

# Transesterification and cyclization of polycarbonate–epoxy blends cured with anhydride

Ming-Shiu Li, Yi-Feng Su and Chen-Chi M. Ma\*

*Institute of Chemical Engineering, National Tsing Hua University, Hsin-Chu 30043, Taiwan, R.O.C.*

and Jyh-Luen Chen, Ming-Shiu Lu and Feng-Chih Chang

*Institute of Applied Chemistry, National Chiao Tung University, Hsinchu 30043, Taiwan, R.O.C.*

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Infrared spectra have been investigated to study the curing mechanisms of polycarbonate–epoxy blends using anhydride as a hardener catalysed by tertiary amine. Due to a significant difference in the reaction, curing reactions of the system can be considered as two sequential stages: (1) an anionic alternating copolymerization of cyclic anhydride and epoxy resin, and (2) a homopolymerization of oxirane initiated by a quaternary ammonium salt zwitter ion. The transesterification/cyclization of carbonate groups proceeds in the later stage if the oxirane is still available. Degrees of transesterification/cyclization and homopolymerization are higher when a higher epoxy/anhydride ratio is used. This study positively confirms the mechanism of transesterification/cyclization proceeding through a zwitter ion. The zwitter ion is formed from epoxide and tertiary amine, which attacks the carbonate group. Copyright © 1996 Elsevier Science Ltd.

(Keywords: epoxy; blend; polycarbonate)

## INTRODUCTION

Interaction of carboxylates with oxiranes has been the subject of numerous investigations<sup>1–6</sup>. Funahashi<sup>1</sup> studied the ring opening reactions of oxirane with aryl carboxylates catalysed by tertiary amine, and concluded that the reaction proceeds through zwitter ions,  $R_3N^+CH_2CH(R')O^-$  and  $R_3N^+CH(R')CH_2O^-$ . Nishikubo *et al.*<sup>2</sup> investigated the addition reaction of the pendant epoxy groups with active esters using quaternary salts as accelerators, and proposed the formation of intermediates containing epoxide, ester and quaternary salts. Komarova *et al.*<sup>3</sup> synthesized the polymers from the reaction of oxirane ring and ester groups, and proposed an 'insertion' mechanism of the oxirane ring into the ester bond without scission of the polyester molecular chain. However, relatively little research has been carried out on the interaction of carbonates with oxiranes such as polycarbonate (PC)–epoxy blends. Most prior studies were carried out by adding polycarbonate into epoxy simply as a toughening modifier, and had rarely considered the chemical reactions involved between the epoxide and the carbonate groups of polycarbonate. Yu *et al.*<sup>4</sup> studied the transesterification reaction between carbonate and epoxide resulting in a PC–epoxy crosslinked network structure. Abbate *et al.*<sup>5</sup> utilized FTi.r. spectroscopy to study the PC–epoxy blends cured with nadic methyl anhydride and tertiary

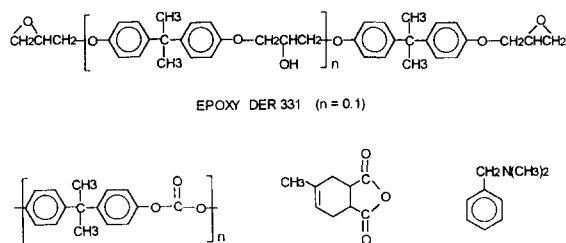
amine as accelerator and reported that the presence of PC does not affect the overall curing mechanism. In our previous study on PC–epoxy blends cured by tertiary amine, the transesterification reaction converted the original aromatic/aromatic carbonate into aromatic/aliphatic and aliphatic/aliphatic carbonates, and a cyclic carbonate structure eventually formed in the later stages of the reaction<sup>6</sup>. The formation mechanism of the cyclic carbonate was assumed to proceed through a zwitter ion and a nucleophile attacking the aromatic/aliphatic or the aliphatic/aliphatic carbonate group. In this study, a PC–epoxy blend system using anhydride as hardener catalysed by tertiary amine is reported. I.r. results indicate that this system is similar to that cured by tertiary amine, which also involves the transesterification/cyclization reactions.

## EXPERIMENTAL

### Materials

The epoxy prepolymer used in this study is DER 331 which is the low molecular weight liquid diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent weight of 188. The polycarbonate used in this study is Calibre 301-15 with a melting index of 15. Both PC and epoxy were purchased from Dow Chemical Company (USA). The hardener used is Lindride 32 (methyl tetrahydrophthalic anhydride, METHPA) which was purchased from Lindau Chemicals Inc. (USA). The tertiary amine used as accelerator is benzyl dimethyl amine (BDMA), purchased from Aldrich Chemical Co. (USA).

