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

Ming-Shiu Li and Chen-Chi M. Ma*
Institute of Chemical Engineering, National Tsing Hua University, Hsinchu 30043, Taiwan, ROC

and Miaw-Ling Lin, Ming-Shiu Lu, Jyh-Luen Chen and Feng-Chih Chang
Institute of Applied Chemistry, National Chiao Tung University, Hsinchu, 30043, Taiwan, ROC

The reaction mechanism of a polycarbonate (PC) and epoxy blend cured with aliphatic amine was investigated. The spectroscopic variations of the PC–epoxy blend cured by aliphatic amines indicate that the carbamates and ureas appeared in the system. Various methods to prepare the blends were used: (1) PC dissolved in epoxy by hot melt method to obtain the PC–epoxy blend and the aliphatic amine then added to cure the blend. (2) PC dissolved in aliphatic amine by solvent to obtain the PC–aliphatic amine mixture and the epoxy added to cure the mixture. Method (1) yields carbamates at the beginning, and the compound is decomposed at 80°C to release isocynates that will react with the hydroxyl group of network to form another carbamate structure. The carbamates formed crosslinked with epoxy at the final stage. Method (2) gives ureas at the initial stage and most of the ureas undergo a substitute reaction with the hydroxyl group of the cured resin to yield the carbamate structure crosslinking with the cured epoxy network. The differences of the resultant products between the two preparing procedures are investigated by calculating the content of crosslinker, plasticizer and chain end. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: epoxy; blend; polycarbonate)

INTRODUCTION

An epoxy thermoset network can be obtained through a curing procedure using low molecular weight epoxy prepolymer. Curing can occur either by a homopolymerization reaction initiated by a catalytic curing agent or a polyaddition/copolymerization reaction with a multifunctional curing agent[1]. One of the multifunctional hardners frequently used is amine. For example, a primary aliphatic amine can react with epoxy rapidly and results in a product with overall properties suitable for a variety of commercial applications, whilst an aromatic amine gives a relatively slow curing rate but yields a higher performance product[2]. The various reactivities of amines used to cure polycarbonate (PC)–epoxy blends may result in different structures for the cured products.

A few articles have reported on a PC–epoxy blend cured by aromatic amines[3-6]. Yu and Bell[3] studied the chemistry of epoxide–polycarbonate copolymer networks using phenol-terminated oligocarbonates. D.s.c. dynamic analysis was utilized to investigate the cure reaction and revealed that the presence of oligocarbonates accelerates the epoxy-diaminodiphenylmethane

(DDM) reaction. Li et al.[4] studied PC–epoxy blends cured by diethyltoluenediamine (DETDA) and found that the crosslinking density of the blending system is increased. This result is explained by the extra knots generated from the transesterification between carbonate of PC and hydroxyl group formed from the ring opening reactions of oxirane with amine. Wu et al.[5] showed a single T_g and homogeneous morphology in a PC–epoxy blend cured with diaminodiphenylsulfone (DDS) and attributed the miscibility in the cured network to the chemical interactions between the components. Lu et al.[6] studied PC–epoxy blends cured by metaphenylenediamine (MPDA) and found the transesterification of the system through spectrometric identification. Curing kinetics showed the phenol chain end of PC generated by transesterification accelerates the epoxy–MPDA reaction. Lu et al. also reported that the transesterification reaction scissors the long chain of PC to short segments and decreases the T_g of the blend system[6]. By summarizing the results of three model reactions carried out by Lu et al., it can be confirmed that PC may react with the hydroxyl group of the cured epoxy to a far greater extent than that with the aromatic amine and oxirane present in the PC–epoxy blend system.

Contrasting with the wider research activity of aromatic amine cured PC–epoxy blends, the chemistry
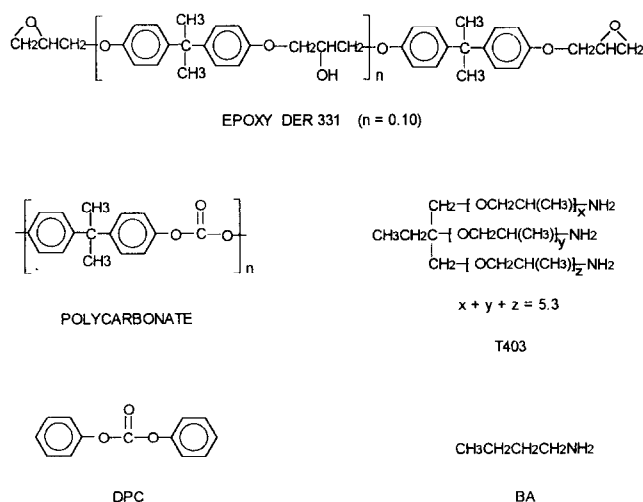
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* To whom correspondence should be addressed

aspect of the PC–epoxy blend cured by aliphatic amine has been little explored[7–9]. Mera and Umetani[7] reported that the PC–epoxy blends cured by bis(4-amino-3-methylcyclohexyl)methane (C-260) improve the processability and thermal and mechanical properties. They found the PC–epoxy blend showed a shift in the position of the carbonyl group in the i.r. spectrum. Rong and Zeng[8] investigated the PC–epoxy blends cured by tetraethylenepentamine (TEPA). They revealed the stretching band of carbonyl groups in the i.r. spectra of cured blends shifted from 1776 to 1725 cm^{-1} and proposed the formation of hydrogen bonding resulting in a molecular level mixing of the blend system. Chen et al.[9] used diethylenetriamine (DETA) to cure a PC–epoxy blend system which resulted in a miscible blend. They explained that the homogeneous morphology observed is attributed to both blend components containing the bis-phenol A structure in their repeat units, and hydrogen-bonding involving the carbonyl groups in the PC and the hydroxyl residues in the epoxy resin. Foldi and Campbell[10] prepared copoly-(carbonate/urethanes) from polycarbonates and various amines and reported that the aliphatic amines are more effective in degrading PC, while aromatic amines need more stringent conditions in order to be effective. In this study, model reactions of various ratios of aliphatic amine and carbonate were utilized and the end products were analysed by i.r. and ^{1}H n.m.r. spectrometry. The results of model reactions are utilized to explain the observed spectroscopic variations of the PC–epoxy blends cured with aliphatic amine.

