miscible [23,24,35−37]. The miscibility is ascribed to the non-negligible entropic contributions to mixing free energy (ΔG_m) since the molecular weights of epoxy precursors are very low. However, the curing agents (*viz*. MOCA and DDS) have quite different effects on the miscibility of epoxy thermosets with PCL after curing.

All the PEO-containing epoxy blends cured with MOCA and DDS at various curing temperatures displayed single, intermediate and composition-dependent glass transition temperatures (T_g's) in the entire composition as revealed by means of differential scanning calorimetry (DSC) [35,37], indicating that the thermosetting blend systems are miscible. The miscibility of the thermosetting blends was attributed to the formation of the intermolecular hydrogen bonding interactions between the hydroxyl groups of amine-cured epoxy and ether oxygen atoms of PEO [23,35−37]. However, the miscibility and phase behavior of the binary thermosetting blends of epoxy with PCL are quite dependent on the type of curing agents used. In the previous work, the miscibility of the thermosetting blends cured with MOCA has been established by means of differential scanning calorimetry (DSC) [35,37]. For the DDS-cured blends, some investigators [27,28] have reported the phenomenon of reaction-induced polymerization. In the present work, it is necessary to examine the phase behavior of the binary thermosets containing the PCL with the identical molecular weight as in the PEO-*b*-PCL diblock copolymer. All the epoxy and PCL blends cured with DDS are translucent, implying that the blends could be phase-separated. The fracture ends of the DDS-cured blends were subjected to scanning electron microscopy (SEM) and atomic force microscopy (AFM) for the morphological observation. The SEM micrograph of the blend containing 10 wt% of PCL are representatively presented in Fig. 3. In the SEM experiment, dichloromethane was used as the solvent to rinse PCL-rich phase while the epoxy phase remained unaffected. It is seen that a heterogeneous morphology was obtained after the sample was etched. The spherical holes were ascribed to PCL-rich phase. The spherical PCL-rich particles (0.2−0.5 μm in diameter) were dispersed uniformly in the continuous epoxy matrix. The morphology of the blends was further investigated by means of atomic force microscopy (AFM). A typical AFM height image of the binary epoxy thermosetting blend containing 10 wt% of PCL is presented in Fig. 4. It is seen that the surface appears to be free of visible defects and quite smooth. The phase contrast image showed a heterogeneous

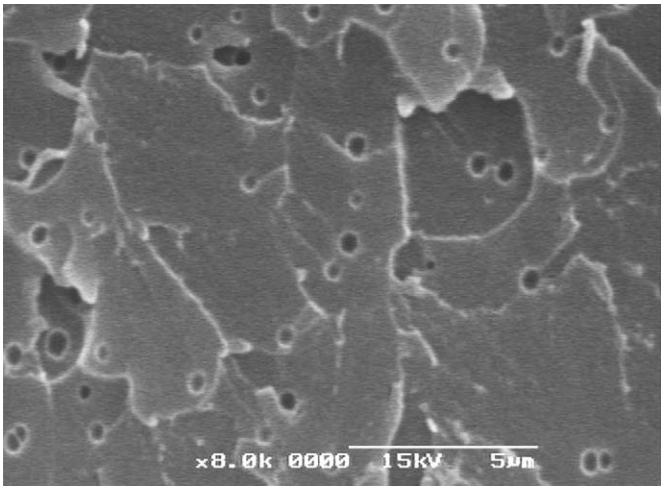


Fig. 3. The SEM micrograph of DDS-cured epoxy blends containing 10 wt% of PCL.

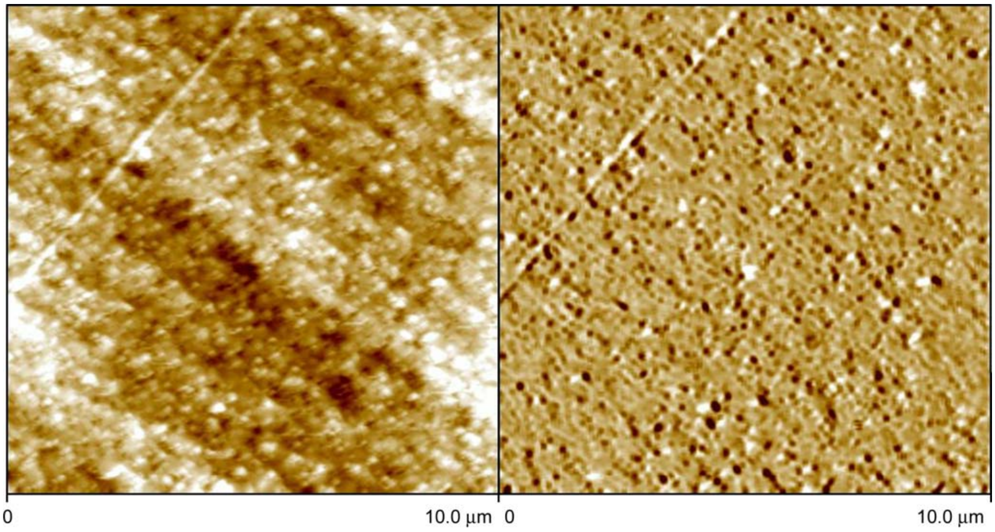


Fig. 4. The AFM images of DDS-cured epoxy blends containing 10 wt% of PCL. Left: topography, right: phase contrast.

