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The mechanism and model reactions of epoxy–polycarbonate blends cured with aromatic amine

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Three model reactions are designed to investigate the transesterification between carbonate of PC and hydroxyl group formed from the ring opening reactions of oxirane with amine. Results show that the observed PC–epoxy blend cured by aromatic diamine-metaphenylene diamine (MPDA) and the i.r. absorption band of carbonate group shifts to low frequency during the curing procedure. The product of transesterification reaction accelerates the reaction between epoxy and amine. The transesterification reaction scissors the long chain of PC to short segments, decreasing the T_gs of the blend system. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: epoxy; blend; polycarbonate)

INTRODUCTION

It is well known that bisphenol-A polycarbonate (PC) undergoes the transesterification reaction with amine, alcohol and ester, etc. For example, PC reacts interchangeably with polycaprolactone[1], phenoxy[2], poly(ethylene terephthalate)[3], and poly(butylene terephthalate)[4] during melt blending. The carbonate group of PC can react with other functional groups of the above mentioned polymers since the carbonated-carbon is connected to the aromatic substitute group. Inductive effect occurring in this structure causes the carbonated-carbon to possess high electrophilicity, which can be easily attacked by nucleophilic reagents. However, most of the prior literature is focused on the transesterification of polycarbonate with other thermoplastics. Relatively fewer studies on the PC-thermosets blending systems involving the PC transesterification with thermosets have been reported[5–7].

Yu and Bell[5] studied the transesterification between carbonate and epoxide catalysed by quaternary ammonium salts and resulted in a PC–epoxy crosslinked network structure. Our previous study[6] utilizing tertiary amine to cure the PC–epoxy blend, resulted in transesterification reactions by converting the original aromatic/aromatic carbonate of PC to aromatic/aliphatic and aliphatic/aliphatic carbonates. A cyclic product produced from the cyclization reaction following the transesterification was identified by a model reaction. We also studied the curing mechanisms of PC–epoxy blends using anhydride as a hardener catalysed by tertiary amine[7]. 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 zwitterion. The transesterification/cyclization of carbonate groups proceed in the later stage if the oxirane is still available.

Some phenomena occurred when PC–epoxy blend cured with primary amine may be attributed to the transesterification. For example, Chen *et al.*[8] used diethylenetriamine (DETA) to cure PC–epoxy blends and found that Young's modulus (*E*) of the resultant blends decrease after post-cure. It was attributed to the degradation of the epoxy resin. Li *et al.*[9] studied the PC-epoxy blends cured by diethyltoluenediamine (DETDA) and reported that the crosslinking density of blending system increases with the increasing of the PC content. This is due to the extra knots generated by the transesterification reaction. However, both articles did not provide the positive spectrometric identification to support their claims. Mera and Umetani[10] reporting on the PC–epoxy blends cured by bis(4-amino-3-methylcyclohexyl) methane (C260), found a shift in the position of the carbonyl group in the i.r. spectrum. Rong and Zeng[11] used tetraethylene pentamine (TEPA) to cure the PC–epoxy blends. They revealed that the stretching band of carbonyl groups in the i.r. spectra of the cured blends shifted to lower frequencies, and they attributed to such i.r. absorption shift as hydrogen bonding. However, Lin *et al.*[12] investigated the spectroscopic variations of PC–epoxy cured by aliphatic amines were attributed to the carbamates and ureas formed in these systems. The

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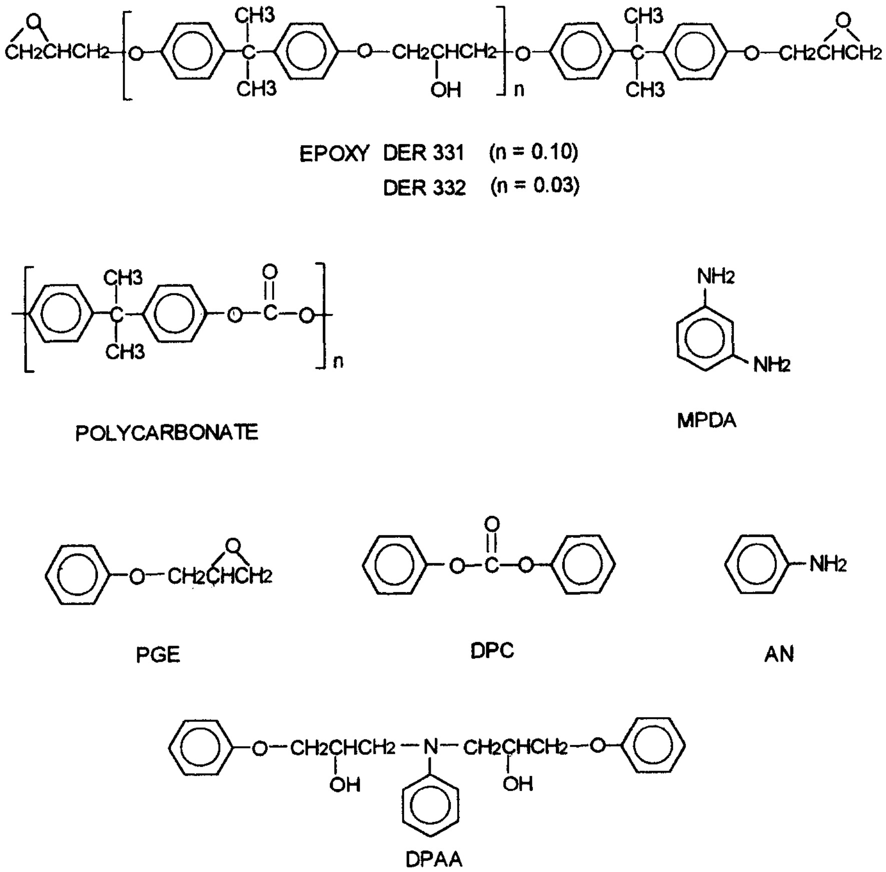


Scheme 1

Table 1 The codes and compositions of the model reaction and PC–epoxy blend

Code	Composition
M1	DER 332 (700 g) + PC (300 g)
M2	DPAA (1965 g) + DPC (214 g)
M3	AN (186 g) + DPC (214 g)
R1	DER 331 (100 g) + MPDA (16 g)
R2	DER 331 (100 g) + MPDA (16 g) + PC (7.4 g)
R3	DER 331 (100 g) + MPDA (16 g) + PC (15.8 g)

differences of the resultant products between two preparing procedures were also studied.