EXPERIMENTAL

Materials

The bisphenol-A base natural grade polycarbonate with a melt flow rate of 15 used in this study was Calibre 301-15 from the Dow Chemical Company. The epoxy prepolymer, DER 331, was also purchased from Dow and is a low molecular weight liquid diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight of 186–192. The polyoxypropylene triamine used as a hardner was T403 with a molecular weight of 403 (Jefferson Chemical Co). The model compounds, butylamine (BA) and diphenyl carbonate (DPC) were from Merck Co. The solvent used to dissolve the DPC
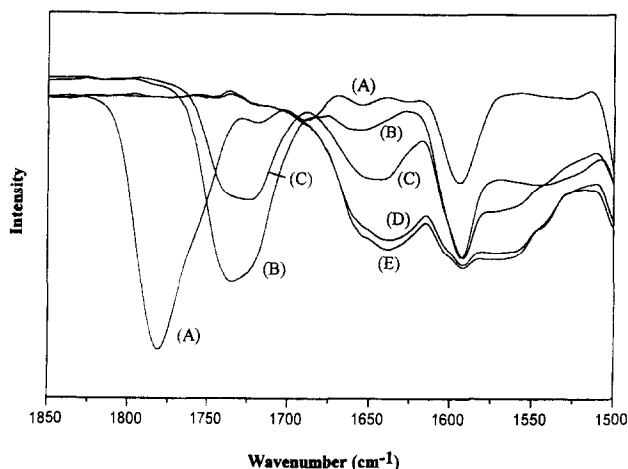
was dichloromethane (Aldrich Chemical Co.). The silica gel used in column chromatography, silica gel 60, was also from Merck.

Procedures and instrumentation

The model reaction was carried out by mixing the DPC–dichloromethane solution with BA at room temperature. The resultant products of various compositions obtained from the model reactions were separated by silica gel column chromatography using dichloromethane as eluent. The identification of the structure of the resultant products obtained from column chromatography was determined by high resolution ^{1}H n.m.r. and i.r. spectrometry. The ^{1}H n.m.r. spectra were measured with a Bruker 400 FT-n.m.r. spectrometer with a magnetic field strength of 9.4 Tesla (^{1}H = 400 MHz).

Table 1 The codes and compositions of the model reactions

Code	DPC/BA weight ratio	Carbonate/amine mole ratio	Carbonate/amine equivalent ratio
M1	214/73	1/1	1/2
M2	214/146	1/2	1/4
M3	214/292	1/4	1/8

Figure 1 I.r. spectra in the carbonyl stretching region: (A) DPC; (B) DPC/BA = 214/73 at 25°C for 3 min; (C) DPC/BA = 214/73 at 80°C for 2 h; (D) DPC/BA = 214/73 at 150°C for 2 h

EPOXY DER 331 (n = 0.10)

POLYCARBONATE

T403

x + y + z = 5.3

DPC

BA

CH3CH2CH2CH2NH2

Figure 2 I.r. spectra in the carbonyl stretching region: (A) DPC; (B) DPC/BA = 214/146 at 25°C for 3 min; (C) DPC/BA = 214/146 at 80°C for 2 h; (D) DPC/BA = 214/146 at 150°C for 2 h

Figure 3 I.r. spectra in the carbonyl stretching region: (A) DPC; (B) DPC/BA = 214/292 at 25°C for 3 min; (C) DPC/BA = 214/292 at 80°C for 2 h; and (D) DPC/BA = 214/292 at 150°C for 2 h

The samples were diluted by deuterated chloroform (CDCl$_3$). I.r. spectra were obtained on a Perkin-Elmer 842 infrared spectrometer with a resolution of 2.4 cm^{-1} in the transmission mode.

The PC–epoxy blends cured by aliphatic amine (T403) were observed by the following two procedures: (1) PC dissolved in epoxy by the hot melt method at 220°C under nitrogen gas for 1 h. After cooling to room temperature, the hardner T403 was added to cure the blend. (2) PC was dissolved into dichloromethane at room temperature to make a solution of 16.7% by weight and the T403 was added to make a solution with weight ratio of PC/T403 at 100/209.5. The resulting solution was distilled under vacuum at 80°C for 2 h to remove the dichloromethane. The semi-solid end product was mixed with epoxy resin at 80°C to proceed the curing reaction. One drop of the above blend was pasted into a thin film between two sodium chloride plates and then mounted on a sample holder located in the i.r. instrument. The heating process was set at 80°C for 2 h, at 150°C for 2 h and at 180°C for 2 h. The blend compositions, together with their codes, are listed in *Table 1*.

RESULTS AND DISCUSSION

The model reaction of aliphatic amine and carbonate

To study the reaction of aliphatic amine with carbonate groups, we chose DPC and BA. Curve A of *Figures 1–3* represents the i.r. spectrum of DPC in the carbonyl region. Curves B–D of *Figure 1* show the absorption band of the end products from DPC/BA = 214/73 composition (Code M1 in *Table 1*, mole ratio 1/1) at 25, 80 and 150°C for 2 h, respectively. These curves reveal that DPC can react with BA rapidly. Even at 25°C, immediately after mixing of DPC and BA, most of the carbonyl absorption of DPC at 1780 cm^{-1} shifted to 1720 cm^{-1} and only a small original carbonyl absorption remained. The spectra at higher temperatures (80 and 150°C) are almost identical to the one at lower temperature (25°C), an indication of nearly complete reaction at 25°C. This phenomenon indicates a new compound resulting from the reaction of DPC and BA with high conversion.