\*To whom correspondence should be addressed



**Procedures and instrumentation**

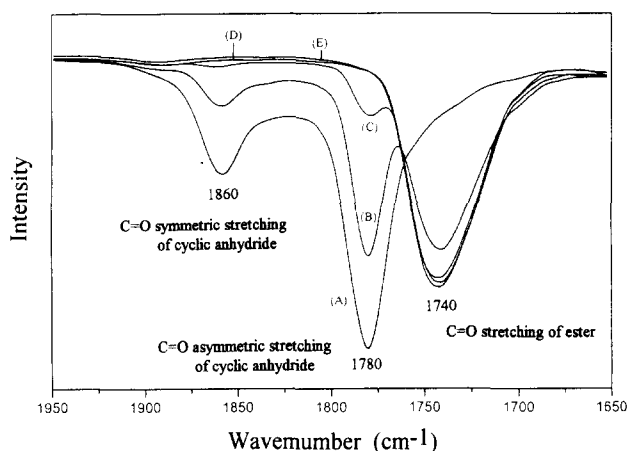
Before dissolving PC into epoxy, both PC and epoxy were dehydrated at 120°C for 24h under vacuum. Polycarbonate (25 phr) was dissolved into the epoxy resin at 220°C by stirring for 1 h under dry nitrogen gas. The resulting solution was clear, homogeneous and viscous. When the mixture is cooled to room temperature, various amounts of METHPA and 2 phr BDMA were added and mixed using a high torque stirrer. One drop of mixture was removed and pasted between two sodium chloride plates which were then mounted on a sample holder in the i.r. instrument. Infrared spectra were obtained on a Perkin-Elmer 842 infrared spectrometer with a resolution of 2.4 cm<sup>-1</sup> using transmission mode. Spectra recorded at elevated temperature were obtained using a heating cell mounted inside the sample chamber. The glass transition temperature of the blend was determined by a Du Pont differential scanning calorimeter (DSC 10) with a heating rate of 10°C min<sup>-1</sup>. The various blend compositions investigated, together with their codes, are listed in Table 1.

**RESULTS AND DISCUSSION**

*Study on the finished product of PC-epoxy blends*

Figure 1 shows the infrared spectra of the epoxy/METHPA/BDMA (100 : 50 : 2) (R50, Table 1) system in

the carbonyl stretching regions during the progress of curing. This system contains excess oxirane (27.2 mol%, Table 2) relative to anhydride. Comparing curve A with curve B shows that the absorptions of C=O symmetric and asymmetric stretch at 1860 and 1780 cm<sup>-1</sup> decrease substantially after 60 min at 80°C. The intensity increase at 1740 cm<sup>-1</sup> is due to the formation of the ester group. The variations of these spectra can be explained as an anionic alternating copolymerization of the epoxide/anhydride/tertiary amine system. The anhydride is believed to undergo a nucleophilic attack by the unbonded electron pair of the tertiary amine to form the quaternary ammonium salt zwitter ion which then reacts with epoxide to yield an alkoxide anion. The alkoxide anion is followed by attacking the anhydride to yield a carboxylate anion, which then repeatedly reacts



**Figure 1** Infrared spectra of the unmodified epoxy system (R50) in the carbonyl stretching region: (A) initial at 80°C, (B) 60 min at 80°C, (C) 120 min at 80°C, (D) 180 min at 80°C, and (E) 300 min at 80°C, 120 min at 100°C and 120 min at 120°C

**Table 1** The compositions and codes of the PC-epoxy blends

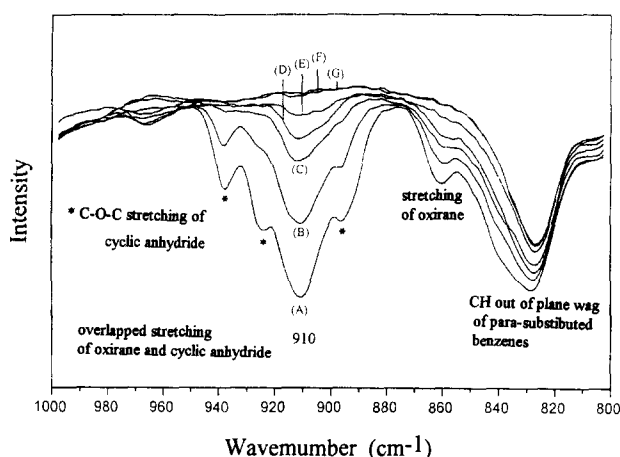
Code	Epoxy	METHPA	BDMA	PC	Epoxy + METHPA + BDMA (wt%)	PC (wt%)
R0	100	0	2	0	100	0
R30	100	30	2	0	100	0
R50	100	50	2	0	100	0
R80	100	80	2	0	100	0
R100	100	100	2	0	100	0
C <sub>6</sub> 0	100	0	2	6.51	94	6
C <sub>6</sub> 30	100	30	2	8.43	94	6
C <sub>6</sub> 50	100	50	2	9.70	94	6
C <sub>6</sub> 80	100	80	2	11.62	94	6
C <sub>6</sub> 100	100	100	2	12.89	94	6
C <sub>12</sub> 0	100	0	2	13.91	88	12
C <sub>12</sub> 30	100	30	2	18.00	88	12
C <sub>12</sub> 50	100	50	2	20.73	88	12
C <sub>12</sub> 80	100	80	2	24.82	88	12
C <sub>12</sub> 100	100	100	2	27.55	88	12