In this study, the transesterification of PC with epoxy during the hot melting stage and during curing process was investigated. The effect of the existence of PC on the kinetics of epoxy curing reaction was also studied.

EXPERIMENTAL

Materials

The Bisphenol-A base natural grade polycarbonate with a melt flow rate of 15 used in this study is Calibre 301-15 from Dow Chemical Company. The epoxy prepolymers, DER 331 and 332, a low molecular weight liquid diglycidyl ether of Bisphenol-A (DGEBA) with an epoxide equivalent weight of 186–192 and 172–176, used in this study were also purchased from Dow Chemical Company. The diamine used as a hardener is metaphenylene diamine (MPDA) which was purchased from Aldrich Chemical Co. The compounds for model reaction, phenyl glycidyl ether (PGE), aniline (AN) and diphenyl carbonate (DPC), were purchased from Merck Co. Dichloromethane used as solvent to dissolve DPC was also purchased from Aldrich Chemical Co. The chemical structures of epoxy, PC, MPDA, PGE, AN, DPC and di(phenyl glycidyl ether)-aniline-adduct (DPAA) synthesized are illustrated in *Scheme 1*.

Procedures and instrumentation

Before dissolving the PC into epoxy, both materials were dehydrated at 120°C for 24 h under vacuum. The mixture of 30 wt% PC in epoxy was prepared by dissolving the PC in the epoxy resin at 220°C after stirring the mixture under dry nitrogen gas for 1 h. The solution is clear, homogeneous and viscous. After cooling to 80°C, additional epoxy resin and MPDA were added to the mixture to adjust the desirable composition of the PC–epoxy blend with various contents of PC. The mixture was cured at 80°C for 2 h, 150°C for 2 h and 200°C for 4 h.

The DPAA used as the model compound was synthesized by blending two moles of PGE with one mole of AN at 80°C for 2 h. The experimental procedure of the model reaction was carried out by dissolving DPC into dichloromethane, then a proper amount of AN or DPAA was added to the mixture. One drop of the above mixture was pasted into a thin film between two sodium chloride plates and then mounted on a sample holder located in an i.r. instrument. The compositions and codes of blends are listed in *Table 1*.

Infrared spectra were obtained on a Perkin–Elmer 842 Infrared Spectrometer with a resolution of 2.4 cm^{-1} in the transmission mode. I.r. spectra at elevated temperatures were obtained using a heating cell mounted inside the sample chamber. The ^{13}C n.m.r. spectra were measured with a Bruker 400 FT-NMR Spectrometer with a magnetic field strength of 9.4 Tesla (e.g. $^{13}C = 100.6$ MHz). The

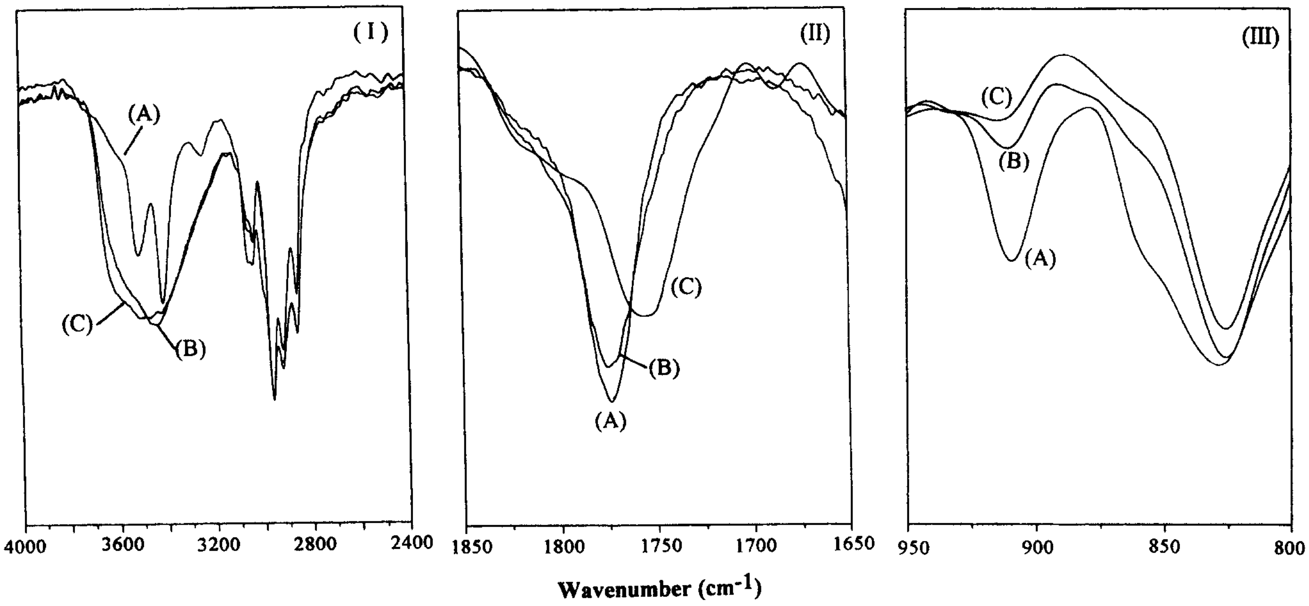


Figure 1 I.r. spectra of the DER 331/MPDA/PC = 100/16/15.8 (Code R3 of *Table 1*) recorded in (I) hydroxyl, (II) carbonyl and (III) oxirane stretching region (A) intial, (B) 80°C for 2 h and (C) 150°C for 2 h