Curves B–D of *Figure 2* illustrate the absorption band of the end products from DPC/BA = 214/146 composition (Code M2 in *Table 1*, mole ratio 1/2) at 25, 80 and
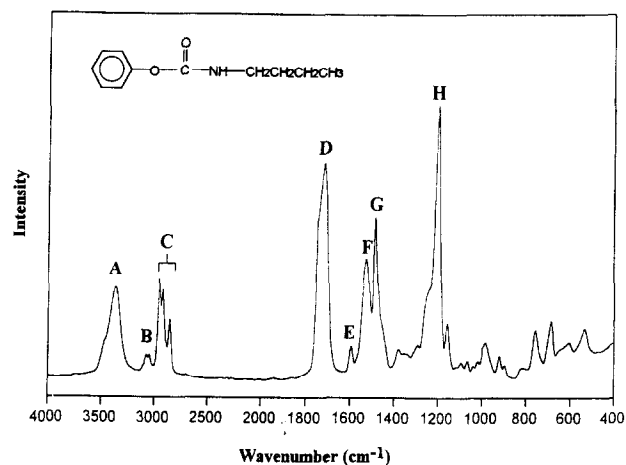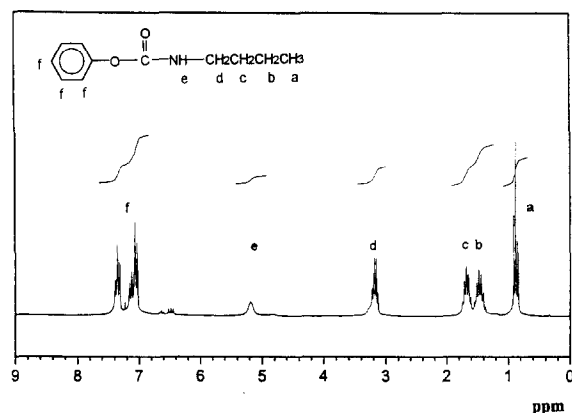

Figure 4 I.r. spectrum of the end product separated from the DPC–BA model reaction mixture with a weight ratio of 214/73 (equivalent ratio of 1/1): (A) the N–H stretch, hydrogen-bonded, 3381 cm^{-1}; (B) aromatic C–H stretch, 3080, 3048 cm^{-1}; (C) aliphatic C–H stretch, 2957, 2928, 2862 cm^{-1}; (D) the C=O stretch, 1719 cm^{-1}; (E) ring C=C stretch, 1595 cm^{-1}; (F) the N–H bend, 1529 cm^{-1}; (G) the C–H bend, 1488 cm^{-1}; (H) the C–N stretch, 1023 cm^{-1}

Figure 5 ^{1}H n.m.r. spectrum of the end product separated from the DPC–BA model reaction mixture with a weight ratio of 214/73 (equivalent ratio of 1/1)

150°C for 2 h, respectively. Again, the absorption of DPC at 1780 cm^{-1} disappears completely and forms a new carbonyl absorption at 1720 cm^{-1} similar to *Figure 1*. From curve B to curve D, the intensity at 1720 cm^{-1} decreases with increasing reaction temperature.

Curves B–D of *Figure 3* show the initial absorption band of DPC/BA = 214/292 composition (Code M3 in *Table 1*, mole ratio 1/4) at 25°C and after 2 and 24 h, respectively. Curve E of this figure shows the i.r. spectrum of the same composition at 80°C for 2 h. Comparing these curves, it is obvious that the absorption decreased at 1720 cm^{-1} causes the absorption increase at 1640 cm^{-1}, either at longer time or at higher temperature.

The spectroscopic results of the three model reactions reveal that the products formed are influenced by the feed ratio of DPC and BA. The silica gel column chromatography was used to separate and purify the end products of these model reactions. The end products from curve D of *Figure 1* (Code M1) and *Figure 3* (Code M3) after purification were characterized by i.r. and ^{1}H n.m.r. spectrometry.

The i.r. and ^{1}H n.m.r. spectra of the purified component from the DPC/BA = 214/73 composition (Code M1) are shown in *Figures 4* and *5* while those
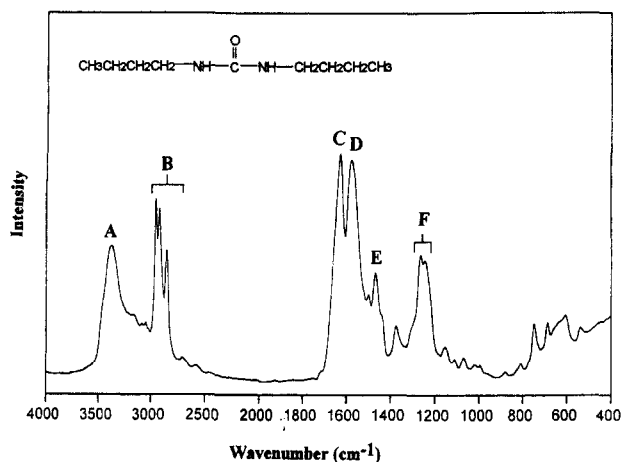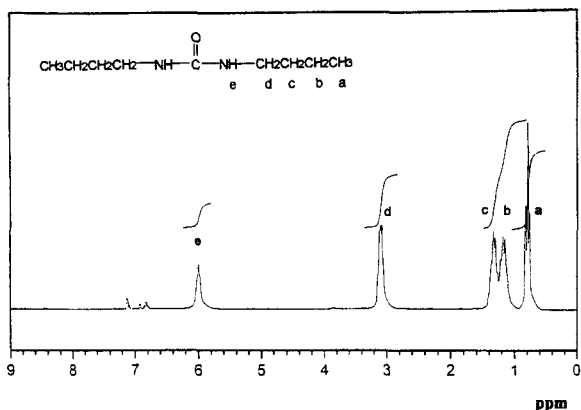
Figure 6 I.r. spectrum of the end product separated from the DPC–BA model reaction mixture with a weight ratio of 214/292 (equivalent ratio of 1/4): (A) the N–H stretch, hydrogen-bonded, $3378\,cm^{-1}$; (B) aliphatic C–H stretch, 2957, 2926, 2861 cm^{-1}; (C) the C=O stretch, $1629\,cm^{-1}$; (D) the N–H bend, $1578\,cm^{-1}$; (E) the C–H bend, $1466\,cm^{-1}$; (F) the C–N stretch, 1268, 1245 cm^{-1}