R is the virgin epoxy system not blended with PC  
 C<sub>6</sub> is the PC-epoxy blend system with PC content 6 wt%  
 C<sub>12</sub> is the PC-epoxy blend system with PC content 12 wt%  
 0, 30, 50, 80 or 100 is the phr of METHPA in the blend

**Table 2** The mole ratio of functional groups of the PC-epoxy blends

Code	Oxirane (mol%)	Anhydride (mol%)	Oxir.-Anhy. (mol%)	Carbonate (mol%)	[Anhr.]/[Oxir.]	[Carb.]/[Oxir.-Anhy.]
R0	100.0	00.00	100	0.00	0.00	0.00
R30	74.44	25.56	48.88	0.00	0.34	0.00
R50	63.60	36.40	27.20	0.00	0.57	0.00
R80	52.20	47.80	4.40	0.00	0.92	0.00
R100	46.63	53.37	-6.74	0.00	1.14	0.00
C <sub>6</sub> 0	75.36	00.00	95.36	4.64	0.00	0.06
C <sub>6</sub> 30	71.11	24.41	46.70	4.48	0.34	0.10
C <sub>6</sub> 50	60.80	34.79	26.01	4.41	0.57	0.17
C <sub>6</sub> 80	49.94	45.73	4.21	4.33	0.92	1.03
C <sub>6</sub> 100	44.62	51.08	-6.46	4.30	1.14	-0.66
C <sub>12</sub> 0	90.57	00.00	90.57	9.43	0.00	0.10
C <sub>12</sub> 30	67.66	23.23	44.43	9.11	0.34	0.20
C <sub>12</sub> 50	57.89	33.13	24.76	8.98	0.57	0.36
C <sub>12</sub> 80	47.59	43.57	4.02	8.83	0.92	2.20
C <sub>12</sub> 100	42.54	48.69	-6.15	8.77	1.14	-1.43

See Table 1 for explanation of codes



**Figure 2** Infrared spectra of the unmodified epoxy system (R50) in the oxirane stretching region: (A) initial at 80°C, (B) 60 min at 80°C, (C) 120 min at 80°C, (D) 180 min at 80°C, (E) 300 min at 80°C, 120 min at 100°C and 120 min at 120°C, (F) 300 min at 80°C, 120 min at 100°C, 120 min at 120°C, 120 min at 150°C and 120 min at 180°C, and (G) 300 min at 80°C, 120 min at 100°C, 120 min at 120°C, 120 min at 150°C, 120 min at 180°C and 300 min at 200°C

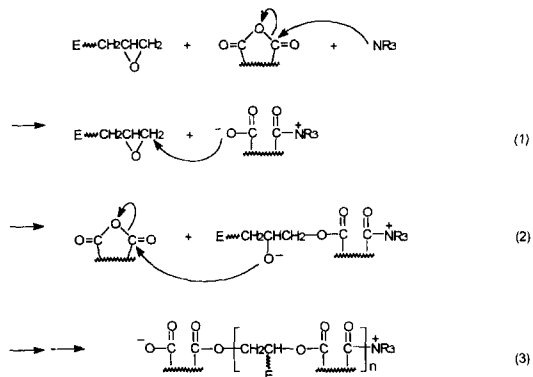
with an epoxide to yield an alkoxide anion<sup>7</sup>. After 180 min at 80°C, the anhydride of the system has been completely converted to ester (curve D).

Figure 2 presents the spectra of the same system as Figure 1 near the oxirane stretching regions of the epoxy. The absorption at 910 cm<sup>-1</sup> is contributed by the overlapping of absorption peaks of oxirane and anhydride. Curve A of Figure 2 is the spectrum at the beginning of reaction. Curve B shows that the band decreased substantially after 60 min. After 180 min at 80°C, the anhydride of the system has been completely converted to ester, confirmed by curve D in Figure 1. Therefore, the absorption at 910 cm<sup>-1</sup> of curve D in Figure 2 is the absorption of oxirane, which indicates that after 180 min, the alternating copolymerization is completed. Curve F in Figure 2 shows that the oxirane