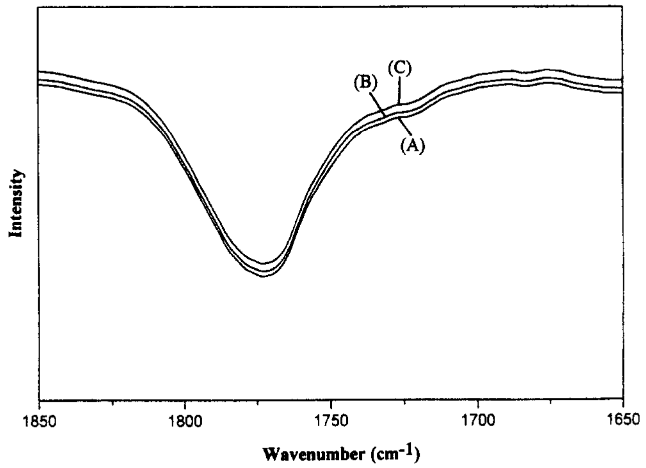


Figure 2 I.r. spectra of PC/DER 332 = 300/700 blend (Code M1 of *Table 1*) in the carbonyl stretching region (A) initial, (B) 80°C for 2 h and (C) 150°C for 2 h

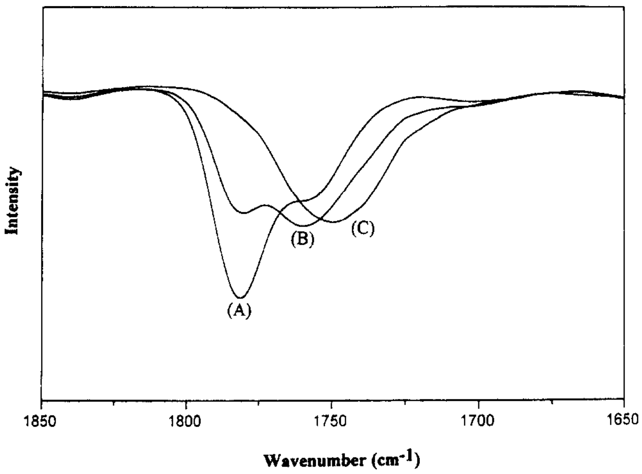


Figure 3 I.r. spectra of the DPC/DPAA = 214/1965 blend (Code M2 of *Table 1*) in the carbonyl stretching region (A) initial, (B) 80°C for 2 h and (C) 150°C for 2 h

samples were diluted by deuterated chloroform ($CDCl_3$). The glass transition temperature and kinetic study of the compound were determined by a Differential Scanning Calorimeter (d.s.c.), a Du Pont 2100, with a heating rate of 10°C min^{-1} in the dynamic scan.

RESULTS AND DISCUSSION

Infrared spectroscopy of PC–epoxy blend

Figures 1I, II and *III* present the i.r. spectra of the PC–epoxy blend cured by MPDA at various temperatures in the region including the hydroxyl, carbonyl and oxirane groups, respectively. *Figure 1 II* reveals the absorption band of the carbonyl group of PC shifting to lower frequency (from 1780 cm^{-1} to 1750 cm^{-1}) at higher temperature (curve C of *Figure 1 II*). Three model reactions were designed to study the variation of carbonyl group in the PC–epoxy blend.

The first model reaction (M1) was carried out by dissolving the PC into epoxy (PC/DER 332 = 300/700, Code M1 of *Table 1*) via hot melt method. The content of hydroxyl group, if any, contributed by the DER 332 might be too low to be detected directly from i.r. spectrum[6]. The DER 332 was used as pure DGEBA to study the reactivity of carbonate and oxirane in the absence of catalyst. *Figure 2* shows the i.r. spectra in the region of the carbonyl group while curve A of *Figure 5* shows the d.s.c. dynamic scan of the same system. As can be seen from *Figure 2*, the carbonyl group absorption does not change significantly during the heating procedure. Curve A of *Figure 5* does not show any exothermic peak in the dynamic scan zone. Both i.r. and d.s.c. results indicate that the carbonate does not react with oxirane in the absence of catalyst.

The reactants of the second model reaction (M2 of *Table 1*) are DPC and DPAA. The DPC–DPAA mixture is utilized to investigate the variations of carbonate in the cured epoxy since the chemical structure of DPAA is similar to the product of epoxy cured by MPDA. The i.r. spectrum of the M2 system in the region of carbonyl

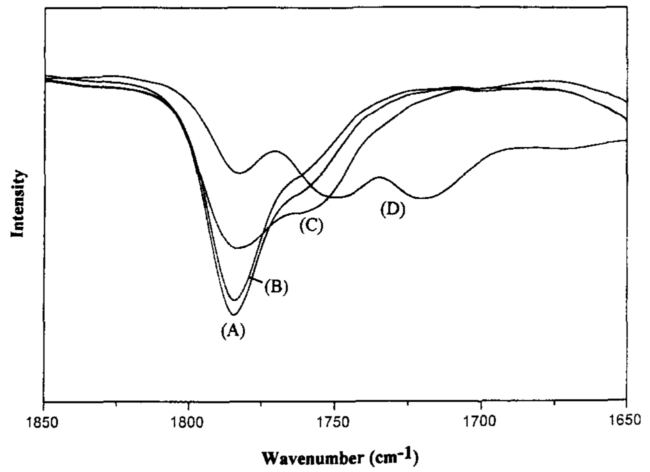


Figure 4 I.r. spectra of the DPC/AN = 214/186 blend (Code M3 of *Table 1*) in the carbonyl stretching region (A) initial, (B) 80°C for 2 h, (C) 120°C for 2 h and (D) 200°C for 1 h

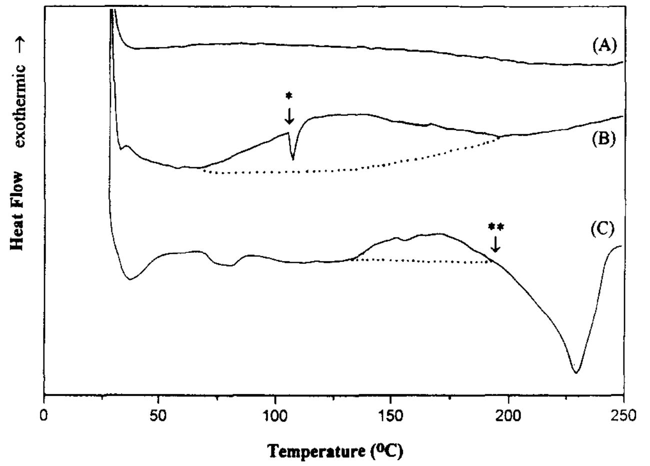
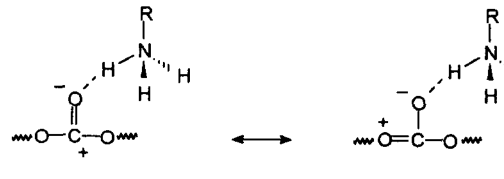