Figure 7 ^{1}H n.m.r. spectrum of the end product separated from the DPC–BA model reaction mixture with a weight ratio of 214/292 (equivalent ratio of 1/4)
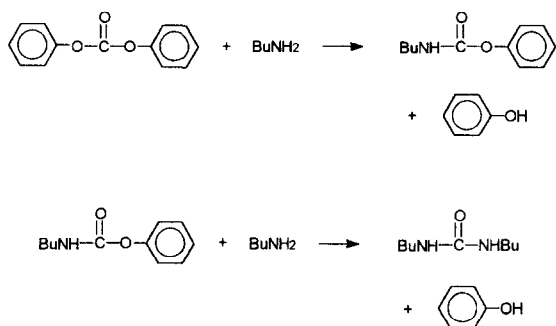
Scheme 1

from the DPC/BA = 214/292 composition (Code M3) are shown in *Figures 6* and *7*, respectively. From the data shown in *Figures 4–7*, we can positively confirm that the component separated from the model reaction of the DPC/BA = 214/73 composition (Code M1) is *N*-butyl phenyl carbamate, and that separated from the DPC/BA = 214/292 composition (Code M3) is *N,N'*-dibutyl urea. The possible mech-
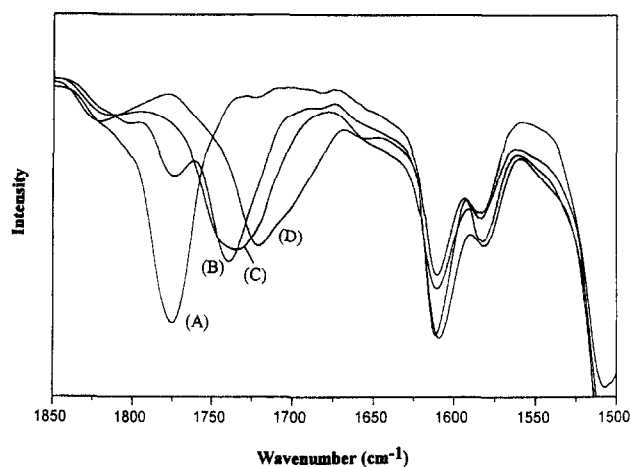

Figure 8 I.r. spectra in the carbonyl stretching region: (A) PC; (B) code H12 blend (PC–epoxy/T403 = 1.91/10/4) at 25°C, 3 min; (C) code H12 blend (PC–epoxy/T403 = 1.91/10/4) at 80°C, 1 h; (D) code H12 blend (PC–epoxy/T403 = 1.91/10/4) at 80°C, 1 h and 150°C, 2 h

anisms to form these two compounds are illustrated in *Scheme 1*.

Infrared spectra of PC–epoxy blends

(i) PC dissolved in epoxy by the hot melt method. PC was dissolved in epoxy resin by stirring the PC pellet with liquid epoxy resin under nitrogen gas at 220°C for 1 h. The i.r. spectrum of the PC in the carbonyl region is illustrated in curve A of *Figure 8*. Curve B represents the spectrum of composition code H12 (*Table 2*), where the hardener T403 was added into the PC–epoxy blend. The spectrum variation of curve A to B of *Figure 8* resembles the code M1 model reaction (*Figure 1*), the i.r. absorption of the carbonate group of PC at $1780\,cm^{-1}$ shifts rapidly to $1740\,cm^{-1}$. This lower frequency band is contributed by the carbonate group formed in the blend. At the same time, the oxirane content of the blend does not change significantly since the absorption ratio of A_{915}/A_{1600} remains nearly constant. This phenomenon indicates that the reactivity of aliphatic amine with carbonate is substantially greater than that with oxirane. Therefore, the aliphatic amine (T403) reacts with the carbonate of PC first (equation (1)), followed by the residual amine ring opening reaction with oxirane (equation (2)).
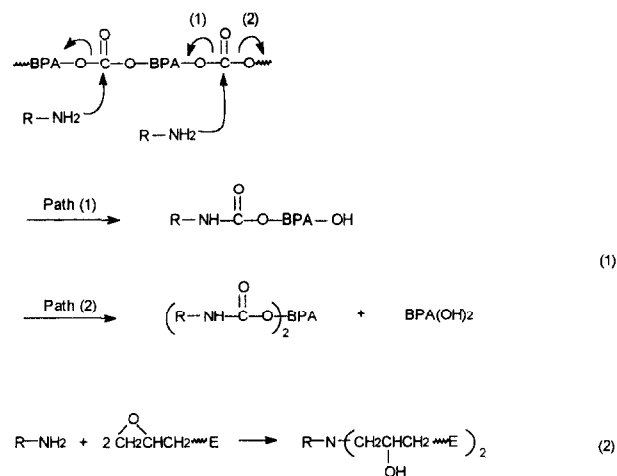
Table 2 The codes and compositions of the PC–epoxy blends

