Transesterification in Homogeneous Poly(ε-caprolactone)–Epoxy Blends

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ABSTRACT: Transesterification has been investigated in poly(ε-caprolactone) (PCL)–epoxy blends. In the hot melt process, the hydroxyl on diglycidyl ether of bisphenol-A (DGEBA) monomers is too low to give a noticeable transesterification reaction. In the postcure process, model reactions reveal that the hydroxyls from a ring-opening reaction are able to react with the esters of PCL. In the meantime, the PCL molecular weight decrease and its distribution becomes broader. Nuclear magnetic resonance spectra reveal that fraction of the tertiary hydroxyls converts to secondary hydroxyls. In the cured DGEBA–3,3′-dimethylmethylene-di(cyclohexylamine)–PCL blend, a homogeneous morphology is achieved. PCL segments are grafted onto the epoxy network after postcuring and result in the lower T_g observed in the differential scanning calorimetry thermogram. A higher transesterification extent also results in broader transition peaks by dynamic mechanical analysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 75–82, 1999

Key words: epoxy; poly(ε-caprolactone); transesterification

INTRODUCTION

Transesterification between polymers have been often used to prepare multiblock copolymers in a rather uncontrolled way.[1] Interchange reactions can take place between ester and hydroxyl groups in the presence of a catalyst or at a high temperature.[2,3] In the phenoxy-polyester blends, the extent of such interchange reactions can be controlled by the processing temperature and time.[4,5] After a prolonged interchange reaction, an immiscible binary blend eventually becomes a uniform random-copolymer structure.

Several polyester–epoxy blends have been studied previously. A high dissolving temperature of some crystalline polyesters, such as liquid crystalline polymers (LCP),[6–12] inhibits the use of hot melt process in dissolving these crystalline polyesters into epoxy monomers. Poly(butylene terephthalate) (PBT) has been incorporated into epoxy networks by either a hot melt or a solution process.[13–19] Cured PBT–epoxy products with homogeneous and heterogeneous morphologies have been reported.[18,19] However, the transesterification between hydroxyl groups from the ring-opened epoxy and the ester groups on PBT at a high temperature of melt dissolving process and at high curing temperatures has virtually been ignored. Our previous studies[20–25] on polycarbonate (PC)–epoxy blends cured with various curing agents revealed that transesterification indeed occurred in these systems. PCL is able to act as a polymeric plasticizer for many polymers.[26] The hydrogen bonding between the network hydroxyls and the ester of PCL results in a homogeneous epoxy–poly(ε-caprolactone) (PCL) blend cured by an amine at a temperature above the PCL melting temperature.[27] Alternatively, a heteroge-

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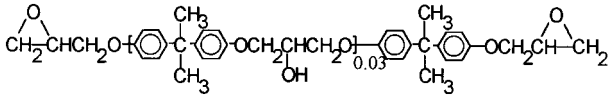
neous morphology was obtained when the same epoxy–PCL blend was cured by an anhydride. An epoxy resin containing hydroxyl groups was modified by the ring-opening polymerization of the ε-caprolactone onto the hydroxyl groups.[28,29] The modified epoxy resin was further combined with anhydride or amine to give a curable composition. Both the modified resin and the compositions are useful in coating.

Since PCL has a relatively lower melting temperature (63°C), it can be dissolved in most epoxy monomers easily. During the hot melt process at 150°C, the possible transesterification between the hydroxyl groups from the epoxy monomer and the ester groups from the PCL has been investigated in this study. Monofunctional epoxy is utilized to model the reactions involved in this system. The effects of transesterification on thermal properties of the cured products are also examined.

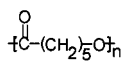
EXPERIMENTAL

Materials

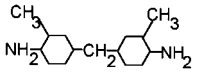
The epoxy monomer, DER 332, purchased from the Dow Chemical Company, is a low-molecular-weight liquid diglycidyl ether of bisphenol-A (DGEBA) with a epoxide equivalent weight of 172–176. PCL used in this study is TONE® Polymer P-787 purchased from the Union Carbide Corporation with an M_n equal to 80,000. The aliphatic amine used as a hardener is the 3, 3′-dimethylmethylene-di(cyclohexylamine) (C-260) from the BASF. Monofunctional epoxy, phenyl glycidyl ether (PGE), was purchased from the Tokyo Chemical Industry Co. The chemical structures of epoxy, PCL, C-260, and PGE are illustrated as follows:



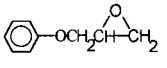
DGEBA (DER 332)



PCL



C-260



PGE

Blending Procedures

The homogeneous mixture of PCL–epoxy equal to 30/70 % by weight was firstly prepared by a hot melt process at 150°C under nitrogen gas for 1 h. After cooling to 100°C, a calculated amount of additional epoxy resin and hardener were added to bring the mixture to the desired composition. The mixture was then cast immediately into steel molds for primary curing in an oven for 2 h at 100°C. These products were postcured at 150, 175, or 200°C for 5 additional hours, respectively. For model reaction, mixtures of PGE–C-260–PCL equal to 60/24/12 % by weight and 60/24/1200 % by weight were prepared by the same procedure.

Characterizations

0.5% by weight solution of the PGE–C-260–PCL blend was prepared in tetrahydrofuran (THF) and analyzed by gel permeation chromatography (GPC) at a 40°C column temperature and a 1.0 mL/min flowing rate. Characterization by Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet 520 spectrometer in the transmission mode with a resolution of 4 cm^{-1}. Samples were pasted onto salt disks and mounted on a temperature-controlled disk holder of the FTIR instrument. FTIR spectra were taken after heating the sample at desired temperature and time. Nuclear magnetic resonance (NMR) analysis was measured with a Bruker-DRX 300 NMR spectrometer. The PGE–C-260–PCL equal to 60/24/12 % by weight blend diluted by deuterated chloroform ($CDCl_3$) was used to observe the ^{1}H-NMR spectra. The glass transition temperature (T_g) of the cured blend was determined by differential scanning calorimetry (DSC) using a heating rate of 10°C/min in the dynamic scan. Dynamic mechanical analysis (DMA) of the cured sample was performed on a TA Instruments DMA 983 using a heating rate of 5°C/min. A Hitachi model S-570 scanning electronic microscope (SEM) was employed to examine the morphology of the fracture surface.

RESULTS AND DISCUSSIONS

Blending Process

Dissolving PCL in the DER 332 epoxy resin by a high-temperature (150°C), hot melt method resulted in a homogeneous and viscous solution. After cooling to room temperature, the PCL crystallized from the solution, and the whole mixture became a white solid mass. By comparing the GPC, retention times of the pure PCL and the

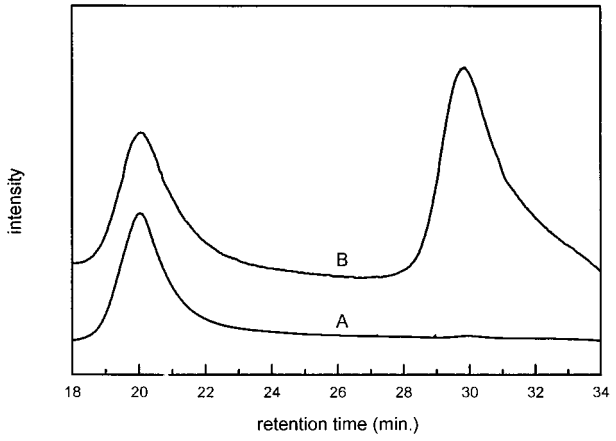


Figure 1 GPC chromatograms of (A) neat PCL and (B) PCL–DER 332 equal to a 30/70 mixture.

PCL–DER 332 equal to a 30/70 mixture (Fig. 1), the retention time of the PCL component in the PCL–DER 332 blend is identical to the pure PCL. That means that the molecular weight of PCL does not change during the hot melt process. Curve (A) of Figure 2 shows the carbonyl absorption (1734 cm^{-1}) of the neat PCL at 100°C. Curve