Figure 5 Dynamic runs of DSC in temperature range between 30–250°C (A) DPC/DER 332 = 300/700 blend (Code M1 of *Table 1*), (B) DPC/DPAA = 214/1965 blend (Code M2 of *Table 1*) and (C) DPC/AN = 214/186 blend (Code M3 of *Table 1*)

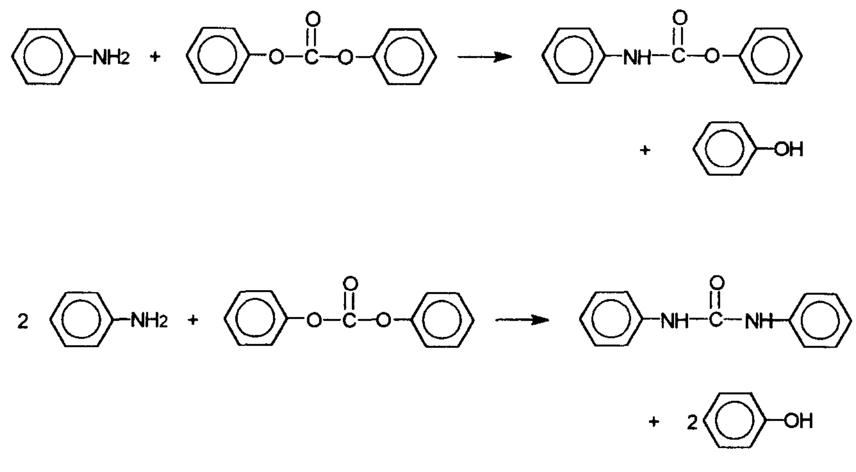


Scheme 2

stretching is shown in *Figure 3* and the d.s.c. dynamic scan is illustrated as Curve B of *Figure 5*. *Figure 3* shows that the carbonyl group band of M2 system at 1780 cm^{-1} shifts to 1750 cm^{-1}. The i.r. variations of the carbonyl stretching absorption can be explained by the transesterification reaction. The transesterification reaction will convert the original carbonate group of DPC, 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). The absorption frequency of the aromatic/aromatic carbonate (Ar–O–CO–O–Ar), aromatic/aliphatic carbonate (Ar–O–CO–O–R) and aliphatic/aliphatic carbonate (R–O–CO–O–R) are 1776 cm^{-1}, 1762 cm^{-1} and 1746 cm^{-1} respectively[13]. Therefore, the original absorption band shown in Curve A of *Figure 3* was broadened and shifted to lower frequency by transesterification between the carbonyl group of DPC and the hydroxyl group of DPAA, which is composed of three different carbonate components with different intensities. Curve B of *Figure 5* also reveals that an obvious reaction occurred and that the exothermic peak is initiated at 65°C. These phenomena provide the evidence that the carbonate will proceed the transesterification reaction with the hydroxyl group yielded from the curing of epoxy and aromatic amine rapidly.

The third model reaction (M3 of *Table 1*) was carried out by mixing the DPC with AN (aniline) to study the reaction between carbonate and aromatic amine. *Figure 4* shows the infrared spectrum in the region of the carbonyl stretching and curve C of *Figure 5* shows the corresponding d.s.c. dynamic scan. Curve A of *Figure 4* is the spectrum at the beginning of reaction. The absorption at 1780 cm^{-1} is contributed by the carbonate of PC stretching and the side band appeared at 1750 cm^{-1} is probably due to the hydrogen bonding caused by the mesomeric hybrid of the polar forms of the carbonyl group of PC. This mesomeric effect can be expressed as shown in *Scheme 2*.

Curves B and C of *Figure 4* show that the intensity of such coupled interactions increased. However, this phenomenon does not warrant a new compound to be produced. Curve D of *Figure 4* clearly reveals a reaction occurred between the carbonate and aromatic amine at higher temperature (180°C). The reaction products obtained as the carbamates and ureas which have the absorption bands located at 1725 cm^{-1} and 1675 cm^{-1}, respectively. The substitute groups of both carbamate and urea are the aromatic species[15] (*Scheme 3*).



