PII: S0032-3861(96)01089-0

Chemical reactions occurring during the preparation of polycarbonate-epoxy blends

Ming-Shiu Li*, Chen-Chi M. Ma*†, Miaw-Ling Lin‡ and Feng-Chih Chang‡

*Institute of Chemical Engineering, National Tsing Hua University and ‡Institute of Applied Chemistry, National Chiao Tung University, Hsinchu, 30043, Taiwan

The chromatographic and spectroscopic variations of polycarbonate (PC)–epoxy blends during the hot-melt process of dissolving PC in epoxy were observed. The characteristics of PC–epoxy blend are influenced by the following factors: (1) the minor components in the epoxy monomer, (2) the ratio of PC to epoxy in the PC–epoxy blend, and (3) the environment in which the blends are prepared. The water contained in the epoxy may hydrolyse the PC and yield two phenolic chain end groups and carbon dioxide. The alcoholic hydroxyls existing in epoxy may transesterify the original aromatic/aromatic carbonate of PC to aromatic/ aliphatic and aliphatic/aliphatic carbonates. The α-glycol present in epoxy would react with the carbonate of PC to form a cyclic carbonate structure. Whether the PC hydrolysis, transesterification or cyclization reaction proceeds during the process of dissolving PC in epoxy depends on the minor components present in the epoxy monomer. The extent of the aforementioned reactions increases with the decrease of the PC content in the PC–epoxy blend. Results show that the oxirane of epoxy would not react with the carbonate of PC in the absence of a catalyst. The possibility of the oxidation of the PC–epoxy blends could be avoided by carrying out the experiment under a nitrogen atmosphere. © 1997 Elsevier Science Ltd.

(Keywords: epoxy; blend; polycarbonate)

INTRODUCTION

Toughening of crosslinked epoxy resin by blending with various thermoplastics has been investigated extensively. One of the numerous thermoplastics employed which has attracted special attention is polycarbonate (PC) due to its high toughness. It has been well recognized that the reactions between PC and epoxy can take place under the following situations: (1) during the preparation of the PC–epoxy mixture, and (2) during the curing of the PC–epoxy blend. Transesterification between PC and epoxy has been reported when the PC–epoxy was cured by tertiary amine[1,2], anhydride[3-6], quaternary ammonium salt[7,8] and aromatic amine[9-14]. The PC could transamidate with amine when the PC-epoxy was cured with aliphatic amine[15-18].

In spite of extensive research on the reactions occurring during the curing of PC–epoxy blends, the chemical aspect of the reactions involved during the preparation of a PC–epoxy mixture has been less explored[5,11,14,18]. In the past, the precured blends of PC and epoxy were made by dissolving the thermoplastics and the epoxy monomer in dichloromethane followed by evaporating the solvent[2,11-14,16,17]. This solvent process has the disadvantage that the solvent has to be driven off, otherwise it may affect the final properties of cured resin. Additionally, the PC may crystallize when the dichloromethane is removed by distillation[11]. The hot-melt method is another process in which the thermoplastics and melt dissolved in the epoxy

monomer directly to overcome the drawbacks of the solvent method[1,3-7,9-11,15,18]. This melt method usually has to be carried out at higher temperature. For example, Martuscelli et al.[4] dissolved PC in novolac type epoxy at 220°C, and Li et al.[10] blended PC with the diglycidyl ether of bisphenol-A (DGEBA) resin at 160°C. Both reported that a clear, homogeneous and viscous solution was obtained. The PC–epoxy blends prepared by the hot-melt method have been analysed by Abbate et al.[5], Rong and Zeng[18], Don and Bell[11] and Wu and Woo[14]. Abbate et al.[5] found that the PC underwent chain-scission reactions and showed a significant decrease in molecular weight during the high temperature dissolution process. They concluded that the chain scission process of PC may occur either by the hydrolysis of the carbonate groups or by the reaction of carbonate groups with alcoholic functionalities present as impurities in the epoxy resin. Rong and Zeng[18] studied the interaction among the components during the dissolution process of the PC–epoxy blend by dynamic mechanical analysis and characterized both PC fractions selectively extracted from the uncured mixture and epoxy remainder. The dynamic mechanical spectrum of the pure PC showed a broad α transition while the PC recovered from the extracted fraction showed a narrower α transition peak with lower T_α. They concluded that this result is due to the occurrence of PC chain scission and plasticizing by the lower molecular weight fraction. Don and Bell[11] also investigated the melt blending process for PC–epoxy blends and found that in a copolymer structure the PC chains were bonded to the epoxy network. The conversion of the carbonyl groups
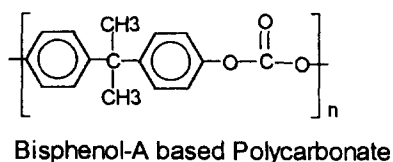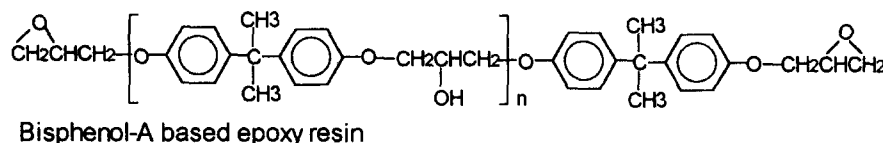
---

† To whom correspondence should be addressed

in the PC was measured as 8% after 6 h at 200°C. Wu and Woo[14] showed that the PC–epoxy blends heated at 190°C for 6–12 h would form a crosslinking structure with a high extent of reaction. No PC could be etched out by the dichloromethane solvent from the cured product. They explained that the DGEBA oligomers have multiple hydroxyl sites per molecule; thus, the exchange reactions between PC and epoxy can lead to a network structure in the absence of any curing agents.

The objective of this study was initiated to clarify the controversy on the reaction between PC and epoxy in the absence of curing agent. Several variables were examined including: (1) the minor structural variation of the epoxy monomer, (2) the PC/epoxy ratio of the blend, and (3) the blending conditions. Infrared (i.r.) spectra and ^{13}C nuclear magnetic resonance (n.m.r.) spectra were employed to reveal the structural changes during the blending procedure. Gel permeation chromatography (g.p.c.) was also utilized to investigate the molecular weights of blends.

EXPERIMENTAL

Materials

The bisphenol-A based natural grade PC with a melt flow rate of 15 used in this study is the Calibre 301-15 from Dow Chemical Co. The epoxy prepolymers, DER 332, 383 and 331, of low molecular weight DGEBA with epoxide equivalent weights of 172–176, 176–183 and 182–192 used in this study were also purchased from Dow. The chemical structures of PC and epoxy are illustrated as follows:
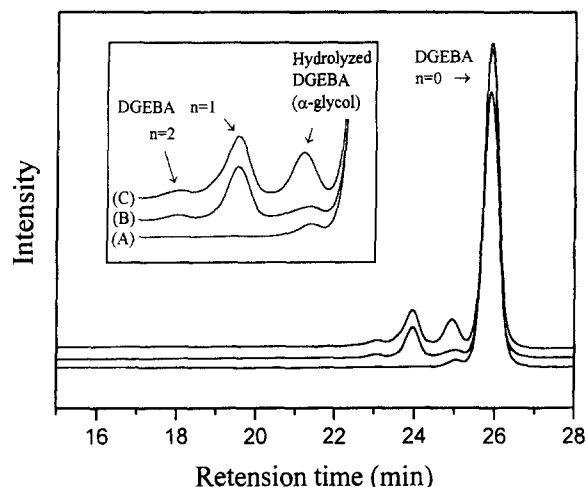
Figure 1 Chromatograms of epoxy used in this study: (A) DER 332 epoxy resin; (B) DER 383 epoxy resin; (C) DER 331 epoxy resin

Associates chromatograph provided with a Waters R403 refractometer.