|	Virgin	H12	H6	S12	S6
Procedures to prepare the blends	epoxy (10 g) + T403 (4 g) ↓ Δ cured epoxy/T403 system (PC 0 wt%)	PC (1.91 g) + epoxy (10 g) ↓ Δ PC–epoxy blend (11.91 g) ↓ + T403 (4 g) ↓ Δ cured PC–epoxy/T403 blend (PC 12 wt%)	⎯ + epoxy (14.23 g) ↓ + T403 (5.69 g) ↓ Δ cured PC–epoxy/T403 blend (PC 6 wt%)	PC (1.91 g) + CH$_2$Cl$_2$ (11.46 g) ↓ PC–CH$_2$Cl$_2$ solution (13.37 g) ↓ + T403 (4 g) ↓ vacuum CH$_2$Cl$_2$ (11.46 g) ↑ +PC–T403 blend (5.19 g) ⎯ ↓ + epoxy (10 g) ↓ Δ cured PC–T403/epoxy blend (PC 12 wt%)	⎯ + T403 (7.61 g) + epoxy (19 g) ↓ Δ cured PC–T403/epoxy blend (PC 6 wt%)
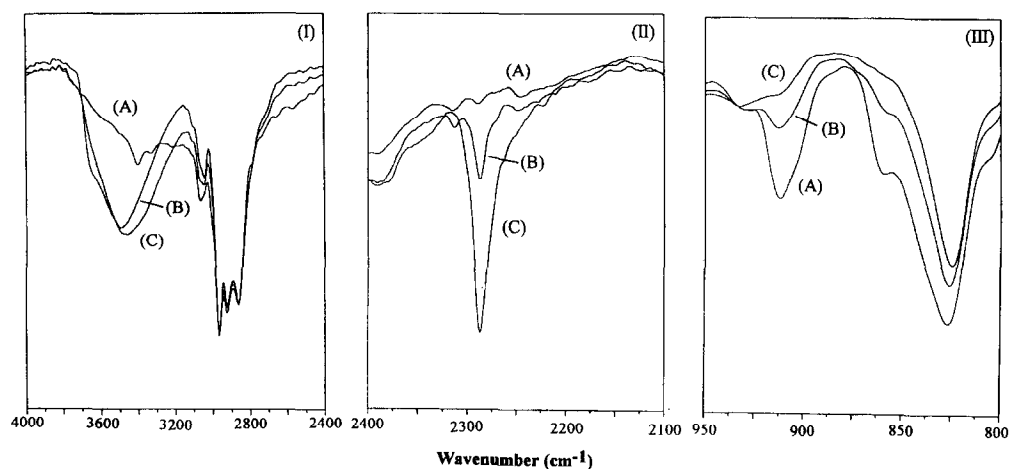
Figure 9 I.r. spectra of code H12 composition (PC–epoxy/T403 blend) recorded in (I) hydroxyl, (II) isocyanate and (III) oxirane stretching region: (A) initial; (B) 80°C for 1 h; (C) 80°C for 1 h and 150°C for 2 h

Curve C of *Figure 8* shows the spectrum of Code H12 composition of the PC–epoxy/T403 blend at 80°C for 1 h. The major absorption at $1730-1740\,cm^{-1}$ indicates that the carbamate is formed and the band representing the original carbonate group of PC disappears completely. Another characteristic revealed in curve C is the band broadening and shifting to lower frequency compared with the corresponding band shown in curve B. Curves A and B of *Figure 9(III)* show that the intensity of oxirane ($915\,cm^{-1}$) decreases substantially and the absorption of N–H symmetric and asymmetric stretching of the aliphatic amine (T403) at 3397 and $3327\,cm^{-1}$ are converted to hydroxyl band at $3300\,cm^{-1}$ [curves A and B of *Figure 9(I)*]. Beside these variations, there is a peak at $2270\,cm^{-1}$. *Figure 9(II)* shows the i.r. spectra of the PC–epoxy/T403 system (Code H12 of *Table 2*) in the region from 2100 to $2400\,cm^{-1}$. Curve A of *Figure 9(II)* presents the spectrum of the system at 25°C. Curves B and C give the spectra of the composition at 80°C for 1 h and at 150°C for 2 h, respectively. The absorption at $2270\,cm^{-1}$ is present and its intensity increased with time and temperature. Such a dramatic variation in i.r. spectra can be explained by the stability of carbamates[11-16]. It is well known that carbamates decompose at higher temperature, and release isocyanate and active hydrogen compounds such as phenol, alcohol, etc. The decomposition temperature is influenced by the substitute groups of the carbamates. Myers and Long[11] reported that the decomposition temperatures of the N-aliphatic aliphatic carbamates (R–NH–CO–O–R), N-aromatic aliphatic carbamates (Ar–NH–CO–O–R), N-aliphatic aromatic carbamates (R–NH–CO–O–Ar), and N-aromatic aromatic carbamates (Ar–NH–CO–O–Ar) are at 250, 200, 180 and 120°C, respectively. The carbamates formed from aliphatic amine (T403) and bisphenol A polycarbonate in this experiment belong to the N-aliphatic aromatic carbonates and should decompose at 180°C according to the reported literature[11]. However, *Figure 9(II)* shows the appearance of the absorption of isocyanate group at $2270\,cm^{-1}$ even at 80°C. This is probably due to the presence of oxirane in the blend system which is able to accelerate the decomposition of the carbamates[16]. Oxirane acts as a weak base or a proton