Scheme 3

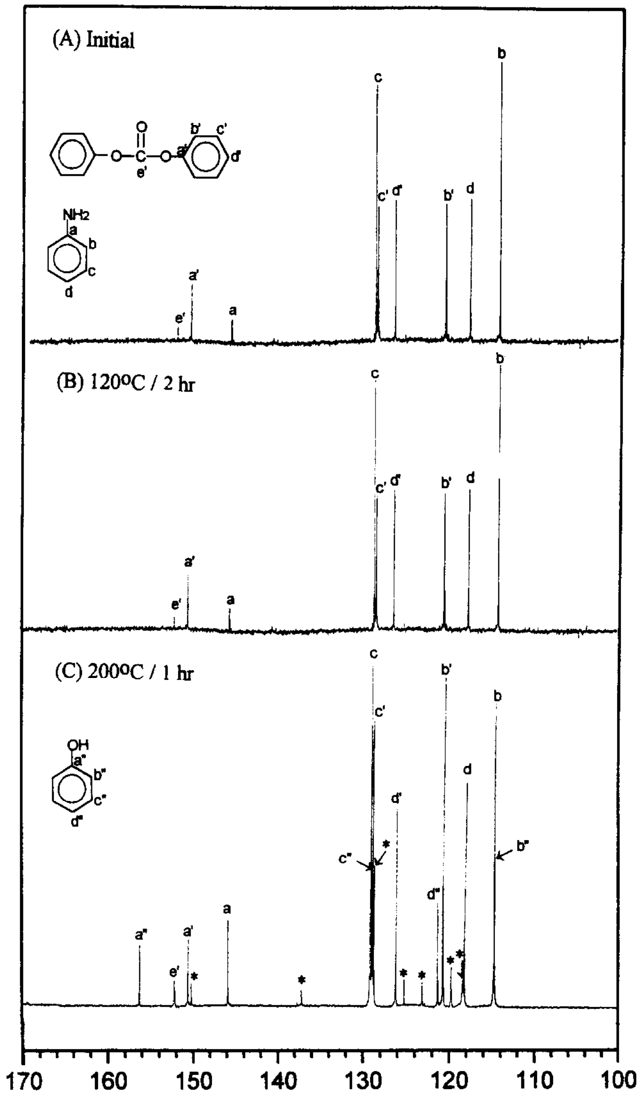
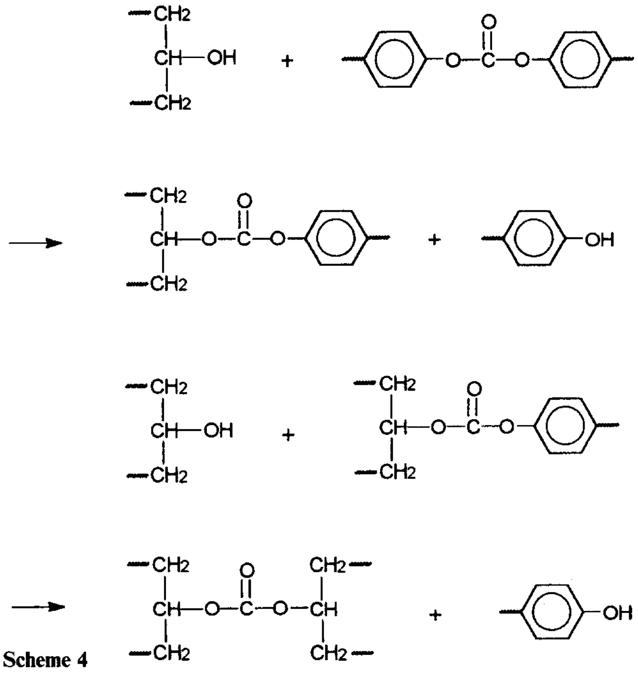


Figure 6 ^{13}C n.m.r. spectra of Code M3 composition [DPC–AN mixture] at (A) initial, (B) 120°C for 2 h and (C) 180°C for 1 h



Scheme 4

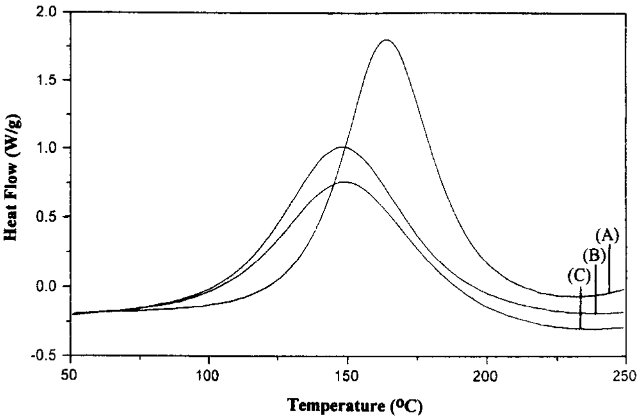


Figure 7 Dynamic runs of DSC in temperature range between 50–250°C (A) DER 331/MPDA = 100/16 blend (Code R1 of *Table 1*), (B) DER 331/MPDA/PC = 100/16/7.4 blend (Code R2 of *Table 1*) and (C) DER 331/MPDA/PC = 100/16/15.8 blend (Code R3 of *Table 1*)

The conclusion of the above reactions were verified by ^{13}C n.m.r. as shown in *Figure 6*[16,17]. Curves A, B and C of *Figure 6* show the ^{13}C n.m.r. spectra of the M3 system at the beginning, 120°C for 2 h and 200°C for 1 h, respectively. The chemical shift of Curves A and B for the carbon atom of carbonate located at 151.7 ppm does not split into two peaks. This result can prove that the i.r. variation of Curve A to B of *Figure 4* is not caused by a new product formation. Curve C of *Figure 6* shows the intensity of the original carbonate at 151.7 ppm decreasing while that of the absorption at 150.1 ppm increasing. Curve C of *Figure 6* also reveals the chemical shift positions of phenol that yielded from AN and DPC. The result coincides with the reaction occurring between AN and DPC. The dynamic d.s.c. of the M3 system is illustrated as curve C of *Figure 5* which presents an exothermic reaction initiated at 130°C. By analysing the results of these three model reactions the variations of the PC–epoxy blend system can be clearly seen. As these model reactions revealed, the carbonate could react with both hydroxyl and amino groups in the PC–epoxy blend cured with MPDA. However, we consider the reactivity between the carbonate with hydroxyl group is significantly higher than that with the amino group in the PC–epoxy blend. The reasons are presented as:

(1) Based on the results of d.s.c. scan (curves B and C of *Figure 5*) and i.r. spectra (curves A and B of *Figures 3* and *4*), it can be seen that the reactivity of the carbonate to the alcoholic hydroxyl group is higher than that of the aromatic amino group.

(2) By comparing curves A and B of *Figures 1 II* and *III*, most of the oxiranes were consumed before the carbonate absorption shifted to lower frequency. In other words, the phenomena indicate that the content of primary and secondary amino groups in the blend system is low when the variations of carbonate occurred.

(3) No absorption peaks at 1720 cm^{-1} or 1675 cm^{-1} were detected which were contributed by the carbamate and urea yielded from the possible reaction of carbonate and amine in the PC–epoxy blend (*Figure 1 II*).