I.r. spectroscopy. One drop of the PC–epoxy blend was pasted onto a thin film between two sodium chloride plates and then mounted on a sample holder located in an i.r. instrument. The i.r. spectra were obtained on a Perkin-Elmer 842 i.r. spectrometer with a resolution of $2.4\,cm^{-1}$ in the absorption mode.

^{13}C n.m.r. The PC–epoxy blend diluted by deuterated chloroform was used to observe the ^{13}C n.m.r. spectra, which were measured with a Bruker 400 Fourier

Bisphenol-A based epoxy resin

Bisphenol-A based Polycarbonate

Procedures and instrumentations

Experimental techniques. Before dissolving the PC in epoxy, both materials were dehydrated at 120°C for 24 h *in vacuo*. The mixture of 30 wt% PC in epoxy was prepared by dissolving the PC (450 g) in the epoxy resin (1050 g) at 200°C after stirring the mixture under dry nitrogen gas for 2 h.

G.p.c. Tetrahydrofuran (THF) was added to the PC–epoxy blend to prepare a 1% solution, which was injected into the chromatograph for the g.p.c. study. The solvent utilized was THF at a flow rate of $1.0\,ml\,min^{-1}$. The results were obtained with a Waters

transform n.m.r. spectrometer with a magnetic field strength of 9.4 T (e.g. ^{13}C = 100.6 MHz).

RESULTS AND DISCUSSION

Compositions of epoxy resin

The commercial DGEBA liquid epoxy resins (LERs) were manufactured by the supplier via the coupling reaction between epichlorohydrin and bisphenol-A with an average molecular weight of approximately 340–380. Not all of the species present in resins are the DGEBA; side reactions may occur during the manufacturing procedure. The amount of the minor products present in any LER, obviously, can be varied by the
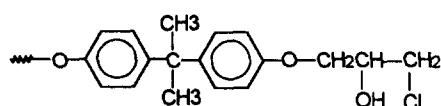
Table 1 Compositions of epoxy used in this study

Items (unit)	Materials		
	DER 332	DER 383	DER 331
Viscosity (cps)[a]	4805	9400	11 623
EEW (g mol^{-1})[a]	173.4	182.1	185.6
DGEBA [n = 0] (%)[b]	98.0	86.1	79.3
[n = 1] (%)	0.0	9.7	11.1
[n = 2] (%)	0.0	1.1	2.2
α-Glycol (%)	—	—	7.7
Others (%)	2.0	3.1	—
Water, max. (ppm)[a]	253.0	334.6	570.0
Hydro. Cl[c] max. (ppm)[a]	201.0	205.5	234.0

[a] Represents the data obtained from the certificate of analysis supplied by Dow Chemical Co.
[b] Represents the fraction of optical density measured by the g.p.c. refractometer
[c] Hydrol. Cl (hydrolysable chloride) represents the 1,2-chlorohydrin, the structure of which is as follows:

Table 2 Main i.r. absorptions of epoxy used in this study

Code	Band (cm^{-1})	Assignment
A	3588	O–H stretch
B	3065	Aromatic C–H stretch
	3046	
C	2966	Aliphatic C–H stretch
	2923	
	2863	
	2737	
D	1608 m	Benzene ring stretch
	1582 w	
	1509 s	
E	1457 w	CH₃ asymmetrical bend
F	1359 w	CH₃ symmetrical bend
G	1294 m	Epoxy ring mode: the C–C, C–O and C–O bonds all stretching in phase
H	1246 s	Ar–O–R asymmetrical bend
I	1182 m	—
J	1032 m	Ar–O–R symmetrical bend
K	910	Epoxy ring mode: the C–C bond contracts while both C–O bonds stretch
L	855 sh	Epoxy ring mode: the C–C bond does not change in length while one C–O bond stretches and the other contracts
M	828	Benzene ring bent out of plane

s = strong; m = medium; w = weak; sh = shoulder

processes chosen and the processing conditions. Therefore, LERs may have similar epoxide equivalent weight (EEW), but with different properties[19]. *Figure 1* shows the g.p.c. chromatograms for various LERs with similar EEWs. Curve A of *Figure 1* is the chromatogram for the DER 332 epoxy resin. This curve indicates that this resin was made up mostly of monomeric DGEBA (n = 0) and the content of impurity is only 2.0% by area. The impurity defined here is any component other than the DGEBA (n = 0). The g.p.c. chromatogram for DER 383 is shown in curve B of *Figure 1*, where the component distribution for n = 0, 1 and 2 are 86.1, 9.7 and 1.1%, respectively. Other components make up about 3.1%. Curve C of *Figure 1* shows the component distribution of DER 331 where n = 0, 1 and 2 and 79.3, 11.1 and 2.2%, respectively. Another special characteristic of this DER 331 resin is a major

peak appearing between monomeric DGEBA (n = 0) and homologus DGEBA (n = 1). This absorption peak is mainly the hydrolysed resin containing α-glycol that makes up 7.7% in the DER 331 epoxy resin. DER 331 was prepared from DER 383 by partially hydrolysing the epoxide into α-glycol to increase the hydroxyl content.

The compositions of these epoxy resins are summarized in *Table 1*. *Figure 2* shows the i.r. spectra of those epoxy resins; the characteristics of the main absorption peaks are listed in *Table 2*[19–21]. Most of the peak positions and their relative intensities of DER 332 epoxy resin are similar to those of DER 383 and 331 epoxy resins. The main difference among those resins is the hydroxyl stretching region at 3200–3700 cm^{-1}. Curve A of *Figure 2* indicates that the hydroxyl content and the possible contaminated water of the DER 332 epoxy is too low to be detected directly from the i.r. spectrum. Curve C of *Figure 2* clearly shows the presence of the hydroxyl stretching absorption band in the DER 331 epoxy resin. The absorption intensity of DER 383 epoxy resin (curve B, *Figure 2*) in this region is higher than that of DER 332, but lower than that of DER 331. These observed phenomena are coincident with the results of g.p.c. analysis mentioned previously. Since DER 332 epoxy resin consists mainly of pure monomeric DGEBA (n = 0), the small hydroxyl stretching band may come from the water contaminating this resin. The absorption of DER 383 epoxy resin in the hydroxyl group region may be due to the homologous DGEBA (n ⩾ 1) and some water present. The hydroxyl stretching absorption of DER 331 epoxy resin comes from the hydrolysed α-glycol, homologus DGEBA (n ⩾ 1) and water present in this resin. The chlorohydrins (hydrolysable chloride) present in these three resins may also contribute to the absorption in this region. The maximum contents of the hydrolysable chloride are only 300–500 ppm; hence, the contribution from these trace fractions on the influence of hydroxyl groups during the hot-melt procedure for PC with epoxy may be ignored.

Products of the PC-DER 332 blend

When PC was dissolved in DER 332 epoxy resin by the hot-melt method at 200°C for 2 h a clear, homogeneous and viscous solution was found at high temperature. When this homogeneous PC–DER 332 mixture was cooled down slowly, the PC crystallized from the mixture at lower temperature and the whole mixture solidified like a wax. For example, a PC–DER 332 mixture with a weight ratio of PC to DER 332 of 3/7 became cloudy at 147°C. This cloudy mixture consists of large PC spherulites which can be observed as well developed Maltese crosses with crossed polarizers. The morphology and the micrographs of the PC–DER 332 mixture will be reported later.