acceptor that can react with the proton of the carbamates to form the intermediate oxonium complex and isocyanate. The ring opening of the epoxide ring results in an increase in hydroxyl level for the epoxy resin (equation (3)).
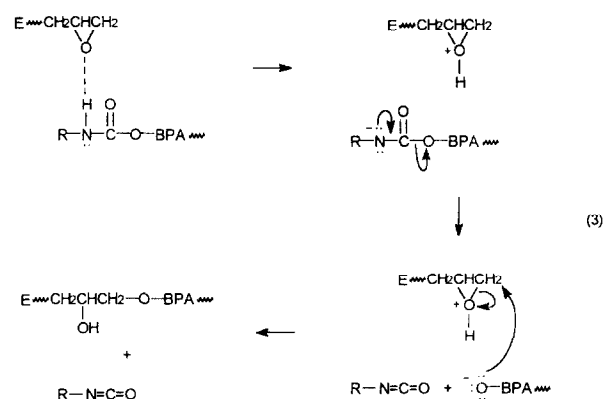
To the end, the isocyanates in equation (3) will react with the hydroxyl group present in the network (equations (2) and (3)) to form a carbamate structure (equation (4)).
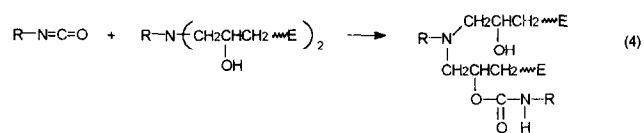
Curve D of *Figure 8* shows that the absorption at $1740\,cm^{-1}$ shifts to $1725\,cm^{-1}$ completely at 150°C for 2 h. Such spectroscopic variations can be explained by the changes of substitute group around the carbamates. As can be seen from equation (1), the aliphatic amine (T403) and bisphenol A polycarbonate yield the N-aliphatic aromatic carbamates with an i.r. absorption peak at $1740\,cm^{-1}$. The N-aliphatic aromatic carbamates decompose to yield the isocyanates which react with hydroxyls of the epoxy to form new N-aliphatic aliphatic carbamates (equation (4)). Comparing the N-aliphatic aliphatic carbamates with the N-aliphatic aromatic
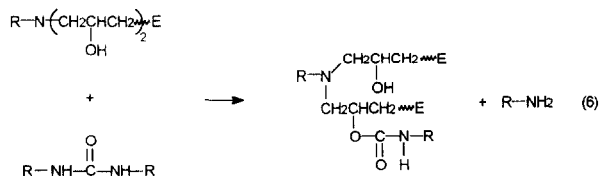
carbamates, the substitute groups of the former has a lower inductive effect than the latter[16]. In other words, the carbonyl stretching absorption of N-aliphatic aliphatic carbamates is lower than that of N-aliphatic aromatic carbamates, at $1725\,cm^{-1}$. From the observation of the i.r. spectra, the results coincide with the proposed mechanism which represents the carbamates crosslink in the network structure of epoxy cured with amine.

(ii) PC dissolved in aliphatic amine by solvent. PC dissolved in aliphatic amine (T403) was prepared by dissolving PC pellets into the dichloromethane solvent at room temperature. The PC solution was then added into the aliphatic amine and heated under vacuum to remove the solvent. The solventless mixture was a yellow, transparent semi-solid. The i.r. spectrum of PC in the carbonyl region is shown in curve A of *Figure 10*. Curve B shows the initial i.r. spectrum of the PC–T403/epoxy blend (Code S12 of *Table 1*) which is similar to that of the resultant product from the model reaction of the DPC/BA = 214/292 blend (Code M3 of *Table 1*), the i.r. absorption band appears at $1650\,cm^{-1}$. This phenomenon indicates that the carbonate groups of PC react with aliphatic amine (T403) to yield the ureas during the dissolving procedure. The reaction mechanism of PC with aliphatic amine is illustrated as follows (equation (5)):

$$R{-}NH_2 \; + \; \text{\tiny www} BPA{-}O{-}\overset{\overset{\textstyle O}{\|}}{C}{-}O{-}BPA\text{\tiny www} \longrightarrow R{-}NH{-}\overset{\overset{\textstyle O}{\|}}{C}{-}NH{-}R \; + \; BPA(OH)_2 \quad (5)$$

Curve C of *Figure 10* represents the i.r. spectrum of the PC–T403/epoxy blend at 80°C for 1 h. This spectrum indicates that the urea structure is virtually unchanged at 80°C. Curve D of this figure gives the spectrum at 150°C for 2 h. The peak at $1725\,cm^{-1}$ appears while the intensity of the band at $1650\,cm^{-1}$ decreases. The band at $1725\,cm^{-1}$ is contributed by the N-aliphatic aliphatic carbamate formed from the isocyanates with the hydroxyl group of the epoxy network previously mentioned. However, there is no absorption band of isocyanate at $2270\,cm^{-1}$. This result indicates that the band at $1725\,cm^{-1}$ obtained does not proceed through the reaction involving the isocyanate group.

The formation of N-aliphatic aliphatic carbamates is proposed to be by the substitute reaction of ureas and hydroxyl groups of epoxy network as shown below[18]:

$$
\begin{array}{c}
R{-}N{\{}CH_2CHCH_2{\}_2}E \\
\quad\quad\quad | \\
\quad\quad\quad OH \\
+ \\
\quad O \\
\quad \| \\
R{-}NH{-}C{-}NH{-}R
\end{array}
\;\longrightarrow\;
\begin{array}{c}
\quad\quad CH_2CHCH_2\text{\tiny www}E \\
R{-}N' \quad\quad | \\
\quad | \quad\quad OH \\
\quad CH_2CHCH_2\text{\tiny www}E \\
\quad\quad\quad | \\
\quad\quad\quad O{-}C{-}N{-}R \\
\quad\quad\quad\quad \| \; | \\
\quad\quad\quad\quad O \; H
\end{array}
\; + \; R{-}NH_2 \quad (6)
$$

In other words, the ureas can react with the cured epoxy and crosslink in the network structure. The aliphatic amines released in equation (6) will react with residual oxirane as shown in equation (2). Curve E of *Figure 10* shows the i.r. spectrum of the resultant product of the PC–T403/epoxy blend (Code S12 of *Table 1*) at 180°C for 2 h. The intensity of carbamate absorption at $1720\,cm^{-1}$ increases substantially, but the residual absorption of the ureas is at $1660\,cm^{-1}$.
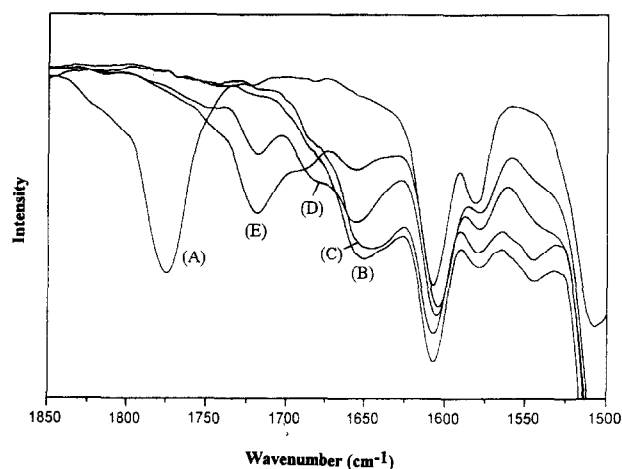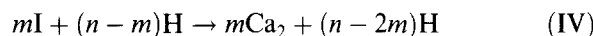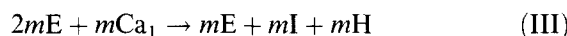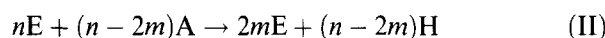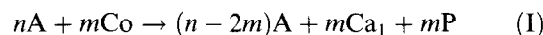