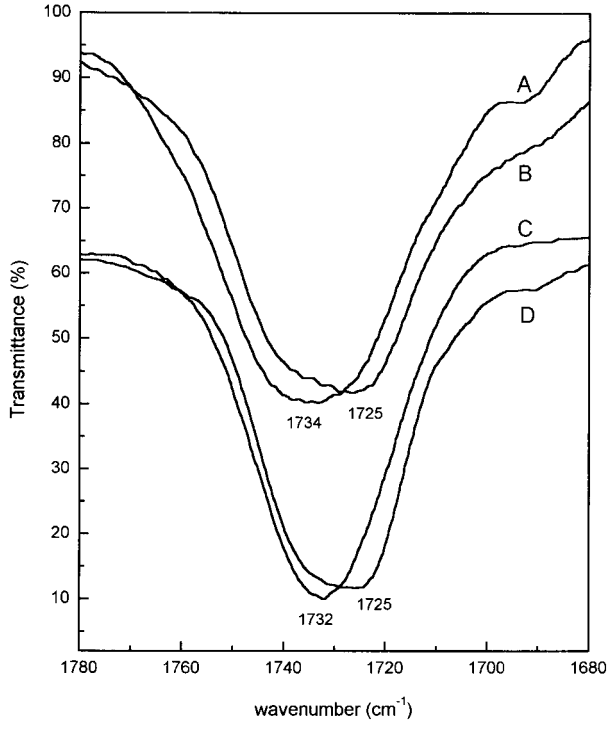


Figure 2 The carbonyl stretching absorption in the FTIR spectra of (A) neat PCL at 100°C, (B) neat PCL at 25°C, (C) PCL–DER 332 equal to 30/70 at 100°C, and (D) PCL–DER 332 equal to 30/70 at 25°C.

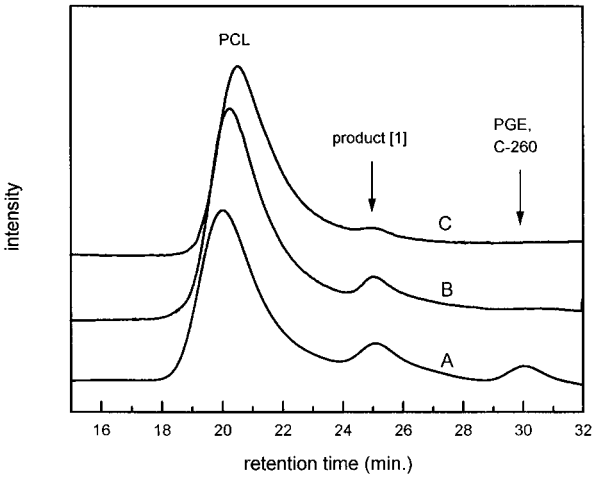


Figure 3 GPC chromatograms of PGE–C-260–PCL equal to the 60/24/1200 blend: (A) 100°C for 2 h, (B) 100°C for 2 h, then 200°C for 2 h, and (C) 100°C for 2 h, then 200°C for 5 h.

(B) gives the spectrum at room temperature when most of the PCL is crystallized, and the absorption at 1725 cm^{-1} corresponds to the oriented carbonyl in crystal lattice. Curves (C) and (D) in Figure 2 display the absorptions of PCL–DER 332 blend at 100°C and room temperature, respectively, giving the same trend as the pure PCL, except for reduced band widths. PCL in the PCL–DER 332 solution has a higher mobility to orientate itself to a more ordered state and results in

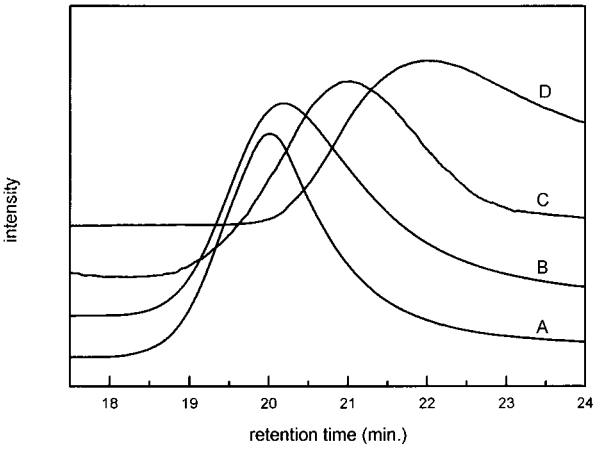


Figure 4 PCL absorptions in GPC chromatograms of (A) neat PCL, (B) PGE–C-260–PCL equal to 60/24/12 after postcuring at 150°C for 5 h, (C) PGE–C-260–PCL equal to 60/24/12 after postcuring at 175°C for 5 h, and (D) PGE–C-260–PCL equal to 60/24/12 after postcuring at 200°C for 5 h.