Curve A of *Figure 3* presents the g.p.c. chromatograms for the original PC, and Curve B of *Figure 3* shows that of the PC–DER 332 mixtures after melt mixing in a special weight ratio. Comparing these two curves indicates that the molecular weight of the original PC decreased during the hot-melt process. This phenomenon can be interpreted as PC hydrolysis due to the slight amount of water present in the DER 332 epoxy resin. It is well known that the hydrolysis of an aromatic
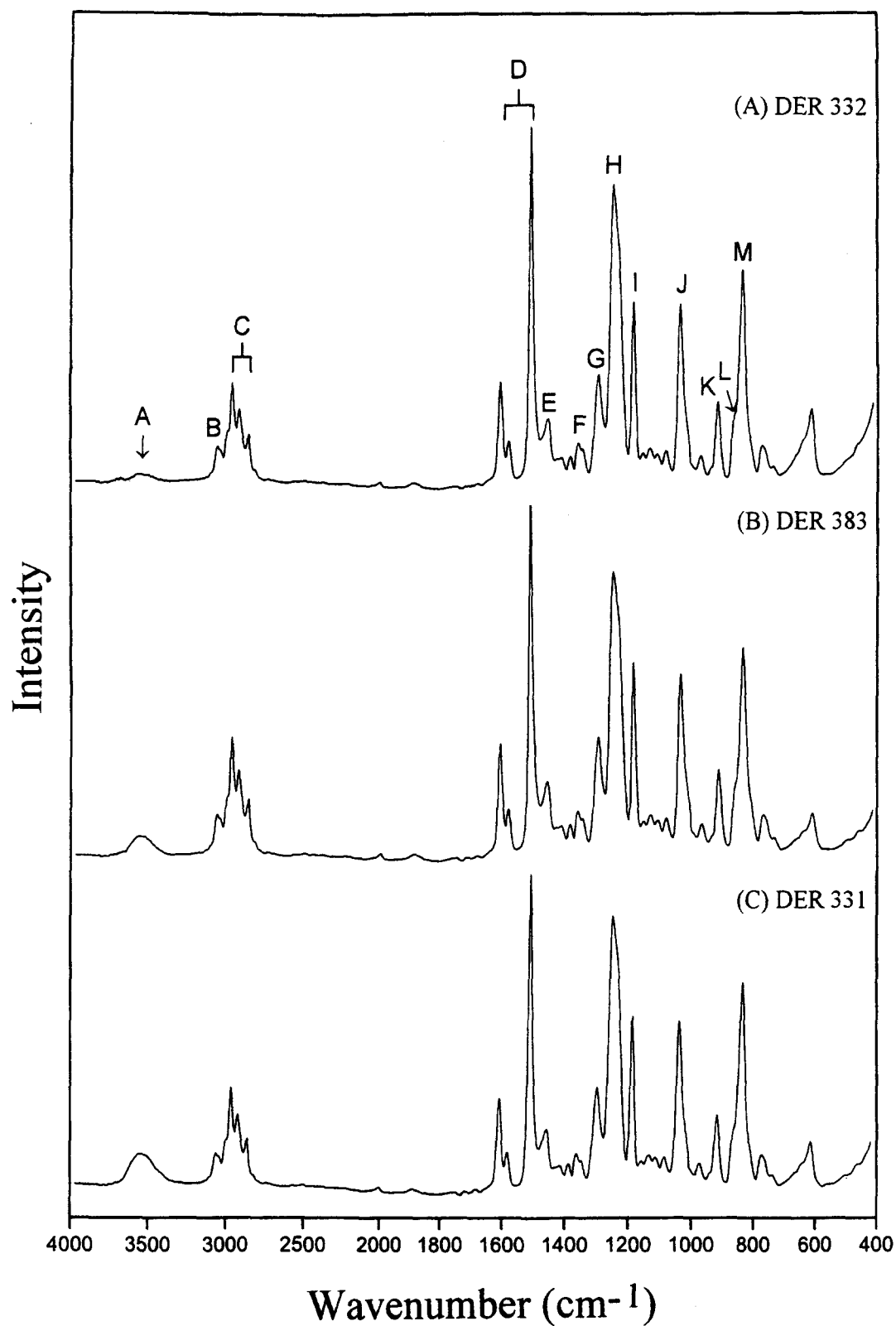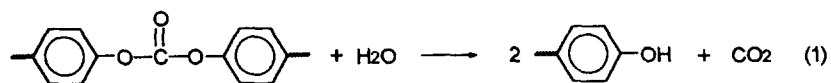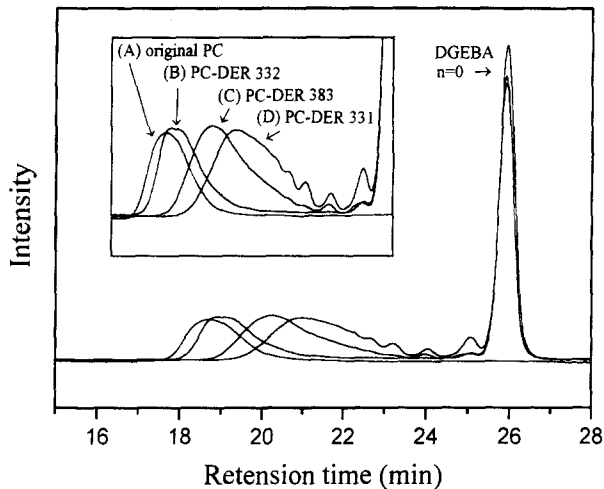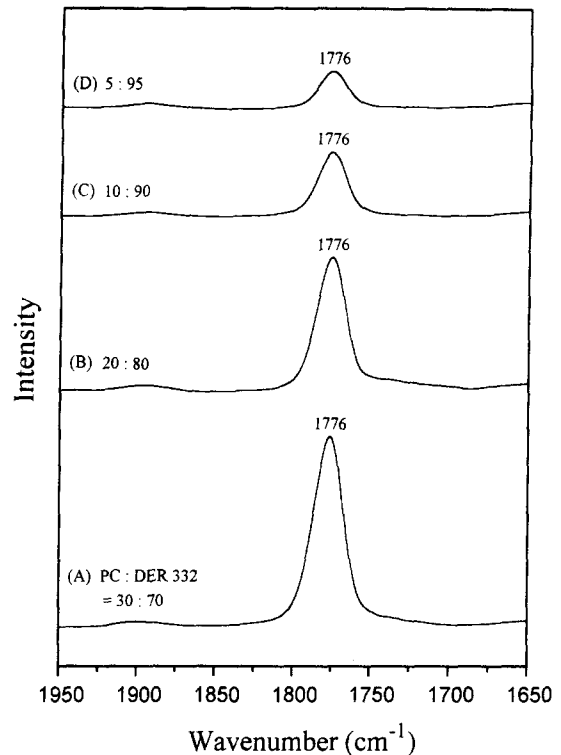
Figure 2 The i.r. spectra of epoxy used in this study: (A) DER 332 epoxy resin; (B) DER 383 epoxy resin; (C) DER 331 epoxy resin

carbonate yields two phenolic end groups and carbon dioxide as below[22]:

$$\text{—}\bigcirc\text{—O—}\overset{\overset{\text{O}}{\parallel}}{\text{C}}\text{—O—}\bigcirc\text{—} \; + \; H_2O \; \longrightarrow \; 2 \; \text{—}\bigcirc\text{—OH} \; + \; CO_2 \quad (1)$$
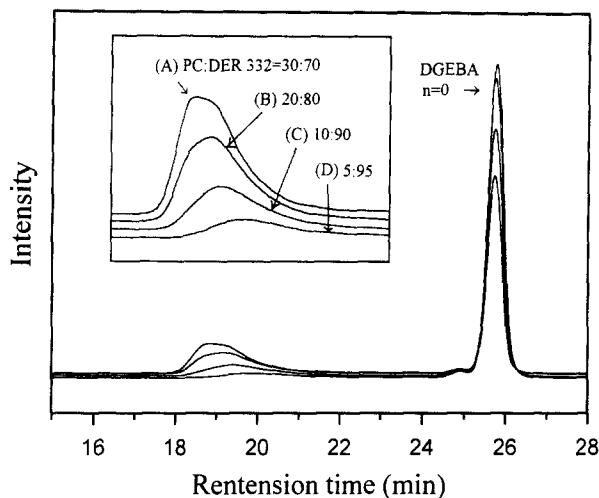
Figure 3 Chromatograms of (A) original PC and PC–epoxy blend with a weight ratio of PC to epoxy of 3/7 (w/w). Epoxies used are: (B) DER 332 epoxy resin; (C) DER 383 epoxy resin; (D) DER 331 epoxy resin
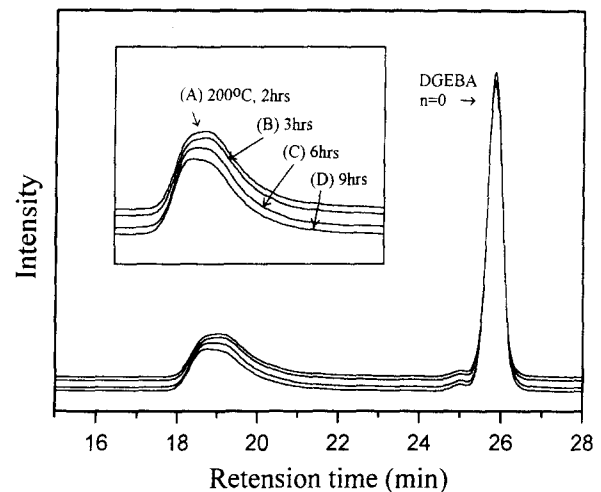

Figure 4 Chromatograms of PC–DER 332 blend with various weight ratios of PC to DER 332 epoxy resin: (A) 3/7; (B) 1/4; (C) 1/9; (D) 1/19

Figure 5 The i.r. spectra of PC–DER 332 blend with various weight ratios of PC to DER 332 epoxy resin: (A) 3/7; (B) 1/4; (C) 1/9; (D) 1/19

Figure 6 Chromatograms of PC–DER 332 blend with weight ratio of PC to epoxy of 30/70 (w/w) heated at 200°C for various times: (A) 2 h; (B) 3 h; (C) 6 h; (D) 9 h

Figure 4 shows the chromatograms of PC–DER 332 blends with various weight ratios of PC to DER 332 epoxy resin. The g.p.c. chromatograms show that the PC molecular weights decreased very significantly with increasing epoxy content in the blend. Compared to the blend with higher PC content, the blend with lower PC content has more water in the epoxy resin to react with the carbonyl groups of the PC and causes more chain scissions in the PC molecule. *Figure 5* illustrates the i.r. spectra of the PC–DER 332 blend with different weight ratios of PC to DER 332 epoxy resin in the carbonyl stretching region. *Figure 5* shows that the characteristic of the carbonyl stretching band at a frequency $\nu = 1776\,\text{cm}^{-1}$, a width $w = 10.44\,\text{cm}^{-1}$ and an amplitude $A = 0.76$ Gaussian does not vary with the PC content in the PC–DER 332 blend. This spectroscopic result confirms that the residual carbonate groups of PC in the blend are essentially the same as the original carbonate of PC. *Figure 6* shows the g.p.c. chromatograms of the PC–DER 332 blend (3/7) after heating at 200°C under nitrogen. This result indicates that the molecular weights of PC and DER 332 in the blend are

nearly unchanged. *Figure 7* shows the i.r. spectra in the region of the carbonyl group, where the carbonyl group absorption does not change noticeably during heating. Both g.p.c. and i.r. results show that the carbonyl does not react with oxirane in the absence of a catalyst. In other words, no other reaction occurs after the water contained in the original DER 332 epoxy resin is consumed by the PC hydrolysis.

Don and Bell[11] reported that the reactions between phenolic or carbonate groups of PC with the epoxide group of epoxy take place at 200°C. The reaction between carbonate and epoxide was confirmed by shifting to lower frequency in the i.r. absorption. The conversion of the carbonate groups was measured as 8%
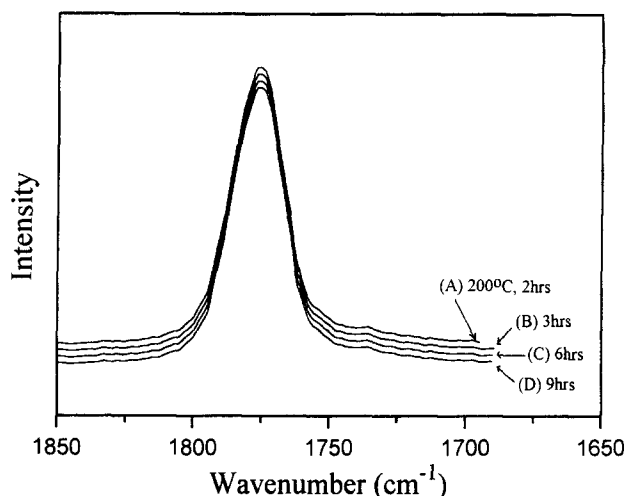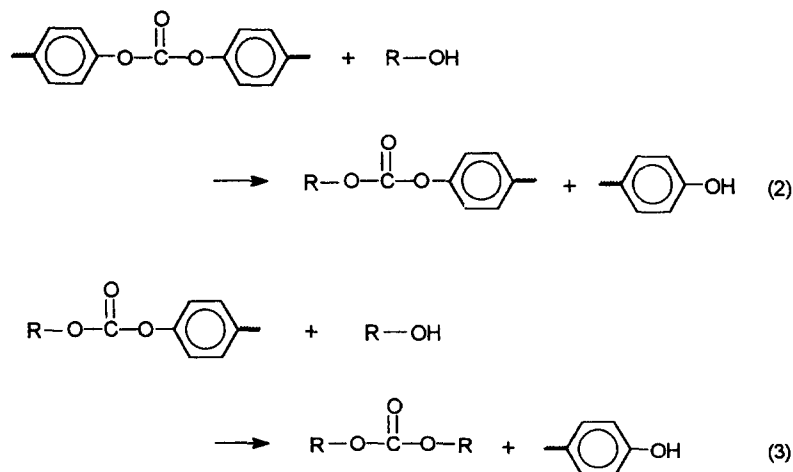
Figure 7 The i.r. spectra of PC–DER 332 blend with weight ratio of PC to epoxy of 3/7 (w/w) heated at 200°C for various times: (A) 2 h; (B) 3 h; (C) 6 h; (D) 9 h

TGDDM (tetraglycidyl-4,4'-diaminodiphenylmethane) by heating the blend in the absence of any curing agents. The TGDDM epoxy possesses two tertiary amine sites in every monomer molecule which are able to initiate transesterification and cyclization reactions between PC and epoxy[1]. In other words, the system which Su and Woo employed is not the same as in this study.

Products of the PC-DER 383 blend

The mixture obtained by dissolving the PC in DER 383 via the hot-melt method at 200°C for 2 h is a clear, homogeneous and viscous solution at high temperature. The PC can be crystallized after cooling. However, the amount and size of the PC spherulites of this blend are substantially smaller than those of the PC–DER 332 blend system. This phenomenon can be explained by the result of *Figure 3*. Curve C of *Figure 3* presents the chromatogram for the PC–DER 383 blend (3/7). Comparing curve C with curve B of *Figure 3*, the molecular weight of PC in the PC–DER 383 blend (3/7) is lower than that in the PC–DER 332 blend (3/7). It is reasonable to assume that the extent of crystallization decreases when part of the PC reacts with epoxy. In the PC–DER 383 blend (3/7), the reduction of molecular weight of PC is caused by two possible paths: (1) PC was hydrolysed by the water contained in the DER 383 epoxy resin; or (2) PC transesterifies with the alcoholic hydroxyls in the DER 383 epoxy resin. The alcoholic hydroxyls come from the homologous DGEBA $(n \geqslant 1)^{22}$. These aliphatic hydroxyl groups can transesterify with the carbonate groups of PC and scissor the PC chain to shorter segments as follows:

while the extent of epoxide disappearance was 30% after heating at 200°C for 6 h. A similar result can be expected if the i.r. spectrum is measured by coating the blend as a thin film between two sodium chloride plates at elevated temperature. However, if the PC (450 g) is dissolved in epoxy resin (1050 g) at 200°C under dry nitrogen gas, the opposite result would be observed. Comparing these two experimental procedures revealed that the spectroscopic variations observed by Don and Bell[11] may be due to the occurrence of some oxidation.