morphology, *i.e.*, the spherical PCL-rich particles were homogeneously dispersed in the continuous epoxy matrix. The AFM result is in good agreement with that of SEM, *i.e.*, reaction-induced phase separation occurred in the thermosetting blends of epoxy and PCL with the identical molecular weight with the length of PCL subchain in the diblock copolymer when the blends were cured with DDS. It should be pointed out that the variation in curing circles did not alter the formation of the heterogeneous morphologies of the binary thermosetting blends, suggesting that the formation of the phase-separated structure is governed by the immiscibility between DDS-crosslinked epoxy resin and PCL [27,35,37].

3.3. Thermosetting blends of epoxy and PEO-b-PCL

The blends of epoxy resin with PEO-*b*-PCL diblock copolymer were cured with MOCA and DDS, respectively. Before curing, all the mixtures of epoxy precursors (*viz*. DGEBA and the curing agents) and the block copolymer are transparent in the melt. After curing, all the epoxy thermosets containing PEO-*b*-PCL were also transparent, indicating that no macroscopic phase separation occurred.

3.3.1. Blends cured with MOCA

The thermosetting blends cured with MOCA were subjected to morphological observation by means of AFM. The representative AFM images of the blend containing 20 wt% of PEO-*b*-PCL are presented in Fig. 5. It is seen that the surface appears to be free of visible defects and quite smooth. The phase contrast image (Fig. 5, right) shows a homogeneous surface, indicating that the surface of fractured ends is compositionally homogeneous, *i.e.*, no localized domains were observed at the scale of several nanometers. The AFM result indicates that the MOCA-cured epoxy blends with PEO-*b*-PCL are homogeneous. This result was further confirmed by means of small-angle X-ray scattering (SAXS) (the featureless scattering curves are not shown here for brevity).

3.3.2. Blends cured with DDS

Shown in Fig. 6 are the AFM topology and phase images of the epoxy resin and PEO-*b*-PCL blends cured with DDS. In the phase images, the light continuous regions are ascribed to the crosslinked epoxy networks, which were miscible with the PEO blocks of the diblock copolymer whereas the dark areas correspond to PCL-rich microdomains. For the thermoset containing 10 wt% of PEO-*b*-PCL, the spherical particles with the size of *ca.* 10–20 nm in diameter were dispersed in the continuous epoxy matrix (Fig. 6A). With increasing the content of the diblock copolymer, the PCL-rich microdomains began to coagulate and some interconnected domains began to appear while the concentration of the diblock copolymer is 20 wt% or higher (Fig. 6B and C). The AFM results were further confirmed by transmission electron microscopy (TEM). Representatively shown in Fig. 7 is the TEM micrograph of the thermoset containing 20 wt% of PEO-*b*-PCL diblock copolymer. The spherical microdomains with the size of *ca.* 10 nm in diameter were discernible and dispersed in the epoxy matrix, which is comparable to the results of AMF. It should be pointed out that due to the lack of unsaturated C=C double bonds for the efficient staining with OsO_4, the TEM micrograph could not reflect the real nanostructure of the thermoset. Nonetheless, the compositional inhomogeneity at the nanometer scale revealed by TEM is indeed an indicative of the formation of the nanostructure.

The nanostructured thermosets were subjected to differential scanning calorimetry (DSC) and the DSC curves of the nanostructured thermosets are presented in Fig. 8. The glass transition temperature (T_g) of the control epoxy is about 153 °C. The DSC curve of PEO-*b*-PCL diblock copolymer displays a ramp melting peak at *ca.* 55 °C, which is due to the overlapped melting transitions of both PCL and PEO blocks. It is noted that the T_g's of the nanostructured thermosets decreased with increasing the content of PEO-*b*-PCL. The decreased T_g's are ascribed to the plasticization of PEO chains on the epoxy matrix. In addition, the glass transition range of