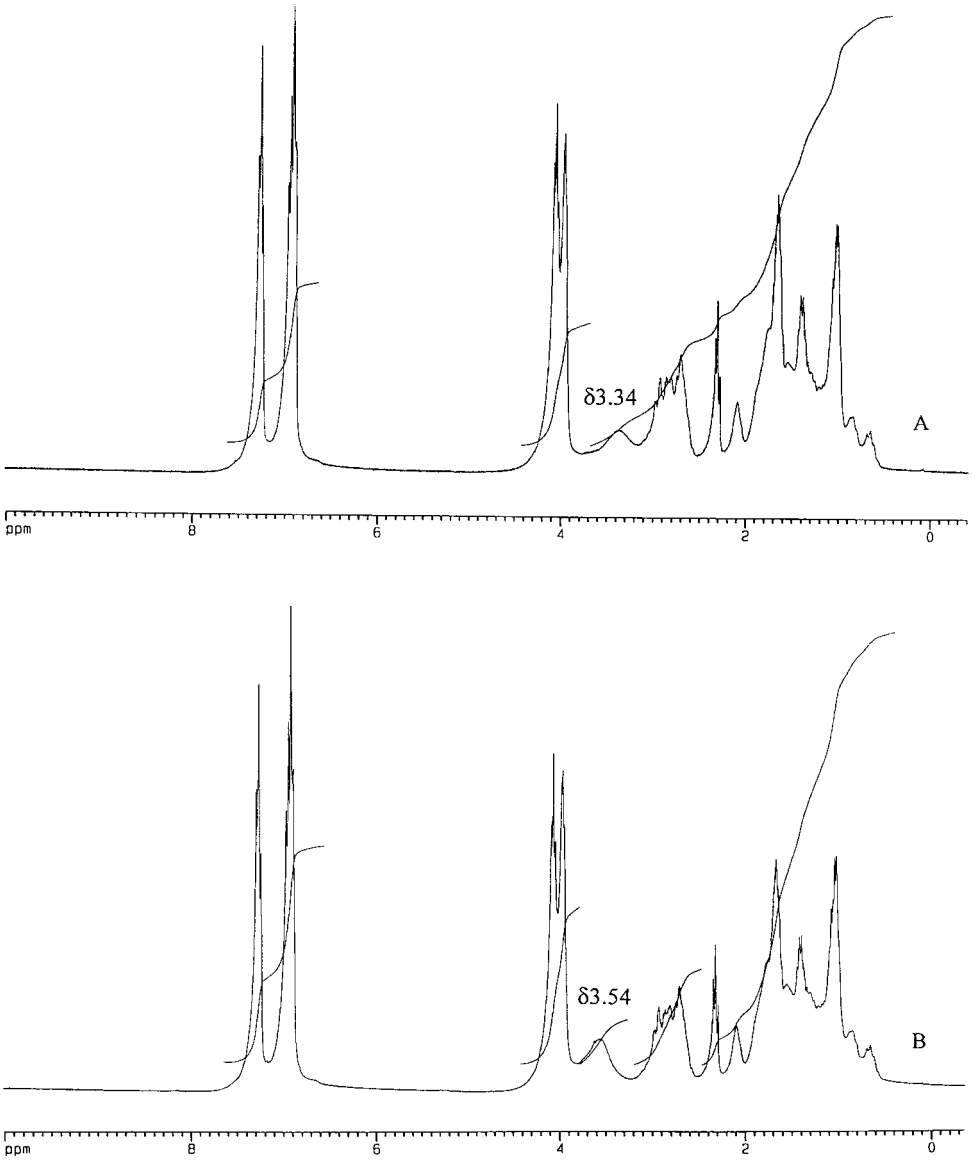
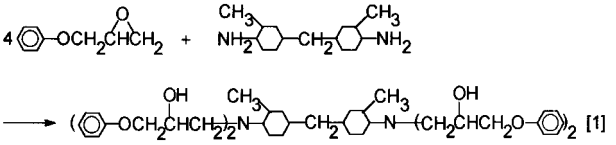


Figure 5 ^{1}H-NMR spectra of PGE–C-260–PCL equal to 60/24/12 postcured at (A) 150°C or (B) 200°C for 5 h.

narrow band widths of the absorption peaks. Therefore, only physical interaction is involved in this system, and no chemical reaction occurs in the hot melting process.