Su and Woo[2] studied and proposed the possible mechanisms of the chemical reactions between PC and

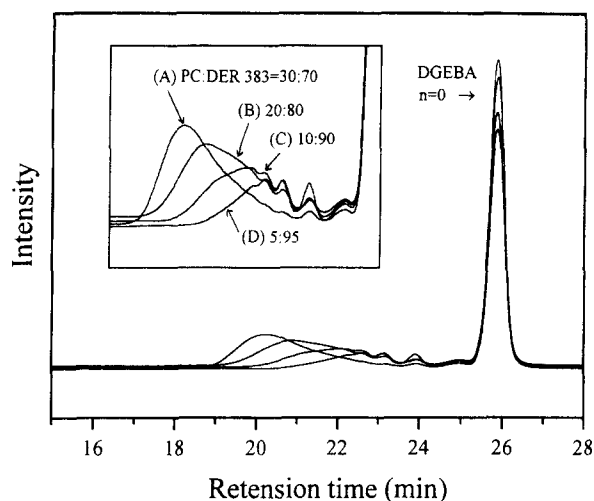where R–OH represents the aliphatic hydroxyl of the homologue of DGEBA $(n \geqslant 1)$ as:
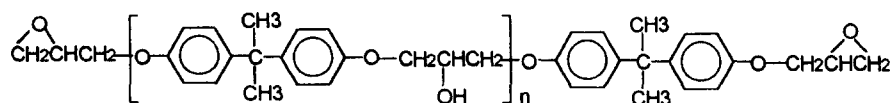
Figure 8 Chromatograms of PC–DER 383 blend with various weight ratios of PC to DER 383 epoxy resin: (A) 3/7; (B) 1/4; (C) 1/9; (D) 1/19
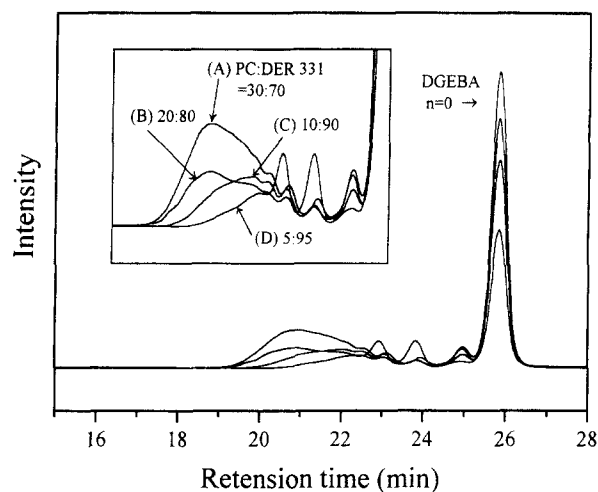

Figure 10 Chromatograms of PC–DER 331 blend with various weight ratios of PC to DER 331 resin: (A) 3/7; (B) 1/4; (C) 1/9; (D) 1/19
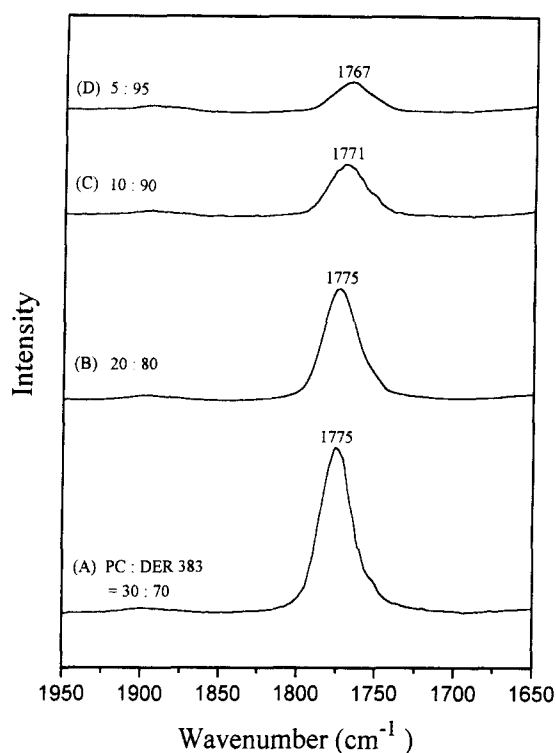

Figure 9 The i.r. spectra of PC–DER 383 blend with various weight ratios of PC to DER 383 epoxy resin: (A) 3/7; (B) 1/4; (C) 1/9; (D) 1/19
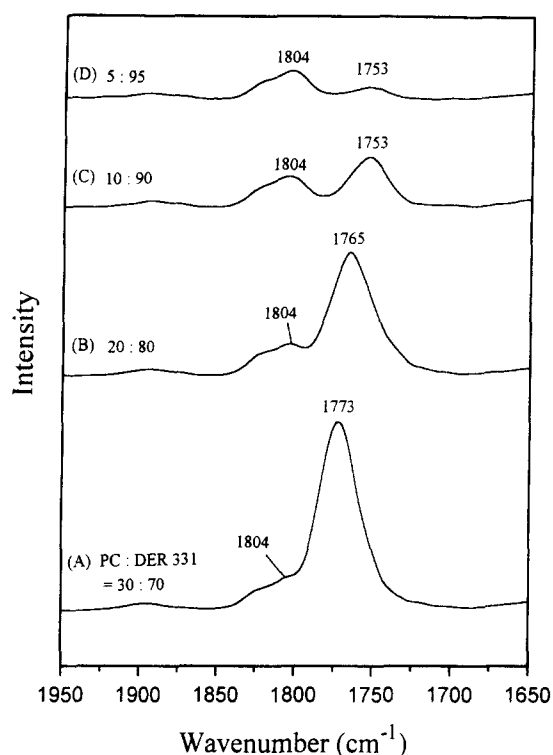

Figure 11 The i.r. spectra of PC–DER 331 blend with various weight ratios of PC to DER 331 epoxy resin: (A) 3/7; (B) 1/4; (C) 1/9; (D) 1/19

Figure 8 shows the g.p.c. chromatograms for the PC–DER 383 blends containing various weight ratios where the molecular weight of PC decreases with the decrease in PC content. *Figure 9* presents the i.r. spectra of PC–DER 383 blends containing various weight ratios of PC to epoxy in the carbonyl stretching region. *Figure 9* shows that the carbonate absorption band of the PC was broadened and shifted to a lower frequency by decreasing the PC content in the PC–DER 383 blend. The blend (PC/DER 383 = 30/70) has an absorption peak at $1775 \, \text{cm}^{-1}$ (curve A of *Figure 9*) while the absorption peak of the blend (PC/DER 383 = 1/19) is at $1767 \, \text{cm}^{-1}$ (curve D of *Figure 9*). This phenomenon can be explained by the transesterification converting the original carbonate group of 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). The absorption frequencies 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, 1762 and $1746 \, \text{cm}^{-1}$, respectively[24]. Therefore, the variation of the carbonate adsorption band shown in *Figure 9*, due to transesterification, consists of three major components with different intensities. The distribution of these three different carbonate moieties is a function of the extent of reaction.