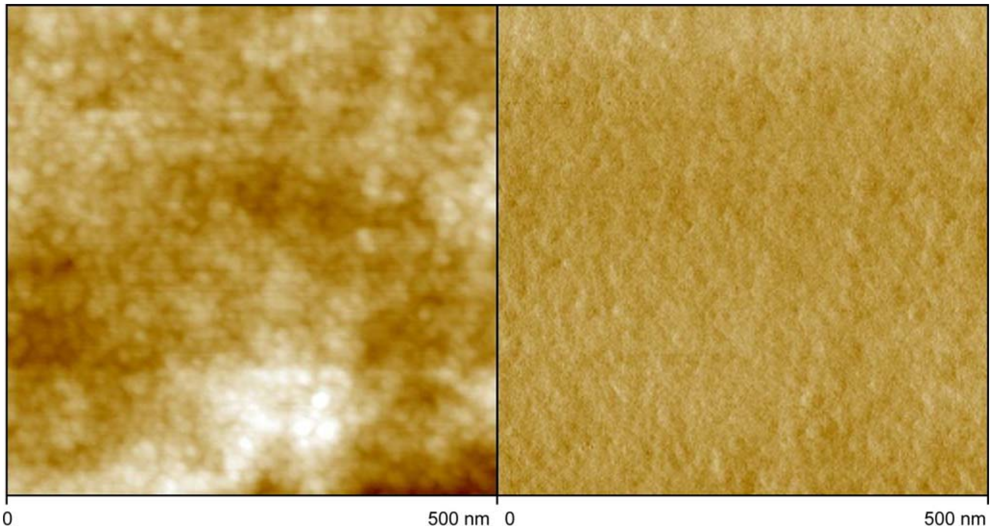


Fig. 5. The AFM images of the blend containing 20 wt% of PEO-*b*-PCL cured with MOCA. Left: topography, right: phase contrast.

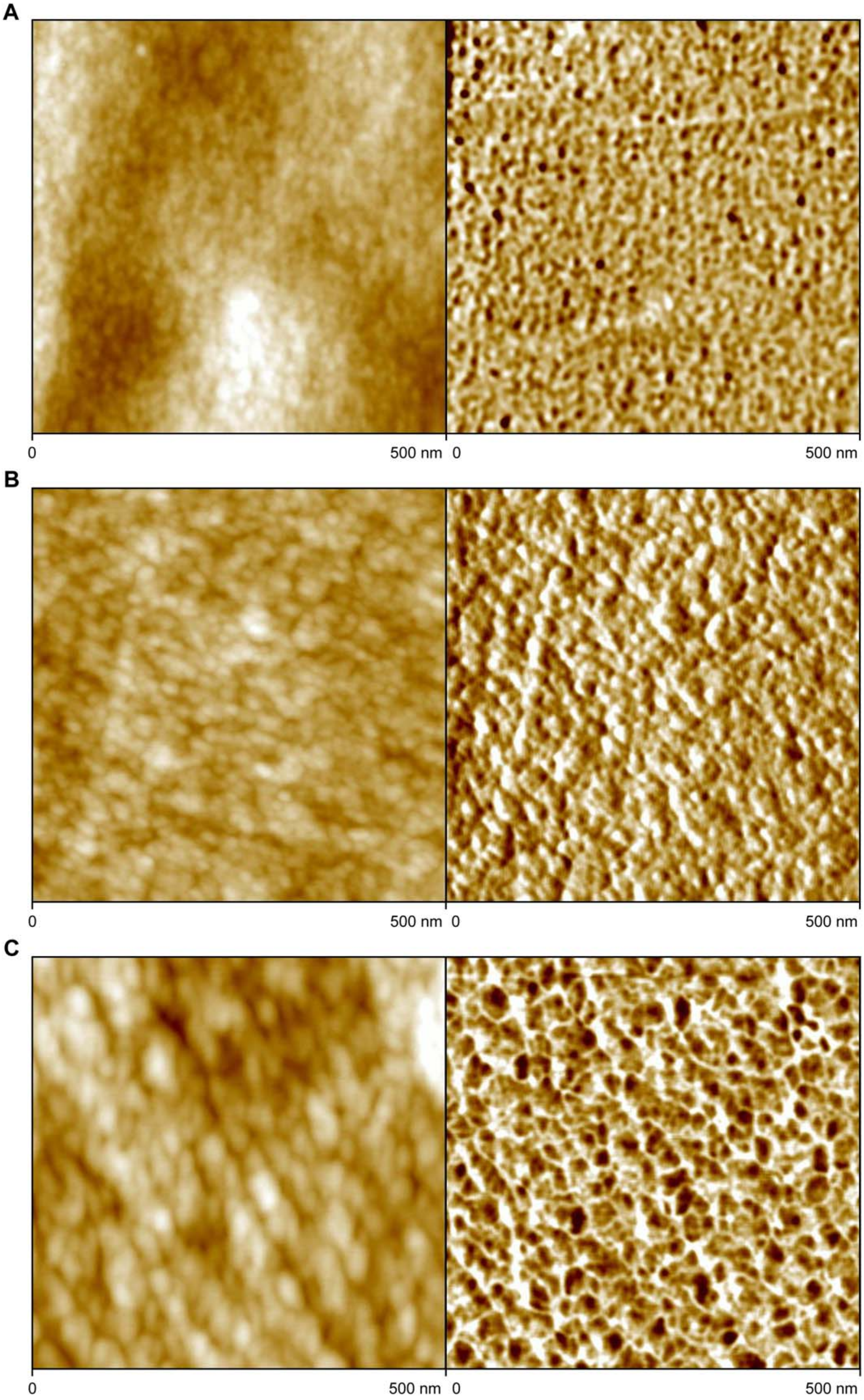


Fig. 6. The AFM images of the epoxy thermosetting blends with PEO-*b*-PCL cured with DDS. Left: topography, right: phase contrast. (A) 10 wt% of PEO-*b*-PCL, (B) 20 wt% of PEO-*b*-PCL and (C) 30 wt% of PEO-*b*-PCL.