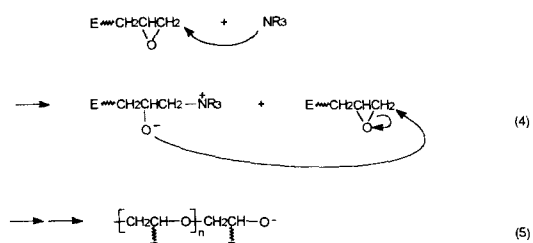
peak disappears, and curve G shows no further change was detected thereafter. This phenomenon can be interpreted as the homopolymerization of the oxirane groups of the epoxy resin during the later stages of curing. The tertiary amine attacks the oxirane to form a quaternary ammonium salt zwitter ion, which then reacts with the residual oxirane to yield an alkoxide anion. The alkoxide anion then reacts with other oxirane to complete the homopolymerization. The homopolymerization of oxirane competes with the copolymerization of epoxy/anhydride/tertiary amine during the curing procedure, however, the reactivity of homopolymerization is significantly lower than that of copolymerization<sup>8</sup>. Therefore, the curing reaction of the system can be considered as two sequential stages: (1) an anionic alternating copolymerization of cyclic anhydride and epoxy resin, and (2) a homopolymerization of oxirane initiated by a quaternary ammonium salt zwitter ion. The mechanisms of the copolymerization of epoxy/anhydride/tertiary amine and the homopolymerization of oxirane are shown in Scheme 1.

Figure 3(I) shows the aromatic/aromatic carbonate absorption peak of polycarbonate at 1775 cm<sup>-1</sup>. Curve A of Figure 3(II) shows the spectra of the C<sub>12</sub>80 composition (epoxy/METHPA/BDMA/PC, 100:80:2:24.82). The system contains only a slight excess of epoxy over the anhydride (4%, as illustrated in Table 2). After 300 min at 80°C and 120 min at 100°C, the absorption peaks at 1860 and 1780 cm<sup>-1</sup> have been reduced significantly and the band at 1745 cm<sup>-1</sup> is apparent (curve C). The 1745 cm<sup>-1</sup> band is the characteristic band of the ester group formed in the reaction between epoxy and METHPA. The 1780 cm<sup>-1</sup> band is due to the overlapping of the absorption peaks of polycarbonate and anhydride. Curing proceeded after 300 min at 80°C, 120 min at 100°C, 120 min at 120°C and 120 min at 150°C, the absorption of C=O symmetric stretch from the METHPA at 1860 cm<sup>-1</sup> disappeared completely (curve D, Figure 3(II)). At this stage of curing, the absorption of C=O asymmetric stretch contributed from the METHPA at 1780 cm<sup>-1</sup> should also disappear at the

COPOLYMERIZATION



HOMOPOLYMERIZATION



Scheme 1 Copolymerization of epoxy/anhydride/tertiary amine and the homopolymerization of oxirane

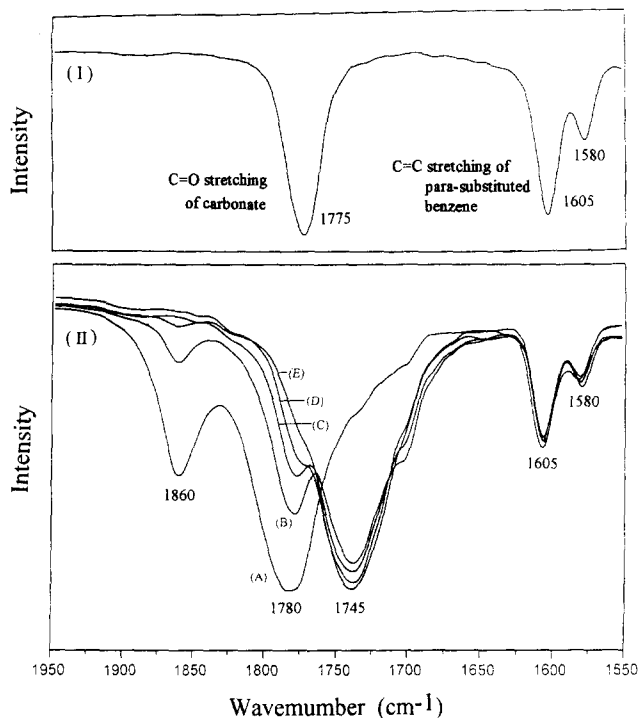


Figure 3 (I) Infrared spectrum of polycarbonate in the carbonyl stretching region. (II) Infrared spectra of PC-epoxy blend with 12 wt% PC (C<sub>12</sub>80) in the carbonyl stretching region: (A) initial at 80°C, (B) 180 min at 80°C, (C) 300 min at 80°C and 120 min at 100°C, (D) 300 min at 80°C, 120 min at 100°C, 120 min at 120°C and 120 min at 150°C, and (E) 300 min at 80°C, 120 min at 100°C, 120 min at 120°C, 120 min at 150°C, 120 min at 180°C and 300 min at 200°C

same time. The band shown at 1775 cm<sup>-1</sup> should be the one contributed solely by the carbonyl group of polycarbonate (curve D). As curves D and E reveal, the intensity of the band at 1775 cm<sup>-1</sup> is gradually reduced.