Figure 10 I.r. spectra in the carbonyl stretching region: (A) PC; (B) code S12 blend (PC–T403/epoxy = 1.91/4/10) at 25°C, 3 min; (C) code S12 blend (PC–T403/epoxy = 1.91/4/10) at 80°C, 1 h; (D) code S12 blend (PC–T403/epoxy = 1.91/4/10) at 80°C, 1 h and 150°C, 2 h; (E) code S12 blend (PC–T403/epoxy = 1.91/4/10) at 80°C, 1 h, 150°C, 2 h and 180°C, 2 h

Comparison of the two blend methods

Based on the variations of the i.r. spectra shown in the *Figures 8* and *9(II)*, the evidence suggests deblocking of the PC–epoxy/T403 blend occurred at 80°C and the isocyanates are released (equation (3)). The released isocyanates will further react with the network of epoxy to form a carbamate structure (equation (4)). The ureas formed in the PC–T403/epoxy blend (equation (5)) will react with the network of epoxy at 180°C (equation (6) and *Figure 10*). Both curve D of *Figure 8* and curve E of *Figure 10* show the same absorption band at $1720\,cm^{-1}$, regardless of the blending procedure. This phenomenon reveals that the chemical structure of PC–epoxy/T403 blend is similar to that of the PC–T403/epoxy blend provided that the curing temperature is high. However, some differences still exist between the two blend systems.

(i) PC–epoxy/T403 blend. In the stoichiometric system of epoxide and amine, n equivalents of amine are added into the PC–epoxy blend where the equivalent numbers of carbonate and epoxide are m and n, respectively. The reaction schemes of this system are proposed below:

$$n\text{A} + m\text{Co} \rightarrow (n - 2m)\text{A} + m\text{Ca}_1 + m\text{P} \quad\quad \text{(I)}$$

$$n\text{E} + (n - 2m)\text{A} \rightarrow 2m\text{E} + (n - 2m)\text{H} \quad\quad \text{(II)}$$

$$2m\text{E} + m\text{Ca}_1 \rightarrow m\text{E} + m\text{I} + m\text{H} \quad\quad \text{(III)}$$

$$m\text{I} + (n - m)\text{H} \rightarrow m\text{Ca}_2 + (n - 2m)\text{H} \quad\quad \text{(IV)}$$
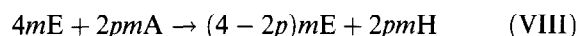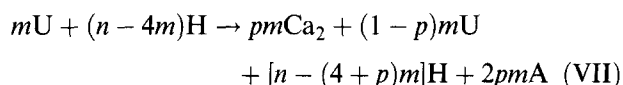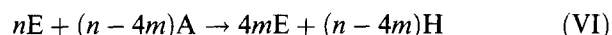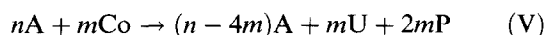
where E represents the epoxides; A represents the amines (N–H); Co represents the carbonates (–O–CO–O–); Ca_1 represents the N-aliphatic aromatic carbamates (R–NH–CO–O–Ar); Ca_2 represents the N-aliphatic aliphatic carbamates (R–NH–CO–O–R); I represents the isocyanates (R–NCO); P represents the phenolic hydroxyls (Ar–OH) and H represents the alcoholic hydroxyls (R–OH).

To summarize the four reactions, the net reaction of the PC–epoxy/T403 blend can be expressed as below:

$$n\text{E} + n\text{A} + m\text{Co} \rightarrow m\text{E} + m\text{Ca}_2 + (n - 2m)\text{H} + m\text{P}$$
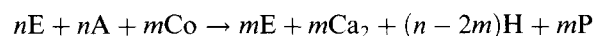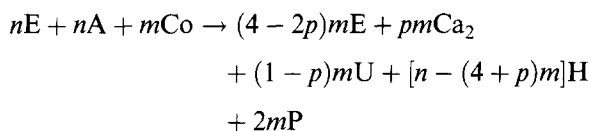
This result indicates the blend with n equivalents of epoxide and m equivalents of carbonate mixed with n equivalents of amine will yield m equivalents of N-aliphatic aliphatic carbamates, $(n - 2m)$ equivalents of hydroxyl group of alcohols release m equivalents of phenol hydroxyl group and m equivalents of the unreacted epoxide remain. When N-aliphatic aliphatic carbamates are formed from the reaction between the isocyanates and the hydroxyl groups of the network, this structure can be considered as a crosslinker of the network (equation (4)). For the same reason, the half equivalent number of the alcoholic hydroxyls shown in equation (II) represents the crosslinking points formed from the ring opening reaction of the epoxide with the primary aliphatic amine. In other words, the crosslinkers of this blend system could be calculated by the addition of m and $1/2^*(n - 2m)$. That means the equivalent numbers of crosslinkers are $n/2$. The released m equivalents of hydroxyl groups of phenol can be seen as $m/2$ equivalents of bisphenol A, which can act as a plasticizer in the cured resin. The m equivalents of epoxide unreacted in the blend represent the amount of chain ends.