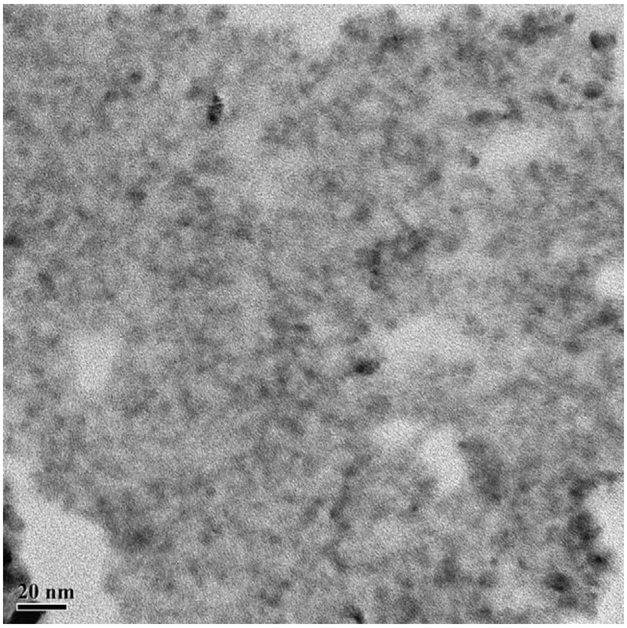


Fig. 7. The TEM micrograph of the epoxy thermosets cured with DDS containing 20 wt% of PEO-*b*-PCL.

the nanostructured thermosets are significantly broadened, which is in marked contrast to the control epoxy, suggesting the presence of microphase-separated structures. It is of interest to note that all the thermosets investigated did not exhibit the melting transition of PCL (and/or PEO) subchains, implying that the PCL (and/or PEO) subchains are not crystalline in the thermosets. It is proposed that the penetration of PEO subchains into epoxy matrix (*i.e.*, the PEO subchains are miscible with the epoxy networks) results in the non-crystallizability. The observation that PCL blocks in the PCL-rich microdomains were not crystalline could be responsible for the partial mixing with the DDS-crosslinked epoxy resin, which can further be confirmed by Fourier transform infrared spectroscopy (FTIR).

The Lorenz-corrected SAXS profiles for the thermosets containing 10, 20, 30 and 40 wt% PEO-*b*-PCL are presented in Fig. 9. A sharp scattering peak is found in the plot of Iq^2 as a function of q for the thermosetting blend containing 40 wt% PEO-*b*-PCL, indicating that the blend possessed a nanoscaled structure. It should be pointed that the SAXS maximum was not from the scattering of spherulitic lamellar of PCL since the DSC results have shown that all the nanostructured thermosets investigated did not display any crystallinity (see Fig. 8). According to the position of the primary scattering maximum the average distance ($L = 2\pi/q_m$) between neighboring domains can be estimated to be 27.4 nm. It is noted that no scattering peaks were found for the thermosetting blends containing 10, 20, and 30 wt% of PEO-*b*-PCL. It is proposed that the observation by no means indicates the homogeneity of the blends at these compositions. There could be the following two factors that resulted in the ''disappearance'' of the scattering peaks. The first situation could be related to the edge of the beam stop, *i.e.*, the positions of the scattering peaks could be beyond the limit of the instrument. The case implies that the average distances between neighboring domains are more than 40 nm according to the calculation of Bragg equation (*viz.* $L = 2\pi/q_m$). The second situation could be due to the lack of the sufficient difference in electronic density between the dispersed PCL-rich microdomains and the continuous epoxy matrix that was plasticized by PEO chains. However, the fact that the blend containing PEO-*b*-PCL of 40 wt% or more exhibited the well-defined scattering peaks (Fig. 9) indicates that the difference in