Products of the PC–DER 331 blend
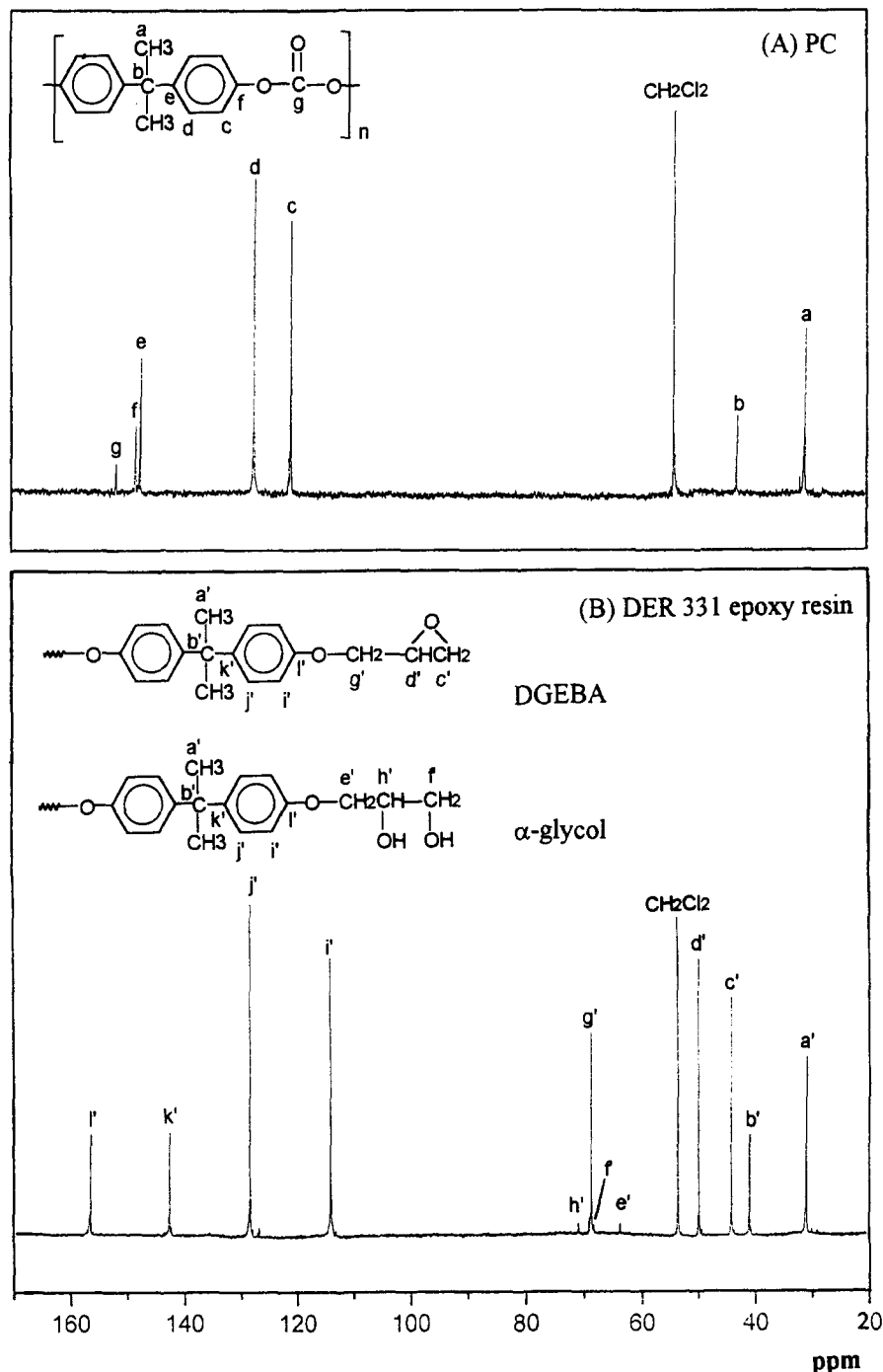
The mixture obtained by dissolving the PC in DER

Figure 12 The ^{13}C n.m.r. spectra of (A) PC; (B) DER 331 epoxy resin; (C) PC–DER 331 blend (PC/DER 331 of 3/7); (D) PMD

331 epoxy resin by the hot-melt method at 200°C for 2 h is also a clear, homogeneous and viscous solution at high temperature. In the mixture, the PC spherulites did not form after cooling. Curve D of *Figure 3* presents the chromatogram of the PC–DER 331 blend (PC/DER 331 = 3/7) where the molecular weight of PC is significantly lower than those of the PC–DER 383 and PC–DER 332 blends. By the Flory–Huggins rule, lowering the molecular weight of PC and the reaction rate between epoxy and PC could increase the miscibility of the blend system. Water and alcoholic hydroxyls in homologous DGEBA ($n \geqslant 1$) and the α-glycol in DER 331 are able to decompose the PC molecular chain. *Figure 10* shows the g.p.c. chromatograms of the PC–DER 331 blends with various weight ratios. Again,

the molecular weight of PC decreases with the decrease of the PC content. *Figure 11* gives the i.r. spectra of PC–DER 331 blends with various weight ratios in the carbonyl stretching region. Curve A of *Figure 11* presents the spectrum of the PC–DER 331 blend (PC/DER 331 = 3/7). Comparing this i.r. spectrum with that of curve A of *Figure 5*, the absorption peak of this PC–DER 331 blend (PC/DER 331 = 3/7) was broadened and shifted to lower frequency (1776 *versus* 1773 cm^{-1}). This spectrum (curve A) of *Figure 11* also shows the appearance of a broad shoulder in the high-frequency region. Curve B of *Figure 11* clearly shows the original carbonyl absorption band splitting into two bands, at 1765 and 1804 cm^{-1}, respectively. Curves C and D of *Figure 11* clearly show that the
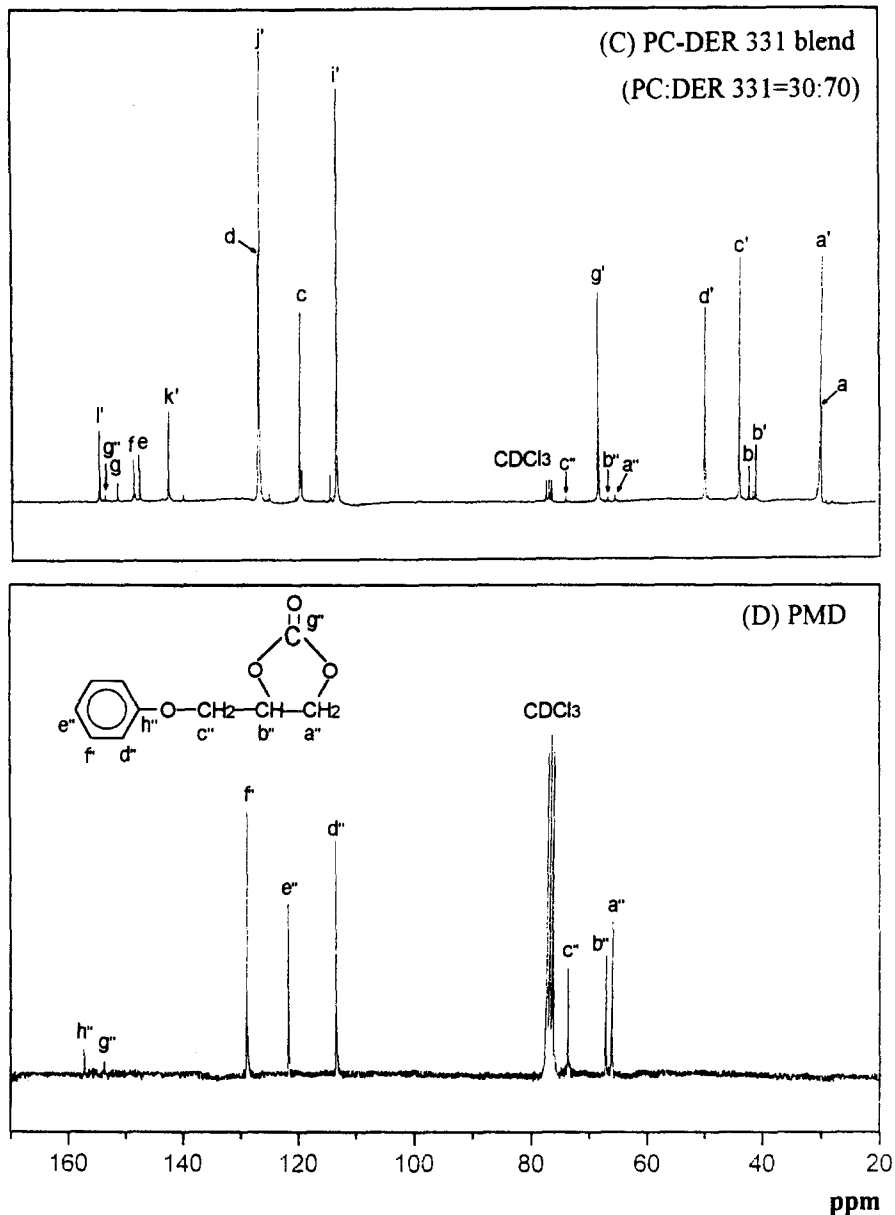
Figure 12 (Continued)