By analysing the results from these three model reactions, we can conclude that the absorption band of

Table 2 The exothermic initial and peak temperatures (T_i and T_p), heat of reaction (ΔH), reaction order (m and n), activation energy (E_a) and pre-exponential factor (A) of PC–epoxy blend

PC content	0 wt%	6 wt%	12 wt%
T_i (°C)	132.4	100.6	100.4
T_p (°C)	162.4	143.5	148.6
ΔH (J g^{-1})	435.7	410.9	362.1
m	0.45 ± 0.04	0.38 ± 0.12	0.25 ± 0.09
n	1.45 ± 0.09	1.53 ± 0.30	1.94 ± 0.31
E_a (kJ mol^{-1})	37.9 ± 1.7	28.8 ± 4.9	16.3 ± 3.6
log A (l min^{-1})	4.30 ± 0.24	2.95 ± 0.69	1.12 ± 0.51

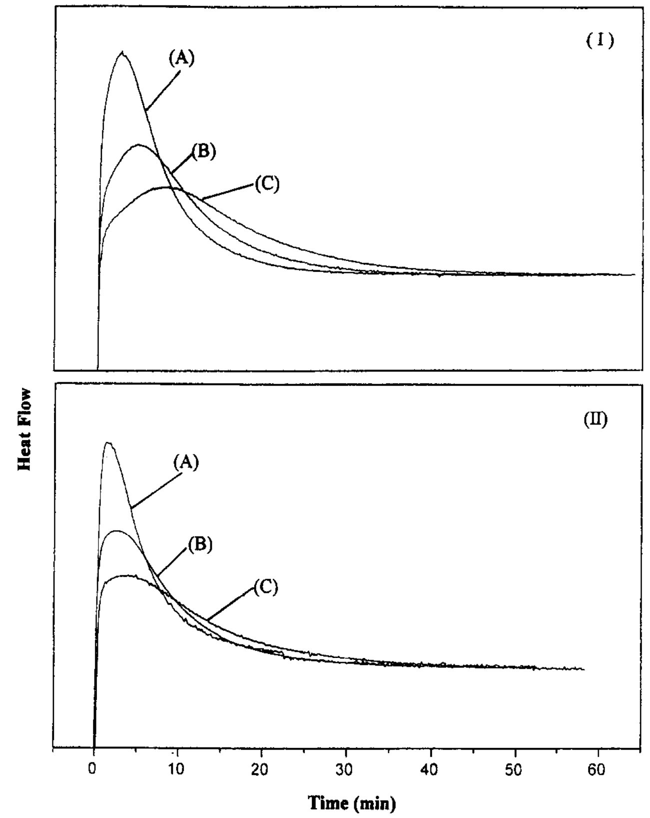


Figure 8 Isothermal runs of d.s.c. (I) DER 331/MPDA = 100/16 blend (A) at 100°C, (B) at 110°C and (C) at 120°C and (II) DER 331/MPDA/PC = 100/16/15.8 blend (A) at 90°C, (B) at 100°C and (C) at 110°C

the carbonyl group in PC–epoxy blend shifting to lower frequency is mainly due to the transesterification reaction occurring between the carbonate group of PC and the hydroxyl group produced in the cured epoxy (*Scheme 4*).

Curing kinetics

D.s.c. scans of the DGEBA/MPDA system and those of the blends containing 6 and 12 wt% PC at the temperature range of 50–250°C are shown in curves A, B and C of *Figure 7*, respectively. With the presence of 12 wt% PC, the exothermic peak temperature (T_p) is lower by 13.8°C and the heat of reaction (ΔH) is only 83.1% of the virgin system. The characteristic dynamic d.s.c. runs for different contents of PC blended with epoxy are presented in *Table 2*. These dynamic d.s.c. runs are used to determine the appropriate isothermal analysis temperature to calculate the kinetic parameters. The isothermal temperatures are selected between the onset of cure and a point midway to the maximum of peak. In this case, the isothermal analysis temperatures are chosen between 90–120°C. As shown in *Figure 8*, the maximum heat evolutions of virgin and blends do not occur in the initial isothermal d.s.c. signal. These results are the characteristics of autocatalysed reactions. The fractional conversion (α) is measured by the partial heat of reaction (ΔH_p) obtained from the isothermal analysis divided by the total heat of the reaction obtained from the dynamic d.s.c. run. The α determined is used to fit the autocatalysed model as

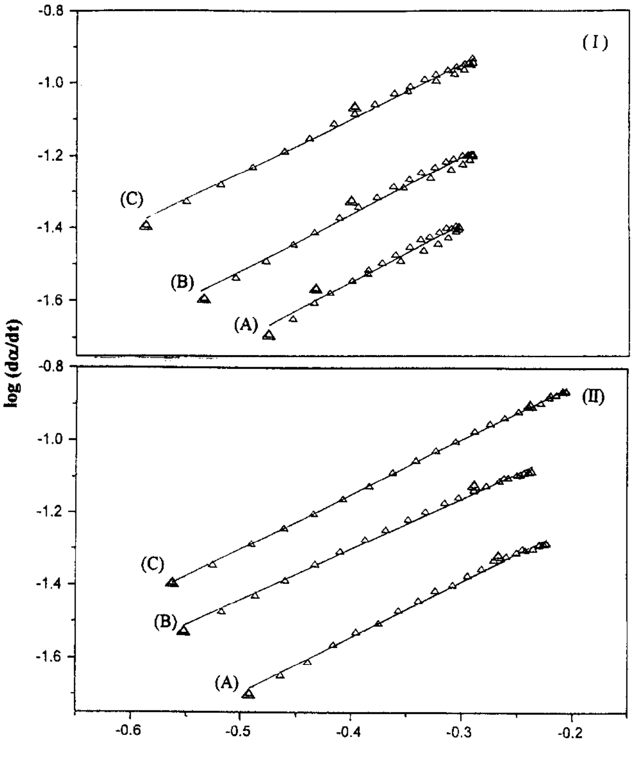


Figure 9 Plots of log ($\mathrm{d}\alpha/\mathrm{d}t$) vs log [$\alpha^{m/n}(1-\alpha)$] (I) DER 331/MPDA = 100/16 blend (A) at 100°C, (B) at 110°C and (C) at 120°C and (II) DER 331/MPDA/PC = 100/16/15.8 blend (A) at 90°C, (B) at 100°C and (C) at 110°C