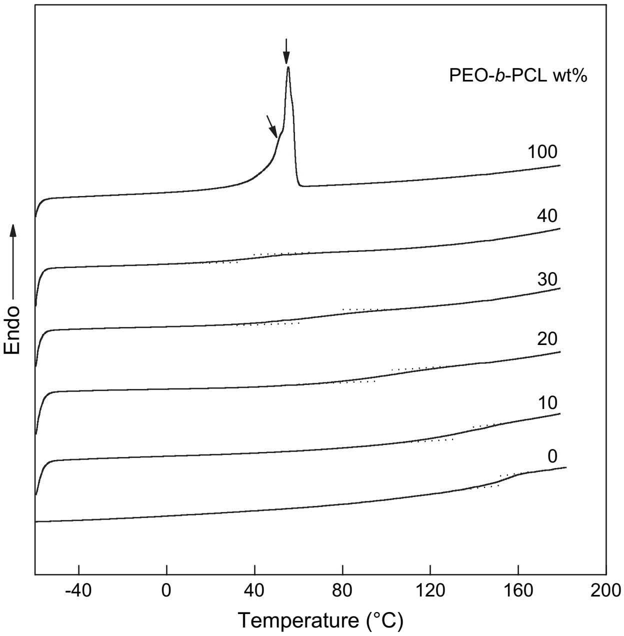


Fig. 8. The DSC curves of the epoxy thermosetting blends with PEO-*b*-PCL cured with DDS.

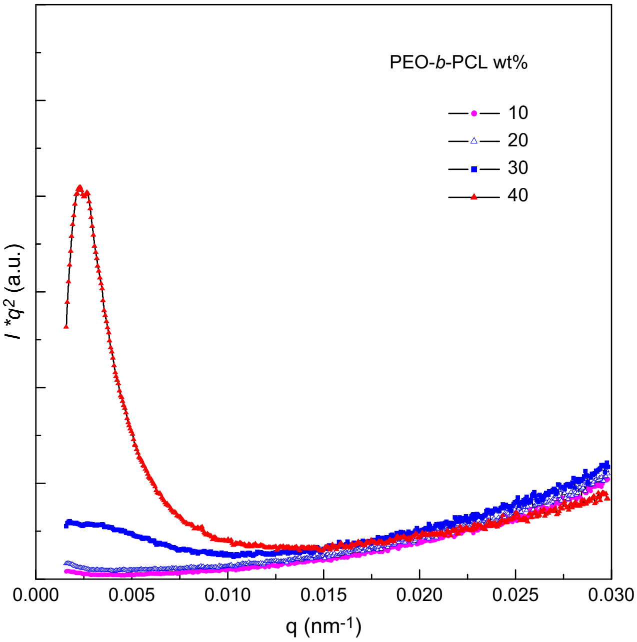


Fig. 9. The Lorenz-corrected SAXS profiles for the thermosets containing 10, 20, 30, and 40 wt% of PEO-*b*-PCL.

electronic density between the dispersed PCL-rich microdomains and the continuous epoxy matrix is sufficient to afford the X-ray scattering phenomenon. Therefore, it is judged that the "disappearance" of scattering peaks should be interpreted on the basis of the positions of scattering peaks. It should be pointed out that the average distances between neighboring domains calculated in terms of the position of scattering maximum unnecessarily correspond to those estimated from the AFM phase images since the two techniques detect the information on microphase behavior from different side views of structure. The former are obtained on the basis of electron density contrast between epoxy matrix and PCL-rich microdomains whereas the latter reflects the information about tip–sample interactions resulting from adhesion [39], surface stiffness [40] and viscoelastic effects [41–43]. Comparatively, the AFM results could be more sensitive to the transition region between PCL microdomains and epoxy matrix that were plasticized by PEO chains and thus the average distances between neighboring domains read from AFM phase images are a little higher than those calculated in terms of SAXS profiles. Nonetheless, AFM, SAXS and TEM results indeed indicate the formation of nanostructures in the epoxy thermosets containing PEO-*b*-PCL diblock copolymer when 4,4′-diaminodiphenylsulfone (DDS) was used as the curing agents.

3.4. Interpretation of morphologies

It has been reported by Horng and Woo that the binary blends of epoxy and PEO are miscible when DDS was used as the curing agent [36]. Our previous work [35] showed that the epoxy and PEO blends cured with MOCA are also miscible in terms of single glass transition behavior. The miscibility of the semi-interpenetrating polymer networks is ascribed to the formation of the strong intermolecular hydrogen bonding interactions between hydroxyl groups of the amine-cured epoxy and ether oxygen atoms of PEO. The inter-chain hydrogen bonding interactions were also responsible for the miscibility of binary epoxy blends with PCL when MOCA was used as the curing agent. However, the analyses of differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) showed that the intermolecular hydrogen bonding interactions between epoxy and PEO are much stronger than those between epoxy and PCL [37]. When 4,4′-diaminodiphenylsulfone (DDS) was used as the curing agent, the partial miscibility was found between epoxy and PCL. The partial miscibility was ascribed to the presence of intra-chain hydrogen bonding interactions between sulfonyl and hydroxyl groups within DDS-crosslinked epoxy resin, which could suppress the formation of the strong intermolecular hydrogen bonding interactions between carbonyls and hydroxyls of amine-cured epoxy [37]. In terms of the influence of curing agents on miscibility for epoxy and PCL (and/or PEO) blends, it is expected that the homogeneous and nanostructured epoxy thermosets can be prepared when PEO-*b*-PCL diblock copolymer is incorporated depending on the aromatic amines (*viz*., MOCA and DDS) used as the curing agents.