intensity of the absorption at higher frequency increases and shifts to lower frequency substantially with the decrease of the PC content. The trend of the i.r. band shifting to lower frequency is contributed to the transesterification reaction, which is identical to that of the PC–DER 383 blend as shown in *Figure 8*. However, the appearance of the higher frequency band at 1804 cm⁻¹ indicates that a new compound must be formed. Based on a literature survey, the cyclic carbonate of the five-membered rings has the carbonyl group i.r. absorption at such a high frequency, near 1800 cm⁻¹ [20,21].

Figures 12a and *12b* show the ¹³C n.m.r. spectra of PC and DER 331 epoxy resin, respectively. The ¹³C n.m.r. spectrum of the PC–DER 331 blend (PC/DER 331 = 3/7) is shown in *Figure 12c*. *Figure 12d* is the spectrum of phenoxymethyl-1,3-dioxolan-2-one (PMD), a cyclic carbonate with a five-membered ring, identified from our previous study [1,7]. The variation of the observed ¹³C n.m.r. spectrum from that of the blend, indicating a new carbon at δ 154.02 (*Figure 12c*), may

be generated from the carbonate group of PC at δ 152.51 (*Figure 12a*). This newly generated carbon can be attributed to the carbonate group of the cyclic carbonate that was verified by comparing with the PMD spectrum (*Figure 12d*). Further characteristics of the cyclic carbonate formed can be investigated by comparing *Figures 12c* and *12d*. *Figure 12c* shows the characteristic peaks at δ 65.97, 66.55 and 73.88 that belong to the carbon atom of the cyclic structure (*Figure 12d*). Based on the information obtained by the i.r. and ¹³C n.m.r. spectra we can positively confirm the formation of the cyclic carbonates in the PC–DER 331 blend.

Evidence of the following reactions has been previously reported [25–27] that the cyclic carbonate can be derived from three different types of intramolecular reactions: from the 2-hydroxyethyl carbonate end groups, the aromatic/aliphatic carbonate and the aliphatic/aliphatic carbonate group. The possible routes to obtain the cyclic carbonate structure in the PC–DER 331 blend by reacting PC with α-glycol in the DER 331 are

as below:
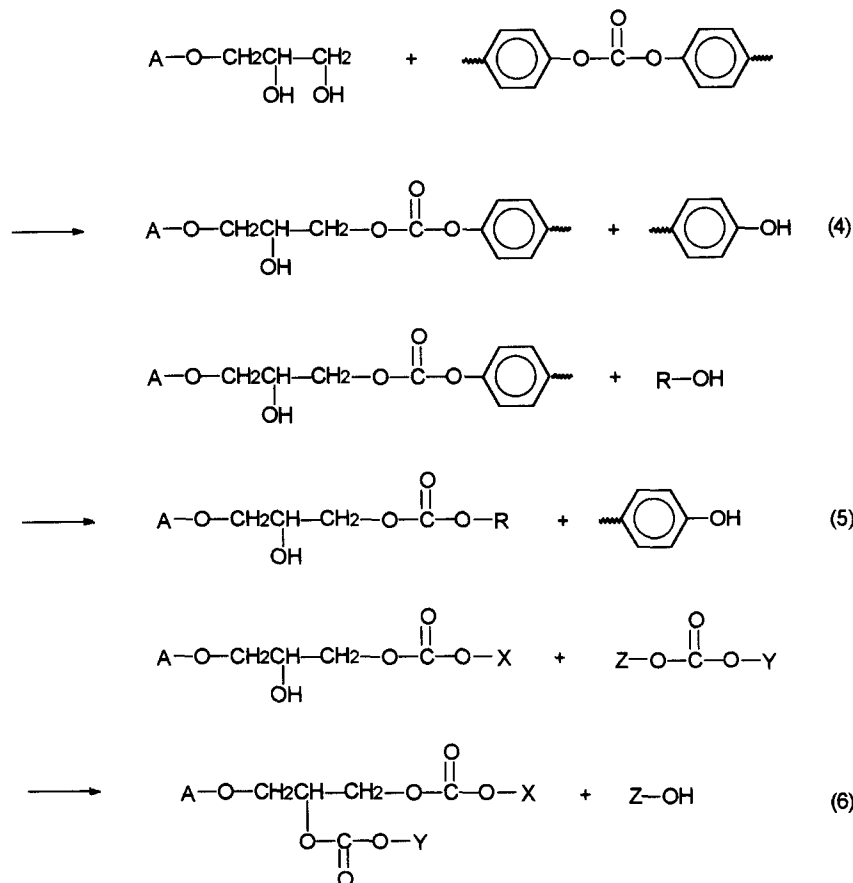
where X, Y and Z represent the aromatic or aliphatic substitutes. A represents the following species:
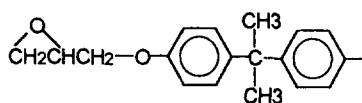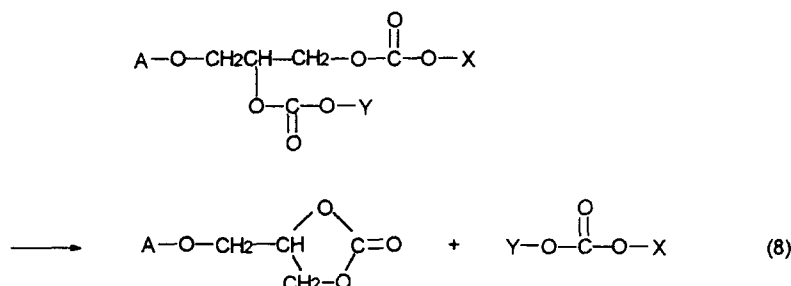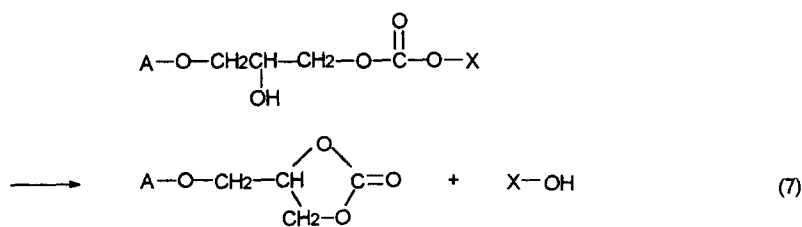

The intramolecular reactions required to yield the cyclic carbonate that was derived from the product of equations (5) and (6) are shown in equations (7) and (8), respectively.