(ii) PC–T403/epoxy blend. In a stoichiometric system, n equivalents of epoxide are added into the PC–T403 mixture while the equivalent numbers of carbonate and amine are m and n, respectively. The reaction schemes of this system are proposed below:

$$nA + mCo \rightarrow (n - 4m)A + mU + 2mP \qquad (V)$$

$$nE + (n - 4m)A \rightarrow 4mE + (n - 4m)H \qquad (VI)$$

$$mU + (n - 4m)H \rightarrow pmCa_2 + (1 - p)mU$$
$$+ [n - (4 + p)m]H + 2pmA \quad (VII)$$

$$4mE + 2pmA \rightarrow (4 - 2p)mE + 2pmH \qquad (VIII)$$

where U represents the ureas $(R-NH-CO-NH-R)$; $(1 - p)$ represents the amount of the ureas remaining in the matrix, where $0 \leq (1 - p) \leq 1$.

To summarize the four reactions, the net reaction of the PC–T403/epoxy blend can be expressed as,

$$nE + nA + mCo \rightarrow (4 - 2p)mE + pmCa_2$$
$$+ (1 - p)mU + [n - (4 + p)m]H$$
$$+ 2mP$$

This result indicates that the mixture of n equivalents of amine and m equivalents of carbonate mixed with n equivalents of epoxy will yield the pm equivalents of N-aliphatic aliphatic carbamates, $[n - (4 + p)m]$ equivalents of alcoholic hydroxyls, $2m$ equivalents of the released hydroxyl group of phenol, $(4 - 2p)m$ equivalents of the unreacted epoxide, and $(1 - p)m$ equivalents of the ureas separated in the matrix. In other words, the crosslinkers of this blend system are $n/2 - 2(1 - p)m$

equivalents. Additionally, there are m equivalents of bisphenol A released as plasticizers and $(1 - p)m$ equivalent of ureas formed as flexibilizers. The chain ends from the unreacted epoxide are $(4 - 2p)m$ equivalents which can be considered as the network defects.

The equivalent numbers of crosslinkers, plasticizers and chain ends are summarized in *Table 3*. The crosslinkers of the PC–epoxy/T403 blend are more than those of the PC–T403/epoxy blend as shown in *Table 3*. Furthermore, the equivalent numbers of plasticizer and chain ends of the PC–epoxy/T403 blend are less than that of the PC–T403/epoxy blend. These phenomena suggest that the T_g of the PC–T403/epoxy blend system would be lower than that of the PC–epoxy/T403 system. *Figure 11* shows the glass transition temperatures of epoxy blended with various contents of polycarbonate obtained from the two preparation procedures.

CONCLUSION

The reactions between carbonates and aliphatic amines result in end products containing carbamates and ureas. The spectroscopic variations of the PC–epoxy blend cured by aliphatic amines are similar to those of the corresponding model reaction system. This study has positively verified the reaction involving PC carbonate and amine to form the carbamates and ureas in the blend. Two different methods were carried out to prepare the blends: (1) PC was dissolved in the epoxy by hot melt to obtain a homogeneous PC–epoxy mixture, then aliphatic amine was added to cure the blend. (2) PC was dissolved in aliphatic amine by solvent to obtain the PC–aliphatic mixture, and then the epoxy was added to cure the mixture. In the PC–epoxy/aliphatic amine blend system by method (1), the aliphatic amine reacts with PC
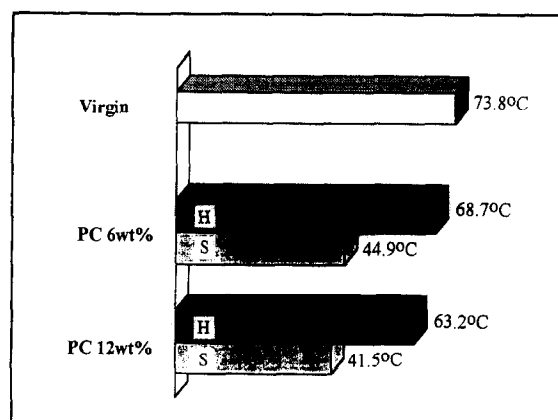

Figure 11 The glass transition temperatures of epoxy blended with various contents of polycarbonate obtained from the two preparing methods at 80°C, 2 h and 150°C, 2 h. H represents the PC–epoxy/T403 blend. S represents the PC–T403/epoxy blend

Table 3 The structure difference between the PC–epoxy/T403 blend and PC–T403/epoxy blend

Structure Unit	PC–epoxy/T403 blend	PC–T403/epoxy blend
Crosslinker (moles)	$n/2$	$n/2 - 2(1 - p)m$
Plasticizer (BPA released) (moles)	$m/2$	m
Flexibilizer (ureas remained) (moles)	—	$(1 - p)m$
Chain end (residue epoxide) (moles)	m	$(4 - 2p)m$

carbonate to yield the carbamates with a much higher rate. The residual amine initiates the normal curing reaction with epoxide. At the same time, the deblock reaction of the carbamates is accelerated by the presence of the oxirane and yields the isocyanate products at 80°C. The isocyanate products will react with the hydroxyl groups of the network and results in a new carbamate structure crosslinking in the cured resin. While in the PC–aliphatic amine/epoxy blend system by method (2), the aliphatic amine reacts with PC carbonate to yield the ureas before the epoxy addition. The residual amine then proceeds the usual ring opening reaction with oxirane. Most of the ureas undergo sub-stitute reaction with the hydroxyl groups of cured resin to yield the cured network structure containing the carbanates crosslinking while a fraction of them remained in the matrix as flexibilizers. Although the i.r. spectra of the end products obtained by both methods are similar, the reactions involved are different. The contents of crosslinkers, plasticizers, chain ends and flexibilizers of the PC–epoxy/aliphatic amine blend system are lower than those of the PC–aliphatic amine/epoxy blend system. This can be utilized to predict that the PC–epoxy/aliphatic amine blends would have a higher T_g and lower fracture energy than the corresponding PC–aliphatic amine/epoxy blends.

ACKNOWLEDGEMENTS

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