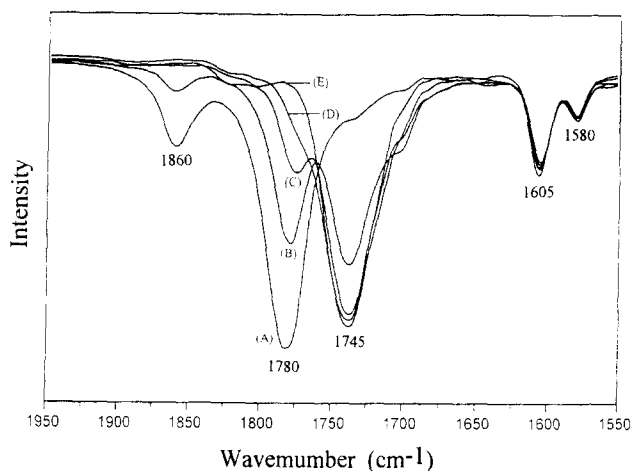


Figure 4 Infrared spectra of PC-epoxy blend with 12 wt% PC (C<sub>12</sub>50) in the carbonyl stretching region: (A) initial at 80°C, (B) 60 min at 80°C, (C) 120 min at 80°C, (D) 300 min at 80°C and 120 min at 100°C, and (E) 300 min at 80°C, 120 min at 100°C, 120 min at 120°C, 120 min at 150°C, 120 min at 180°C and 300 min at 200°C

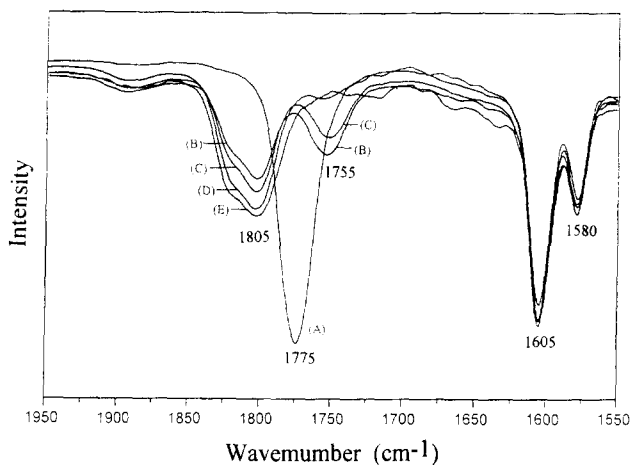


Figure 5 Infrared spectra of PC-epoxy blend with 12 wt% PC (R0) recorded in the carbonyl stretching region: (A) initial at 80°C, (B) 60 min at 80°C, (C) 300 min at 80°C, (D) 300 min at 80°C, 120 min at 100°C and 120 min at 120°C, and (E) 300 min at 80°C, 120 min at 100°C, 120 min at 120°C, 120 min at 150°C, 120 min at 180°C and 300 min at 200°C

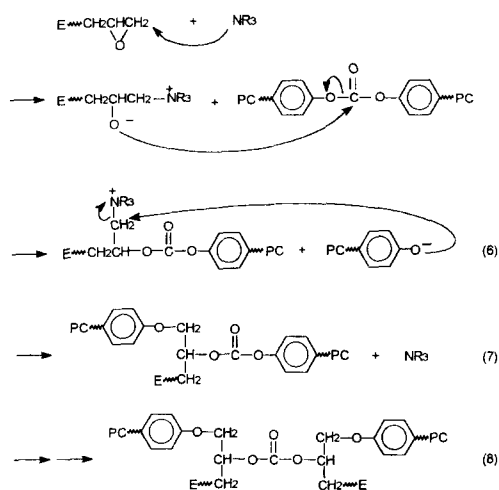
Figure 4 shows the spectra of the C<sub>12</sub>50 composition (epoxy/METHPA/BDMA/PC, 100:50:2:20.73), which are similar to those of R50 (epoxy/METHPA/BDMA/PC, 100:50:2:0) except the presence of 12 wt% PC. Comparing with the previous C<sub>12</sub>80 system, the C<sub>12</sub>50 system contains excessive epoxy relative to METHPA (24.76%, as illustrated in Table 2). Curve A presents the initial spectrum of the epoxide/anhydride/tertiary amine/PC system where the bands at 1860 and 1780 cm<sup>-1</sup> are characteristic of METHPA. Curve C shows that the band at 1860 cm<sup>-1</sup> disappeared completely, an indication of complete consumption of METHPA. Therefore, the remaining peak at 1775 cm<sup>-1</sup> of curve C is the absorption band mainly from the carbonate group of PC. From curves D and E, the absorption band of carbonyl stretching converts to a broad band near 1805 cm<sup>-1</sup>.