For the blends cured with MOCA, PCL subchains of the diblock copolymer did not separate out, *i.e*., the resulting thermosetting blends were homogeneous. The homogeneity was evidenced by the results of AFM and SAXS. The information on mixing degree of PCL subchains of the diblock copolymer with the crosslinked epoxy can be obtained in terms of Fourier transform infrared spectroscopy (FTIR). Shown in Fig. 10 are the FTIR spectra of PEO-*b*-PCL and the thermosets containing PEO-*b*-PCL in the range of 1680–1800 cm^{-1}. In this region, the infrared bands are ascribed to the stretching vibration of carbonyl groups ($>$C=O) in PCL blocks. At the room temperature, the carbonyl band of the PEO-*b*-PCL diblock copolymers consists of two components sensitive to the conformation of PCL chains. The one component centered at 1730 cm^{-1} is characteristic of amorphous chains of PCL whereas the sharp band at 1723 cm^{-1} is ascribed to the carbonyls in the crystalline region of PCL. Upon heating the block copolymer up to 80 °C, the band at 1723 cm^{-1} disappeared, indicating the fusion of PCL crystals. In the thermosets, the bands of the PCL crystals were absent, implying that PCL blocks exist in the amorphous state in the thermosets. There appeared new shoulders at the lower frequency of 1706 cm^{-1} in all the diblock copolymer-containing thermosets. The shoulder bands are ascribed to the stretching vibration of the hydrogen-bonded carbonyls. 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 $F^{\mathrm{f}}_{\mathrm{co}}$ is the fraction of the non-associated carbonyl bands, calculated from the values of absorbency for the associated and the non-associated band contributions:

$$F^{\mathrm{f}}_{\mathrm{co}} = \frac{A_{\mathrm{f}}}{A_{\mathrm{f}} + \left(\varepsilon_{\mathrm{f}}/\varepsilon_{\mathrm{a}}\right)A_{\mathrm{a}}} \tag{1}$$

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 $\varepsilon_{\mathrm{f}}/\varepsilon_{\mathrm{a}}$ for the non-associated and associated carbonyl bands. Using the $\varepsilon_{\mathrm{f}}/\varepsilon_{\mathrm{a}}$ 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. [44,45], we calculated the fraction of non-associated carbonyl bands. The variation of $F^{\mathrm{f}}_{\mathrm{co}}$ as a function of temperature is shown in Fig. 11. It is worth noticing that the fractions of hydrogen-bonded carbonyl for the DDS-cured blends of epoxy with PEO-*b*-PCL are fairly lower than those for the MOCA-cured counterparts, suggesting that in the DDS-cured system there are more carbonyl groups of PCL subchains that remain unassociated with hydroxyl groups of epoxy. In another words, the PCL subchains were only partially mixed with the crosslinked epoxy matrix. It is the difference in miscibility that creates the nanostructure of epoxy thermosets. In the DDS-cured epoxy containing PEO-*b*-PCL, the PCL-rich microdomains are dispersed in the continuous epoxy matrix at the nanometer scale whereas the PEO subchains of the diblock copolymer remain miscible