Model Reactions

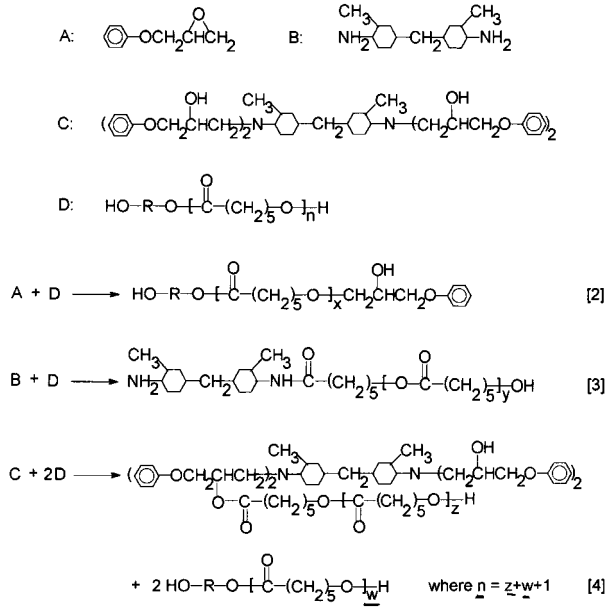
Figure 3 illustrates the GPC chromatograms of the PGE–C-260–PCL equal to a 60/24/1200 mixture that was initially cured at 100°C for 2 h and then at 200°C for an additional 2 and 5 h. When this PGE–C-260–PCL mixture is heated at 100°C for 2 h [Fig. 3, curve (A)], the retention time of the PCL peak remains unchanged at 20 min. The peak at 25 min retention time corresponds to the product from the PGE–C-260 (equal equivalent ratio) mixture after a ring-opening reaction.



Residual of the unreacted reactants are still present in this product at a 30-min retention

time. PGE and C-260 cannot be distinguished by this GPC chromatography. The quantity of the unreacted reactants and this ring-opening product decrease gradually during the postcure process [Fig. 3, curves (B) and (C)]. Meanwhile, the PCL peak shifts to higher retention time (reduced PCL molecular weight). After heating at 200°C for 5 h, only a very small amount this ring-opening product is left while the PCL peak shifts to an even higher retention time. This observation implicates that the molecular weight of PCL is reduced during postcuring in addition to the above reaction.

Figure 4 illustrates the GPC chromatograms of this PGE–C-260–PCL equal to a 60/24/12 mixture after postcuring at 150, 175, and 200°C for 5 h, respectively. The stoichiometric ratio of this mixture is equal to that of DER 332–C-260–PCL equal to 64/24/12. Compared to the peak of the neat PCL [Fig. 4(A)], the PCL molecular weight distribution shifts to a longer retention time with the increase of postcuring temperature [curves (B) to (D)]. This phenomenon implicates that the PCL molecular weight is reduced and the distribution is broadened. Data from Figures 3 and 4 indicate that at a high temperature, the unreacted epoxy and amine may react with PCL as equations (2) and (3). Meanwhile, transesterification of these ring-opened epoxy–amine oligomers scissor PCL chains during postcuring, as shown in equation (4). Copolymers composed of PCL segment, PGE, and C-260 hardener are formed during postcuring. The possible reactions involved are shown as follows:



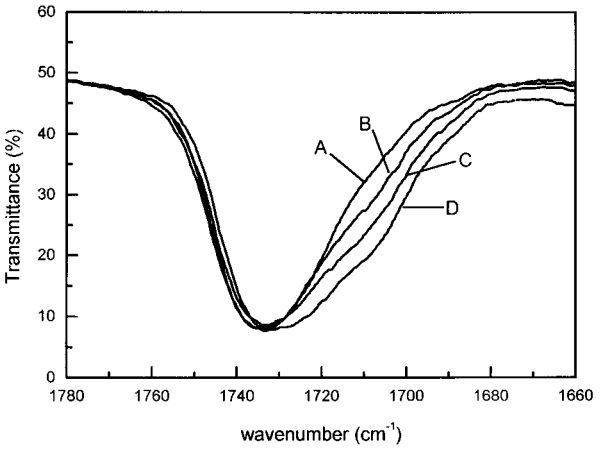
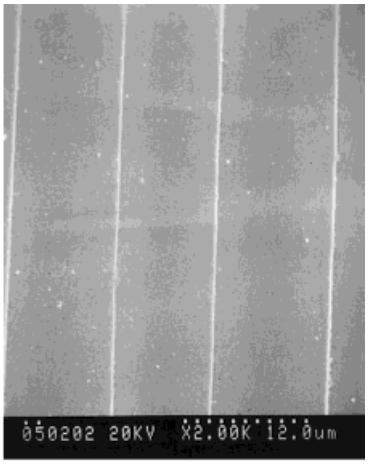


Figure 6 The carbonyl stretching absorption in FTIR spectra of the DER 332–C-260–PCL equal to 64/24/12: (A) 100°C for 2 h, primary curing; (B) 100°C for 2 h then 150°C for 5 h postcuring; (C) 100°C for 2 h, then 175°C for 5 h postcuring; (D) 100°C for 2 h, then 200°C for 5 h postcuring.

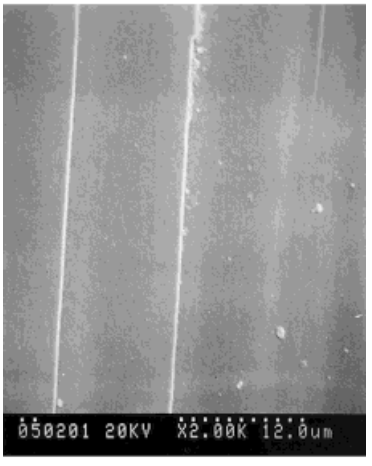
In equation (4), there are 4 tertiary hydroxyls on (C) and 1 secondary hydroxyl chain end on (D) (PCL) (excluding —R—OH) as the potential sites for transesterification. After transesterification, a fraction of tertiary hydroxyls convert to the secondary hydroxyls on the scissored PCL chain end. Hence, the transesterification leads to the increase of the secondary hydroxyls and the decrease of the tertiary hydroxyls. In ^{1}H-NMR spectra, the broad peak centering at δ3.34 represents the mixture containing the tertiary and the secondary hydroxyls postcured at 150°C [Fig. 5(A)]. A higher postcuring temperature (200°C) leads to the greater transesterification extent; thus, the quantity ratio of the tertiary to secondary hydroxyls decreases. This variation results in the broad peak of the hydroxyls shifting to δ3.54 [Fig. 5(B)], which is consistent with the proposed mechanism.

The Cured Epoxy–PCL Blends

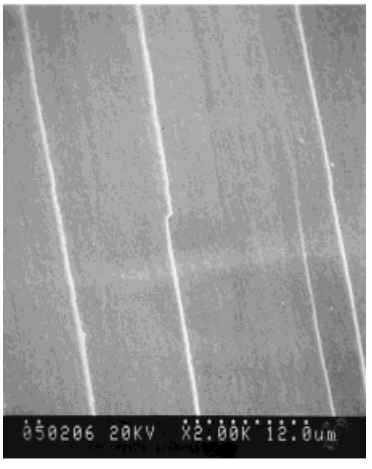
Figure 6 shows FTIR spectra in the carbonyl stretching range of the DER 332–C-260–PCL equal to 64/24/12 blend before and after postcuring at different temperatures. The shoulder at a lower wave number than 1734 cm^{-1} increases with the increase of the postcure temperature. Additional fraction of the hydroxyls of the opened epoxy network is consumed during this transesterification reaction, and another carbonyl with different substituents from the original PCL is



(A)



(B)



(C)

Figure 7 SEM micrographs taken on the fracture surfaces of DER 332–C-260–PCL equal to 64/24/12 postcured at (A) 150°C or (B) 175°C or (C) 200°C for 5 h.