Figure 5 gives the spectra of the C<sub>12</sub>0 system, as illustrated in Table 1, which has a composition with no METHPA (epoxy/METHPA/BDMA/PC,

**Table 3** Characteristic i.r. bands of carbonyl groups

Band (cm <sup>-1</sup> )	Assignment	Ref.
1776	C=O stretch of Ar-O-CO-O-Ar	9
1762	C=O stretch of Ar-O-CO-O-R	9
1746	C=O stretch of R-O-CO-O-R	9
1865	C=O symmetric stretch of anhydride	7
1785	C=O asymmetric stretch of anhydride	7
1740	C=O stretch of ester	7

**TRANSESTERIFICATION**

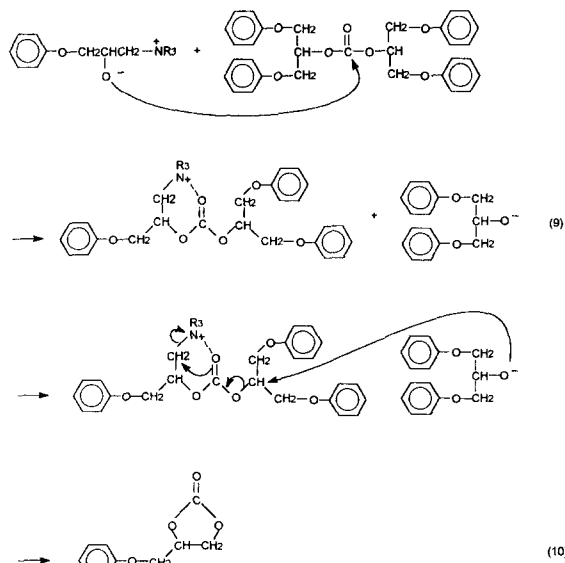


**Scheme 2** Transesterification mechanism

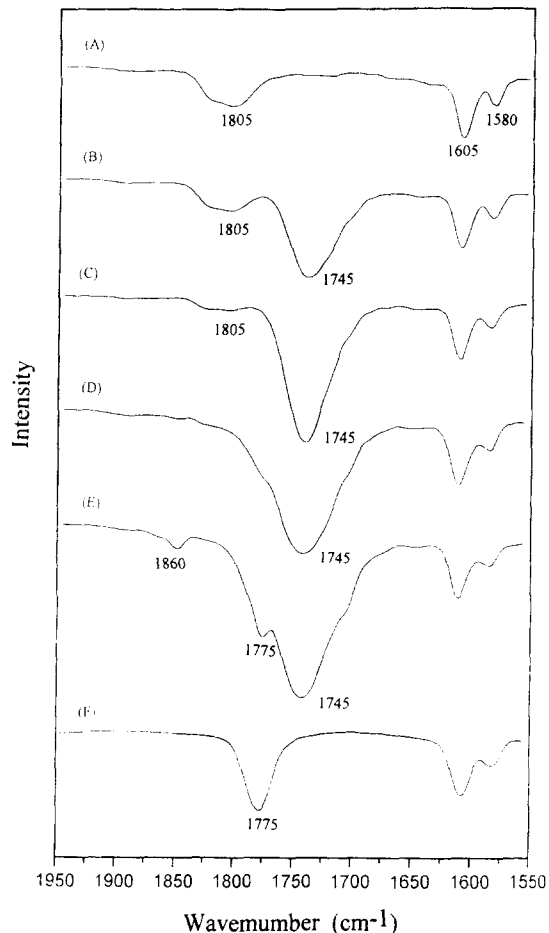
100:0:2:13.91), by varying the reaction time of the system. Curve A shows the absorption band of the carbonate group of polycarbonate at 1775 cm<sup>-1</sup>. Curve B shows that the carbonyl absorption band splits into two bands, 1755 and 1805 cm<sup>-1</sup>. Curves B and C show the band intensity decreases at lower frequencies (1755 cm<sup>-1</sup>), while increasing at higher frequency band (1805 cm<sup>-1</sup>). The shift of absorption of the carbonate at 1775 to 1755 cm<sup>-1</sup> can be interpreted as the transesterification reaction, converting the original carbonate group of the PC between two aromatic nuclei Ar-O-CO-O-Ar, into either one aromatic and one alkyl group Ar-O-CO-O-R or two alkyl groups R-O-CO-O-R by the zwitter ion. Table 3 lists the infrared carbonyl band parameters reported previously<sup>7,9</sup>. The mechanism of transesterification is illustrated in Scheme 2.

After post-curing, the intensity of the higher frequency absorption band increases drastically, while the band intensity at 1755 cm<sup>-1</sup> decreases gradually then disappears (curves C-E). This phenomenon has been studied by a model reaction using diphenyl carbonate and phenyl glycidyl ether, leading to the formation of a cyclic carbonate, 4-phenoxy-methyl-1,3-dioxolane-2-one (PMD)<sup>10</sup>. In other words, a cyclic carbonate structure can be formed from the cyclization of the carbonate substituted with an alkyl group(s). The mechanism to form the cyclic carbonate is assumed to proceed through a zwitter ion and a nucleophile attack of the aromatic/aliphatic or the aliphatic/aliphatic carbonate group. It must be emphasized that this cyclization requires the presence of oxirane in order to form the zwitter ion. That

**CYCLIZATION**



**Scheme 3** Cyclization mechanism to form cyclic carbonate



**Figure 6** Infrared spectra of PC-epoxy blend with 12 wt% PC in the carbonyl stretching region: (A) C<sub>12</sub>0, (B) C<sub>12</sub>30, (C) C<sub>12</sub>50, (D) C<sub>12</sub>80, (E) C<sub>12</sub>100, and (F) pure PC

means excess epoxy related to METHPA in the feed is essential to proceed with this cyclization reaction. The cyclization mechanism is illustrated in Scheme 3.