$$\mathrm{d}\alpha/\mathrm{d}t = k\alpha^m(1-\alpha)^n \qquad (1)$$

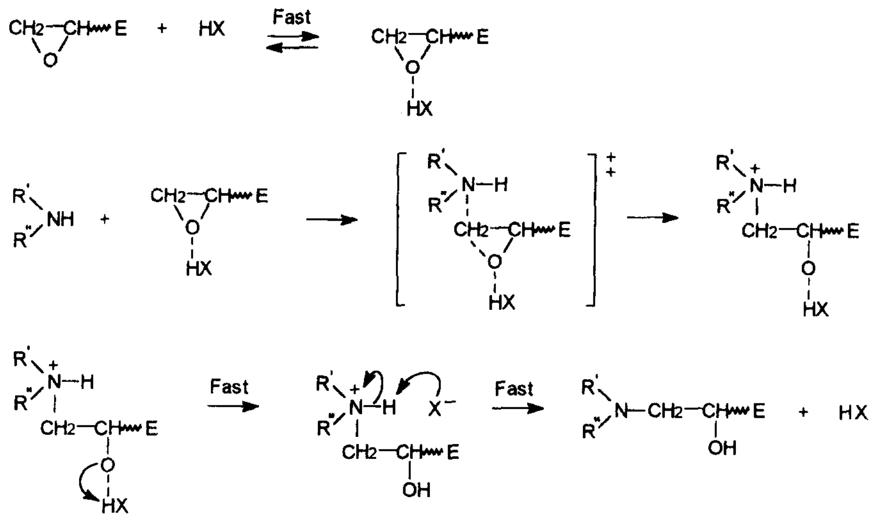
By taking logarithms of both sides of the equation, one can obtain the equations

$$\begin{aligned}\log(\mathrm{d}\alpha/\mathrm{d}t) &= \log k + \log[\alpha^m(1-\alpha)^n]\\ &= \log k + n\log[\alpha^{m/n}(1-\alpha)] \qquad (2)\end{aligned}$$

Figure 9 presents the plots of log ($\mathrm{d}\alpha/\mathrm{d}t$) vs log [$\alpha^{m/n}(1-\alpha)$] of virgin and blend systems at various temperatures. Essentially all the plots of log ($\mathrm{d}\alpha/\mathrm{d}t$) against log [$\alpha^{m/n}(1-\alpha)$] show fairly good straight lines. Such linear relationships indicate that all three systems follow the autocatalysed model. The slope of the line is n and the intercept is log k. The value m is calculated by substituting n and k, and then solving equation (2). If we assume the reaction rate constant (k) obeys the Arrhenius expression

$$k(T) = A\exp(-E_a/RT) \qquad (3)$$

where A = pre-exponential factor (s^{-1}), E_a = activation energy (J mol^{-1}), $R = 8.314$ (J mol K^{-1}), and



Scheme 5

Table 3 The reaction rate constants of PC–epoxy blend

PC content	0 wt%	6 wt%	12 wt%
k 90°C (1 $\min^{-1}$)	–	0.054 ± 0.005	0.046 ± 0.007
k 100°C (1 $\min^{-1}$)	0.104 ± 0.012	0.110 ± 0.014	0.076 ± 0.007
k 110°C (1 $\min^{-1}$)	0.131 ± 0.011	0.163 ± 0.020	0.150 ± 0.023
k 120°C (1 $\min^{-1}$)	0.187 ± 0.016	–	–

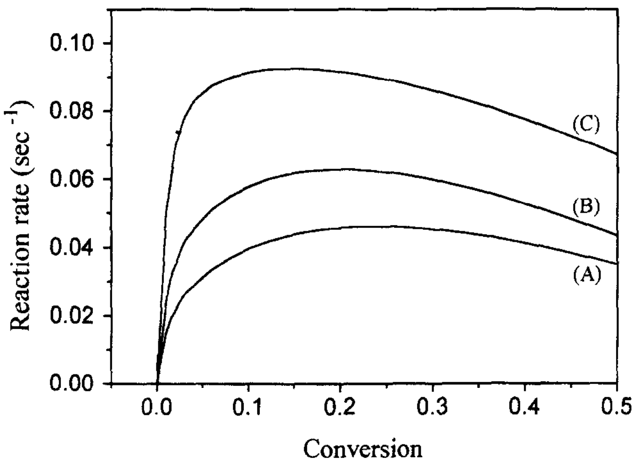


Figure 10 Plots of reaction rate *versus* conversion at 120°C (A) DER 331/MPDA = 100/16 blend, (B) DER 331/MPDA/PC = 100/16/7.4 blend, (C) DER 331/MPDA/PC = 100/16/15.8 blend

Table 4 The glass transition temperatures of the PC–epoxy blend

T_g (°C)	PC content			
Curing procedure	0 wt%	6 wt%	12 wt%	100 wt%
[80/2 + 150/2]	143.3	155.6	136.7	154.0
[80/2 + 150/2 + 200/2]	175.7	156.5	152.7	–
[80/2 + 150/2 + 200/4]	177.2	154.4	147.3	–
$[80/2 + 150/2 + 200/4]_F$	177.2	175.3	173.4	154.0

[80/2 + 150/2] represents the PC–epoxy blend system cured at 80°C for 2 h and 150°C for 2 h

$[80/2 + 150/2]_F$ represents the T_g predicted by the Fox rule

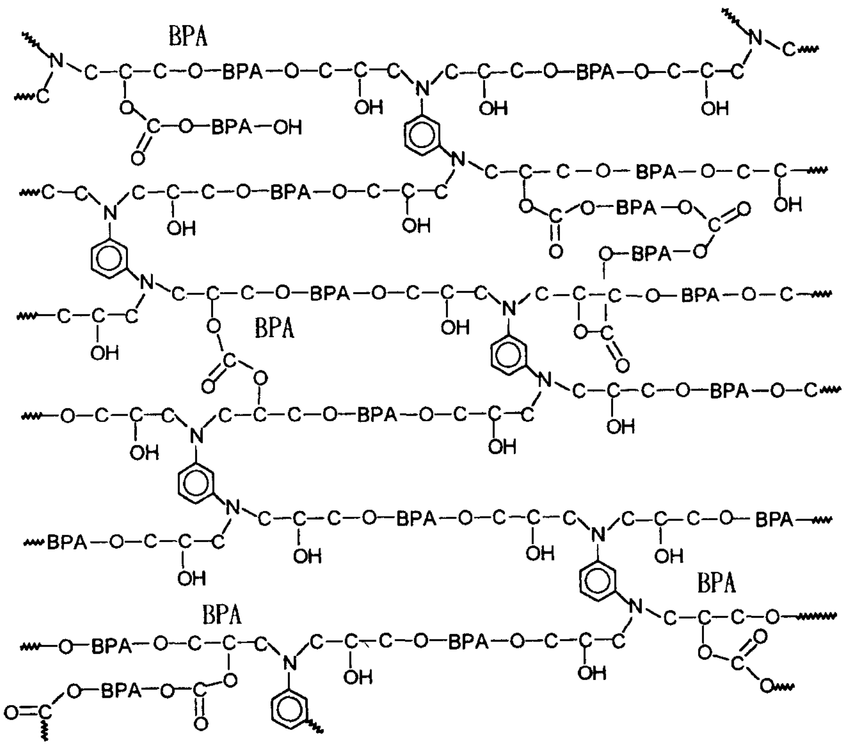
Fox rule:

$$1/T_{g12} = w_1/T_{g1} + w_2/T_{g2}$$

where $T_{g12} = T_g$ of the blend, $T_{g1} = T_g$ of component 1, $T_{g2} = T_g$ of component 2, w_1 = weight fraction of component 1, w_2 = weight fraction of component 2