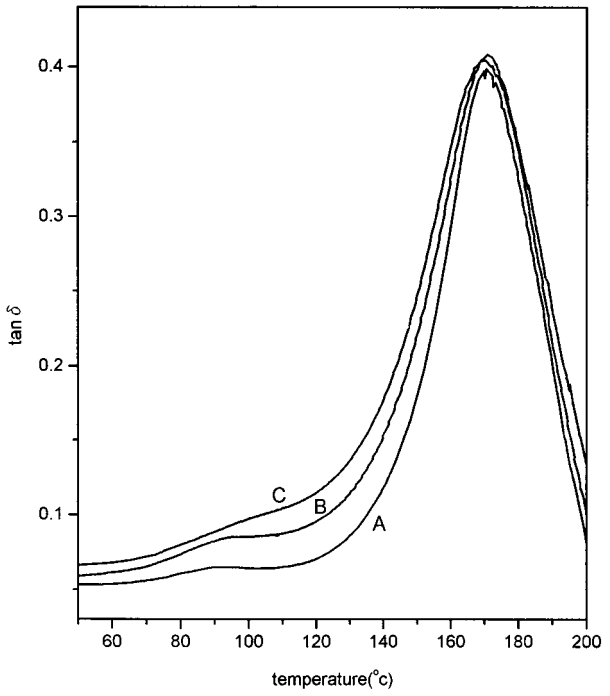


Figure 8 DMA spectra of DER 332–C-260–PCL equal to 64/24/12 postcured at (A) 150°C, or (B) 175°C or (C) 200°C for 5 h.

produced. A portion of these original ester groups from the PCL linking to the methylene is converted to that linking to the methine. The methine is able to stabilize the carbonyl more effectively than the methylene; therefore, the stretching energy of C═O double bond reduction induced by the methine is more significant than that by the methylene. The growth of the shoulder at a lower wave number implicates more ester linking to the methine. A higher heating temperature leads to a higher extent of the transesterification, thus, a higher fraction of the ester connecting to the methine of the epoxy network.

SEM micrographs in Figure 7 display that DER 332–C-260–PCL equal to the 64/24/12 blend remain homogeneous after postcuring at different temperatures. The results observed in model reactions can be applied to these DER 332–C-260–PCL blends. DMA spectra (Fig. 8) indicate that a higher transesterification extent from a higher postcure temperature leads to a broader α-transition peak. Curve (A) displays an evident α-transition at about 170°C and a smaller β-transition peak at 90°C. From curve (A) (150°C) to curve (C) (200°C), this small β-transition peak gradually shifts to a higher temperature and eventually

Table I Glass Transition Temperature (°C) of DER 332–C-260–PCL Blends Postcured at 150, 175, or 200°C for 5 H

	PCL Content				
Temperature	0 Wt %	3 Wt %	6 Wt %	9 Wt %	12 Wt %
150°C postcured	172.1	168.8	165.7	162.2	155.6
175°C postcured	178.3	166.0	158.0	154.6	146.0
200°C postcured	182.2	164.1	154.3	152.2	141.3

combines with the main α-transition peak at curve (C). Transesterification results in a uniform chemical structure composed of the PCL and the PCL-containing epoxy network. The softer parts (PCL segments) reduce the initiating temperature of relaxation. Hence, a broader tan δ peak is observed in the specimens of higher transesterification extent.

Table I lists the glassy transition temperatures (T_gs) of various DER 332–C-260–PCL compositions and postcure temperatures. For the pure epoxy (PCL equal to 0% by weight), the higher postcuring temperature results in higher conversion and a higher T_g, as would be expected. At a relatively lower postcuring temperature (150°C), T_g reduction with the increase of PCL content is less substantial (from 172.1 to 155.6°C). At higher postcuring temperatures (175 and 200°C), T_g reductions are more drastic (178.3 to 146.0°C and 182.2 to 141.3°C). This can be interpreted as more soft PCL segments linking to the rigid epoxy network at higher postcuring temperature and, thus, results in lower T_g.

CONCLUSIONS

Homogeneous DER 332–C-260–PCL blends are obtained after initial curing at 100°C and postcuring at higher temperatures. Model reactions using monofunctional epoxy provide the evidence that transesterification reaction indeed occurs during the postcuring step. This result can be applied to the cured epoxies. After transesterification, PCL chains are scissored into segments and grafted onto the epoxy network. These grafted PCL segments influence the thermal properties of the epoxy network more significantly than by the semi-IPN structure. The broader glass transition behavior observed corresponds to the PCL graft–network structure.

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