Comparing Figure 5 with Figures 3(II) and 4, we can assume that the carbonyl group at 1775 cm<sup>-1</sup> is split into

two bands, 1755 and 1805  $\text{cm}^{-1}$ , which is due to the transesterification/cyclization reaction. Another characteristic feature of the spectra from this epoxy/anhydride/tertiary amine/polycarbonate system is that the transesterification/cyclization reaction occurs mainly during the later stage of homopolymerization. The phenomenon observed is consistent with the previously proposed mechanism of transesterification/cyclization proceeding through a zwitter ion by tertiary amine and oxirane<sup>10</sup>. An approach to verify this mechanism was made by varying the epoxy/anhydride ratio of the epoxy/anhydride/tertiary amine system (Table 2). Curves A-E of Figure 6 show the i.r. spectra of the end products of the PC-epoxy blends with various epoxy/anhydride ratios ( $C_{12}0$ ,  $C_{12}30$ ,  $C_{12}50$ ,  $C_{12}80$  and  $C_{12}100$ , Table 2). Curve F of Figure 6 represents the i.r. absorption of PC. By comparing curves A-C of Figure 6, the intensity of absorption at 1805  $\text{cm}^{-1}$  decreases with decreasing epoxy/anhydride ratio, an indication of a decrease of the homopolymerization fraction. With only a slight excess of epoxy relative to anhydride, curve D of Figure 6 shows the presence of the unreacted carbonate absorption of PC, while the absorption of cyclic carbonate at 1805  $\text{cm}^{-1}$  is not present. This phenomenon can be explained by the cyclic carbonate not being obtained in significant amount from the composites with higher mole ratio of oxirane to anhydride and carbonate. The low fraction of homopolymerization indicates the depletion of the oxirane for possible cyclization reaction to occur. In other words, only some transesterification reactions occurred, thus decreasing the carbonate absorption at 1775  $\text{cm}^{-1}$  (curve D of Figure 6). Curve E of Figure 6 shows the i.r. spectrum of the reaction product from the PC-epoxy blended with slight excess anhydride relative to oxirane where the carbonate absorption of the unreacted PC is higher than that in curve D.

Figure 7 represents the spectra during curing progress for the  $C_{12}100$  composite with excess anhydride relative to oxirane ( $C_{12}100$ , Table 1). The absorption band at 1860  $\text{cm}^{-1}$  indicates that residual METHPA existed and the band at 1745  $\text{cm}^{-1}$  represents the ester formed. The

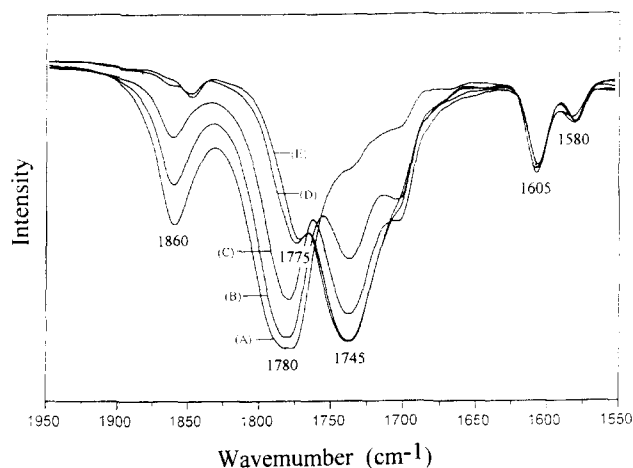


Figure 7 Infrared spectra of PC-epoxy blend with 12wt% PC ( $C_{12}100$ ) in the carbonyl stretching region: (A) initial at 80°C, (B) 60 min at 80°C, (C) 180 min at 80°C, (D) 300 min at 80°C, 120 min at 100°C, 120 min at 120°C, 120 min at 150°C and 120 min at 180°C, and (E) 300 min at 80°C, 120 min at 100°C, 120 min at 120°C, 120 min at 150°C, 120 min at 180°C and 300 min at 200°C

1775  $\text{cm}^{-1}$  band is due to the overlapping band of polycarbonate and anhydride as mentioned earlier. However, no absorption band of cyclic carbonate at 1805  $\text{cm}^{-1}$  could be detected. Abbate *et al.*<sup>5</sup> studied PC-epoxy blended with excess anhydride, the i.r. spectra they obtained also confirmed that the carbonyl group of PC does not participate in the curing process and they did not detect any cyclic carbonate formation as would be expected. These results demonstrate that the system with a higher copolymerization content relative to homopolymerization tends to reduce the degree of transesterification due to the decrease of the residual oxirane to react with tertiary amine to proceed with the transesterification/cyclization.