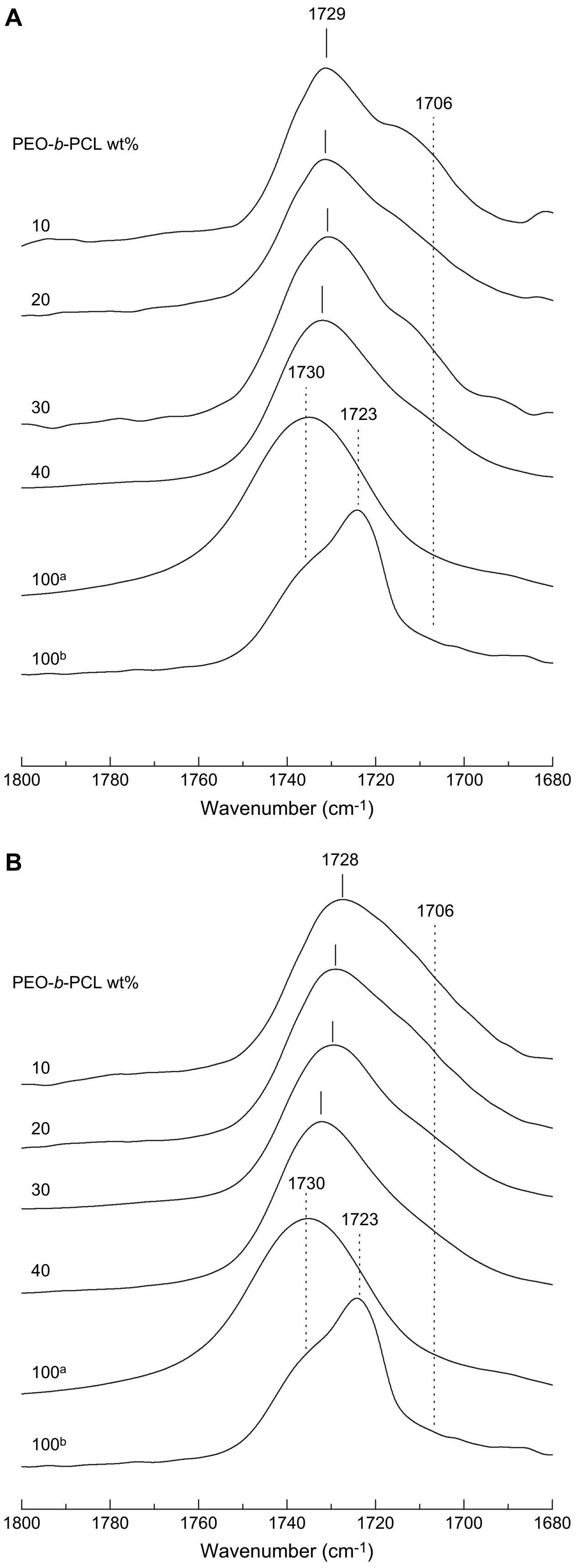


Fig. 10. The FTIR spectra of epoxy resin/PEO-*b*-PCL blends in the range of 1680–1800 cm^{-1}. (A) MOCA-cured and (B) DDS-cured blends. a: at 80 °C and b: at room temperature.

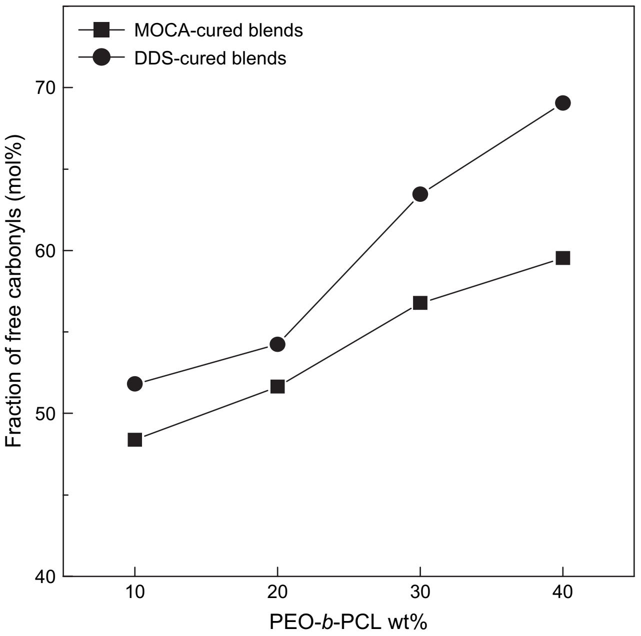


Fig. 11. The plots of fractions of unassociated carbonyl groups as functions of the diblock copolymer for MOCA- and DDS-cured epoxy/PEO-*b*-PCL blends.

with the crosslinked epoxy matrix. The formation of the nanostructures should be attributed to reaction-induced microphase separation, which is in marked contrast to the mechanism of self-assembly [3,4].

4. Conclusions

PEO-*b*-PCL diblock copolymer was incorporated into epoxy thermosets. It is found that the formation of nanostructures of thermosetting blends is quite dependent on the uses of aromatic amine hardeners, which were used for the thermosetting systems. For MOCA-crosslinked thermosetting system, the homogeneous morphology was obtained with the compositions investigated. Nonetheless, the nanostructured thermosets were obtained when the blends were cured with DDS. The DSC results showed that the nanostructured thermosets did not displayed any crystallinity although the subchains of the diblock copolymer are crystalline. The nanostructures were evidenced by means of AFM, SAXS and TEM. The dependence of morphological structures on the types of aromatic amines for epoxy and PEO-*b*-PCL thermosetting blends were interpreted on the basis of the difference in hydrogen bonding interactions resulting from the structure of the curing agents. Considering the complete miscibility of the subchains (*viz.* PEO and PCL) with the precursors of epoxy resin before curing, it is judged that the formation of the nanostructures in the thermosets follows the mechanism of reaction-induced microphase separation, which is in marked contrast to the mechanism of self-assembly, *i.e.*, micelle structures of block copolymers are formed prior to curing, followed by fixing of these nanostructures *via* curing.