Wu and Woo[14] reported that the PC–epoxy blends heated at 190°C for 6 to 12 h could form a crosslinking structure. They explained that the DGEBA oligomers have multiple hydroxyl sites per molecule that can cause the exchange reactions between PC and epoxy. The reaction that occurs has a natural tendency to form a network structure in the absence of any curing agent. Since the DGEBA type LER which Wu and Woo used (Epikote 828, manufactured by Shell Corp., USA, with a EEW of 185–192) is equivalent to the DER 331 employed in this study similar to the resin utilized in this experiment (DER 331, manufactured by Dow Chemical Co., USA, with a EEW of 186–192), there could not be multiple hydroxyl sites contained in each DGEBA oligomer. We can also obtain the cured

PC–DER 332 blend (PC DER 332 = 3/7) by heating at 200°C for 6 h in air. However, the same blend does not form a crosslinked structure after 200°C for 6 h under nitrogen. The difference between the non-crosslinking and crosslinking structures of the PC–epoxy blend may come from the complicated oxidations involved. Whether the heated precured PC–epoxy mixture forms the crosslinking structure or is essentially reacted depends on the type of epoxy monomer selected and environmental conditions during the melt mixing.

CONCLUSIONS

This study has demonstrated that the characteristics of the PC–epoxy blend are influenced by the following factors: (1) the minor components in the epoxy monomer, (2) the PC/epoxy ratio in the PC–epoxy blend, and (3) the environment in which the blends are prepared. Trace amount of water in the epoxy can hydrolyse the PC during melt mixing. This reaction cannot be detected by i.r. directly, but can be judged by a decrease in the PC molecular weight. The aliphatic hydroxyls (from homologues or α-glycol) in the epoxy can transesterify the original aromatic/aromatic carbonate of PC to form the aromatic/aliphatic and the aliphatic/aliphatic carbonates. These transesterifications can be clearly detected by i.r. since the transesterification reactions shift the i.r. absorption peak of carbonate group to lower frequencies. The α-glycol present in epoxy reacts with carbonate of PC and forms a new structure. The i.r.

$$A{-}O{-}CH_2CH{-}CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}X$$
$$|$$
$$OH$$

$$\longrightarrow \quad A{-}O{-}CH_2{-}CH\overset{O}{\diagup \diagdown}C{=}O \quad + \quad X{-}OH \qquad (7)$$
$$\diagdown CH_2{-}O \diagup$$

$$A{-}O{-}CH_2CH{-}CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}X$$
$$|$$
$$O{-}\overset{\overset{\displaystyle}{C}}{\underset{\underset{\displaystyle O}{\|}}{}}{-}O{-}Y$$

$$\longrightarrow \quad A{-}O{-}CH_2{-}CH\overset{O}{\diagup \diagdown}C{=}O \quad + \quad Y{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}X \qquad (8)$$
$$\diagdown CH_2{-}O \diagup$$

absorption band of this new structure shifts to a frequency higher than that of the original carbonate of PC. The ^{13}C n.m.r. spectrum identifies this new structure as a cyclic carbonate. Whether the PC hydrolysis, transesterification or cyclization reaction proceeds during the process of dissolving PC in epoxy depends on the minor components present in the epoxy monomer. The extent of these reactions increases with the decrease of the PC content in the PC–epoxy blend. The possibility of oxidation of the PC–epoxy blends during the heating procedure cannot be neglected, and experiments carried out under a nitrogen atmosphere can avoid the complication of such oxidations.

ACKNOWLEDGEMENTS

REFERENCES

1. Li, M. S., Ma, C. C. M., Chen, J. L., Lin, M. L. and Chang, F. C., *Macromolecules*, 1996, **29**, 2, 499.
2. Su, C. C. and Woo, E. M., *Macromolecules*, 1995, **28**, 20, 6779.
3. Li, M. S., Su, Y. F., Ma, C. C. M., Chen, J. L., Lu, M. S. and Chang, F. C., *Polymer*, (in press).
4. Martuscelli, E., Musto, P., Ragosta, G. and Scarinzi, G., *Angew. Makromol. Chem.*, 1993, **204**, 153.
5. Abbate, M., Martuscelli, E., Musto, P., Ragosta, G. and Scarinzi, G., *J. Polym. Sci., Part B*, 1994, **32**, 395.
6. Di Liello, V., Martuscelli, E., Musto, P., Ragosta, G. and Scarinzi, G., *J. Polym. Sci., Part B*, 1994, **32**, 409.
7. Li, M. S., Ma, C. C. M., Chang, F. C., Lu, M. S. and Lin, M. L., *J. Polym. Sci., Part A*, (in press).
8. Yu, Y. and Bell, J. P., *J. Polym. Sic., Part A*, 1988, **26**, 247.
9. Li, M. S., Ma, C. C. M., Lu, M. S., Lin, M. L., Chen, J. L. and Chang, F. C., *Polymer*, (in press).
10. Li, M. S., Li, Y. S., Chen, J. L. and Ma, C. C. M., *SAMPE Symp. Proc.*, 1995, **40**, 1435.
11. Don, T. and Bell, J. P., *Proceedings of SPE-ANTEC'95*, Soc. Plastics Engr., CT, Boston, MA, May 1995.
12. Lee, D. S., Kim, Y., Park, B. and Kim, J., *J. Appl. Polym. Sci.*, 1996, **59**, 1639.
13. Su, C. C., Kuo, J. F. and Woo, E. M., *J. Polym. Sci., Part B*, 1995, **33**, 2235.
14. Wu, M. N. and Wu, E. M., *Proceedings of International Chinese Symposium on Polymer Blends*, Hsinchu, Taiwan, July 1995.
15. Li, M. S., Ma, C. C. M., Lin, M. L., Lu, M. S., Chen, J. L. and Chang, F. C., *Polymer*, (in press).
16. Mera, H. and Umetani, H., Jap. Patent No. 02-170-822, 1990.
17. Chen, M. C., Hourston, D. J. and Sun, W. B., *Eur. Polym. J.*, 1992, **28**, 1471.
18. Rong, M. and Zeng, H., *Proceedings of International Chinese Symposium on Polymer Blends*, Hsinchu, Taiwan, July 1995.
19. Lee, H. and Neville, K., *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
20. Silverstein, R. M., Bassler, G. C. and Morrill, T. C., *Spectrometric Identification of Organic Compounds*, John Wiley, Singapore, 1991.
21. Colthup, N. B., Daly, L. H. and Wiberley, S. E., *Introduction to Infrared and Raman Spectroscopy*, Academic Press, San Diego, CA, 1990.
22. Pryde, C. A. and Hellman, M. Y., *J. Appl. Polym. Sci.*, 1980, **25**, 2573.
23. Ellis, B., *Chemistry and Technology of Epoxy Resins*, Blackie Academic & Professional, London, 1994.
24. Yang, X., Painter, P. C. and Coleman, M. M., *Macromolecules*, 1992, **25**, 4996.
25. Berti, C., Bonora, V., Pilati, F. and Fiorini, M., *Makromol. Chem.*, 1992, **193**, 1665.
26. Sweeny, W., *J. Appl. Polym. Sci.*, 1961, **16**, 15.
27. Vogdanis, L. and Heitz, W., *Makromol. Chem., Rapid Commun.*, 1986, **7**, 543.