T = absolute temperature (K). These curves obtained from various temperatures can be applied to determine the activation energy (E_a), pre-exponential factor (A), and the reaction order (m and n). The values of the activation energy (E_a), pre-exponential factor (A), and reaction order (m and n) obtained from the regression plots are listed in *Table 2*. As shown in the table, E_a decreases with the increasing of the PC content in the blend. The phenomena should be explained from the view of the epoxy curing mechanism illustrated in *Scheme 5*.

As the mechanism revealed, the oxirane rapidly forming a hydrogen bond with HX is attacked by the amine, and followed by the ring opening of the oxirane. Finally, the sequence is completed by fast proton displacement and a new alcoholic hydroxyl was formed. It should be noted that for each epoxy reacted, a hydroxyl group is formed. The hydroxyl group may lower the energy barrier of the reaction between amine and epoxy group, consequently the reaction is autocatalysed[18]. In the hot melt process by dissolving the PC into epoxy, the transesterification reaction will replace the alcoholic hydroxyl of epoxy to phenolic hydroxyl of PC chain end. In the curing process of the PC–epoxy blends, the hydroxyl groups formed from the reaction between epoxy and amine will transesterificate with carbonate groups and generate a phenol chain end[19]. Phenol has been found to be a more powerful proton donor compound for the reaction than alcohols[20]. This is the reason why the presence of PC is able to decrease the activation energy (E_a) of the epoxy/MPDA system. Since the spectroscopic results indicated that most of the oxiranes are already consumed before the generation of phenolic chain ends as shown in *Figure 1*. The phenolic hydroxyl of PC chain end which is formed during the hot melt process by dissolving the PC into epoxy is the main source to participate the reaction between epoxy and amine. However, the appearance of PC will reduce the concentrations of epoxy and amine, decreasing the effective collisions between them at the same time. The phenomena cause the pre-exponential factor (A) to decrease with the increasing of the PC content in the blend. Compromising these two effects, the observed reaction rate constants calculated by Arrhenius expression decrease with the increase of the PC content. *Table 3* reveals the reaction rate constants of PC–epoxy blend at various temperatures. As the autocatalysed model revealed, the reaction rate ($d\alpha/dt$) may be decreased by decreasing the reaction rate constant (k) but may be



Scheme 6

increased by decreasing the reaction order (*m* and *n*). Both contributions show the opposite effect on the reaction rate. *Figure 10* shows the plots of reaction rate ($d\alpha/dt$) vs conversion (α) that were determined by these observed kinetic parameters. The DGEBA/MPDA system and those of the blends containing 6 and 12 wt% PC are represented as curves A, B and C of *Figure 10*. This figure shows that the reaction rate of the blend system is higher than that of a virgin system. This phenomena indicate that the PC added to the epoxy will accelerate the curing reaction of epoxy and amine.

Thermal properties

The glass transition temperatures of the blends containing various amounts of PC were measured by d.s.c. as shown in *Table 4*. The T_gs of the PC–epoxy blends decrease with the increase of the PC content. However, the T_gs of blends are lower than the temperature predicted by the Fox relationship which is usually used to calculated the T_g of an ideal polymer blend. This explicates a new structure formed in these blending systems by transesterification.

Another character revealed from *Table 4* is that the T_g of the virgin system increases by curing at a higher temperature or a longer time, while that of blend systems decreases. This phenomenon can be explained from the structure of the PC–epoxy blend system formed. The structure of the cured PC–epoxy blend system is illustrated in *Scheme 6*.

The classical network is composed of epoxy and MPDA only. The pendant secondary hydroxyl group is formed from the ring opening reaction of oxirane and amine. The presence of PC carbonate group will be transesterified with the hydroxyl group of cured epoxy network and scissors the long chain into segments. Consequently, the PC segments were grafted or crosslinked in the original network. The BPA monomers and PC oligomers are released at the same time. From this structure diagram, we can consider that the T_g of the resultant blends may be influenced by four factors: (1) crosslinking effect, (2) grafting effect, (3) copolymer effect, and (4) plasticizer effect.

Crosslinking or grafting a short side chain may restrict the motions of the network chains. The copolymer effect attributes the new carbonate crosslinking point or the grafted side chain that is not chemically identical to the rest of the network[21]. For example, the T_g of epoxy crosslinked by carbonate group is at 156°C which is lower than the T_g of epoxy cured with MPDA (177°C)[22]. In other words, due to the compromise from the crosslinking effect and copolymer effect, the extra knots generated by further transesterification at higher temperature will not increase the T_g of the blends. Additionally, the transesterification will release BPA. The presence of BPA in the network acts as a plasticizer of the network, and reduces the T_g of the blend system. Further transesterification at higher temperature will yield more quantity of BPA and decrease the T_g of blend.

CONCLUSION

The i.r. spectra reveal the absorption peak of carbonate group shifts to low frequency when the PC–epoxy blend is cured by the aromatic amine. This is due to the transesterification between the carbonate of PC and the hydroxyl group produced from the curing of oxirane with amine. Three model reactions have been studied which provide the evidence to support the above claimed reactions. The occurrence of transesterification will replace the original alcoholic hydroxyls of epoxy to a phenol chain end of PC, and scissors the long chain of PC into short segments. The result of the former can accelerate the curing reaction while the latter will reduce the T_gs of the blend.

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