The characteristic feature of these results is the drastic difference in reaction rate of copolymerization, homopolymerization, transesterification and cyclization. From the reaction mechanism mentioned above, the copolymerization, homopolymerization and transesterification actually compete with each other. However, the evidence of the experimental results shows that the reactivities of homopolymerization and transesterification are significantly lower than that of copolymerization. This assumption can be proved by investigating the spectrum of curve D, Figure 6. The composition for this spectrum is  $C_{12}80$ , and the mole ratio of oxirane to anhydride is 1.09, near the stoichiometric ratio of pure copolymerization. If the reactivities of homopolymerization and transesterification are not significantly less than the copolymerization, then these reactions will consume a noticeable portion of the oxirane during the first stage of curing (copolymerization), and the anhydride should be in oversupply. However, no absorption of the residual anhydride at 1860  $\text{cm}^{-1}$  can be detected. For the same reason, the reactivity of transesterification is less than the homopolymerization, otherwise the shoulder at 1775  $\text{cm}^{-1}$  which indicates the existence of original PC carbonate would not appear. As the substrate of cyclization is the product of transesterification, there is no doubt that cyclization should occur at the latest stage of curing.

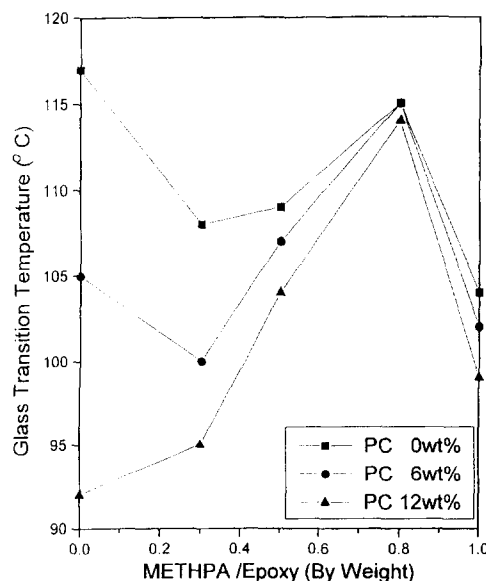


Figure 8 Glass transition temperatures of the blending systems at various polycarbonate contents

The glass transition temperatures ( $T_g$ ) of the finished products of all the blending systems measured by differential scanning calorimetry (d.s.c.) are shown in Figure 8. The  $T_g$  of the blending system decreases with increasing polycarbonate content. All of the  $T_g$ s of these blending systems are lower than that of the pure polycarbonate. These data do not fit the predictions of the Fox relationship. This predicts that the  $T_g$  of an ideal polymer blend is between the pure components<sup>11</sup>. A reasonable explanation is that the transesterification reaction occurs, hence the epoxy was inserted into the polycarbonate, or a chain end was formed in the network in the cyclization reaction. Both reactions may change the chemical structure and decrease the crosslink density of the original system. Thus, increasing the homopolymerization fraction would increase the cyclization reaction and decrease the  $T_g$  of the PC-epoxy blend. For example, the  $T_g$  of the C<sub>12</sub>0 system is 25°C lower than that of the R0 system. The  $T_g$ s of the C<sub>12</sub>30 and C<sub>12</sub>50 systems are 15 and 5°C lower than those of R30 and R50, respectively. The  $T_g$  of the C<sub>12</sub>80 system is almost the same as those of C<sub>6</sub>80 and R80. This result can be explained from the i.r. spectrum (curve D of Figure 6) that there is only a low degree of transesterification reaction and so the cyclization reaction does not occur. However, the  $T_g$  of the blended system which uses excess anhydride decreases with increasing PC content. Although the presence of PC does not affect the overall curing mechanism, it may decrease the final conversion of reactants<sup>5</sup>. The reduced conversion causes a deviation from the Fox law, even the original PC carbonyl group does not transesterificate with the epoxy. These phenomena cause the  $T_g$  of the PC-epoxy blend to be lower than that of the pure components.

## CONCLUSIONS

The curing reaction of the epoxy/anhydride/tertiary amine system can be considered as two sequential stages: (1) an anionic alternating copolymerization of cyclic anhydride and epoxy resin, and (2) a homopolymerization of oxirane. The transesterification/cyclization

reactions in the PC-epoxy blends occur during the later stages of curing. A mechanism has been proposed to explain the formation of the cyclic carbonate compound by proceeding through a zwitter ion followed by a nucleophile attack at the aliphatic/aliphatic carbonate group. Conversion of transesterification/cyclization increases with increasing fraction of homopolymerization. This result confirms that the mechanism of transesterification/cyclization proceeds through a zwitter ion. The cyclization reaction causes a chain end in the network and decreases the  $T_g$  of the blended system, as expected.

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