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References

[1] Pascault JP, Williams RJJ. In: Paul DR, Bucknall CB, editors. Polymer blends, vol. 1. New York: Wiley; 2000. p. 379−415.
[2] Guo Q. In: Shonaik GO, Simon G, editors. Polymer blends and alloy. New York: Marcel Dekker; 1999. p. 155−87 [chapter 6].
[3] Hillmyer MA, Lipic PM, Hajduk DA, Almdal K, Bates FS. J Am Chem Soc 1997;119:2749.
[4] Lipic PM, Bates FS, Hillmyer MA. J Am Chem Soc 1998;120:8963.
[5] Mijovic J, Shen M, Sy JW, Mondragon I. Macromolecules 2000;33:5235.
[6] Guo Q, Thomann R, Gronski W. Macromolecules 2002;35:3133.
[7] Guo Q, Thomann R, Gronski W. Macromolecules 2003;36:3635.
[8] Ritzenthaler S, Court F, Girard-Reydet E, Leibler L, Pascault JP. Macromolecules 2002;35:6245.
[9] Ritzenthaler S, Court F, Girard-Reydet E, Leibler L, Pascault JP. Macromolecules 2003;36:118.
[10] Kosonen H, Ruokolainen J, Nyholm P, Ikkala O. Macromolecules 2001;34:3046.
[11] Kosonen H, Ruokolainen J, Nyholm P, Ikkala O. Polymer 2001;42:9481.
[12] Kosonen H, Ruokolainen J, Torkkeli M, Serimaa R, Nyholm P, Ikkala O. Macromol Chem Phys 2002;203:388.
[13] Grubbs RB, Dean JM, Broz ME, Bates FS. Macromolecules 2000;33:9522.
[14] Rebizant V, Abetz V, Tournihac T, Court F, Leibler L. Macromolecules 2003;36:9889.
[15] Dean JM, Verghese NE, Pham HQ, Bates FS. Macromolecules 2003;36:9267.
[16] Rebizant V, Venet AS, Tournillhac F, Girard-Reydet E, Navarro C, Pascault JP, et al. Macromolecules 2004;37:8017.
[17] Dean JM, Grubbs RB, Saad W, Cook RF, Bates FS. J Polym Sci Part B Polym Phys 2003;41:2444.
[18] Wu J, Thio YS, Bates FS. J Polym Sci Part B Polym Phys 2005;43:1950.
[19] Guo Q, Dean JM, Grubbs RB, Bates FS. J Polym Sci Part B Polym Phys 2003;41:1994.
[20] Zucchi IA, Galante MJ, Williams RJJ. Polymer 2005;46:2603.
[21] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.
[22] Meng F, Zheng S, Zhang W, Li H, Liang Q. Macromolecules 2006;39:711.
[23] Guo Q, Wang Z, Peng X. Polymer 1991;32:53.
[24] Luo X, Zheng S, Zhang N, Ma D. Polymer 1994;35:2619.
[25] Noshay A, Robeson LM. J Polym Sci Part A Polym Chem 1974;12:689.
[26] Clark JN, Daly JH, Garton A. J Appl Polym Sci 1984;29:3381.
[27] Chen JL, Chang F-C. Macromolecules 1999;32:5348.
[28] Vanden Poel G, Goossens S, Goderis B, Groeninckx G. Polymer 2005;46:10758.
[29] Remiro PM, Cortazar MM, Calahorra ME, Calafel MM. Macromol Chem Phys 2001;202:1077.
[30] Guo Q, Harrats C, Groeninckx G, Koch MHJ. Polymer 2001;42:4127.
[31] Guo Q, Harrats C, Groeninckx G, Reynaers H, Koch MHJ. Polymer 2001;42:6031.
[32] Guo Q, Groeninckx G. Polymer 2001;42:8647.
[33] Zheng S, Zheng H, Guo Q. J Polym Sci Part B Polym Phys 2003;41:1085.
[34] Zheng S, Guo Q, Chan C-M. J Polym Sci Part B Polym Phys 2003;41:1099.
[35] Yin M, Zheng S. Macromol Chem Phys 2005;206:929.
[36] Horng TJ, Woo EM. Polymer 1998;39:4115.
[37] Ni Y, Zheng S. Polymer 2005;46:5828.
[38] Bogdanov B, Vidts A, Van Den Bicke A, Verbeeck R, Schacht E. Polymer 1999;39:1631.
[39] Schmitz I, Schreiner M, Friedbacher G, Grasserbauer M. Appl Surf Sci 1997;115:190.
[40] Magonov SN, Elings V, Whangbo MH. Surf Sci 1997;375:L385.
[41] Tamayo A, Garcia R. Langmuir 1996;12:4434.
[42] Chen X, McGurk SL, Davies MC, Roberts CJ, Shakesheff KM, Davies J, et al. Macromolecules 1998;31:2278.
[43] Clarke S, Davies MC, Roberts CJ, Tendler SJB, Williams PM, Lewis AL, et al. Macromolecules 2001;34:4166.
[44] Coleman MM, Graf JF, Painter PC. Specific interactions and the miscibility of polymer blends. Lancaster, PA: Technomic Publishing; 1991.
[45] Hu Y, Motze HR, Etxeberria AM, Fernandez-Berridi HJ, Iruin JJ, Painter PC, et al. Macromol Chem Phys 2000;201:705.