The Kinetics, Thermal and Mechanical Properties of Epoxy-Polycarbonate Blends Cured with Aromatic Amine

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Abstract: PC-DER331 blends are transparent and homogeneous due to the transesterification taking place during hot melting process. This transesterification reaction does not occur or occurs insignificantly during the preparation of PC-DER332 blends. PC is separated from the PC-DER332 melt mixture by slow cooling to room temperature but the mixture remains a single phase by quenching with an ice bath. Two systems of PC-epoxy blends, PC-DER331 blends and PC-DER332 blends are cured by the *m*-phenylene diamine (MPDA) in a stoichiometric ratio. Curing kinetics have been carried out by differential scanning calorimeter (DSC). The presence of PC accelerates the curing reaction. Infrared spectroscopy (IR) indicates the occurrence of transesterification in the PC-DER331/MPDA blends during curing. The flexural modulus increases with the increase of the PC content while the notched Izod impact strength decreases with the increase of the PC content for all the blending systems. The fracture surfaces of the PC-DER331/MPDA blends are smooth, an indication of a homogeneous morphology. The fracture surfaces of the PC-DER332/MPDA blends are rough, an indication of a heterogeneous morphology.

Keywords: Epoxy, Blend, Polycarbonate, Transesterification.

Introduction

It is a well-known technology to prepare copoly(carbonate/urethanes) from polycarbonate (PC) and various amines. The reactivity of amines and PC is influenced by the substitutes of amines. Foldi and Camphell [1] reported that the aliphatic amines are more effective in reacting and degrading PC, while the aromatic amines require more stringent conditions [2,3]. In the PC-epoxy/aliphatic amine blend, the aliphatic amine is able to react with carbonate of PC rapidly to yield carbomates even at room temperature [4]. On the contrary, the aromatic amine does not react with PC at 80 °C for 2 hours in the PC-epoxy blend [5]. Since the long chains of PC are scissored severely by the aliphatic amine, the cured PC-epoxy/aliphatic amine blends are homogeneous [4,6,7]. Most PC-epoxy blends cured by various aromatic amines are homogeneous [5,8-13] except for one that is heterogeneous [14]. Diaminodiphenyl sulfone (DDS) [8,9] and diethyltoulenediamine (DETDA) [10] were used to cure PC-epoxy blends and resulted in homogeneous products with T_g of the blend decreasing with increasing of the PC content. This phenomenon was interpreted by the occurrence of transesterification reaction between the carbonate group of PC and the hydroxyl group of epoxy during the curing process [10]. However, Don et al. [14] were able to obtain a heterogeneous PC-epoxy cured product by curing with diaminodiphenyl methane (DDM). We investigated the cured PC-epoxy/aromatic amine blends and also discovered that the product morphologies depend on methods of preparing of the precured PC-epoxy mixture [15]. Several variables were examined including the minor structural variation of the epoxy monomer, the PC/epoxy ratio of the blend, and the blending conditions. Several reactions were found involved during the process of dissolving PC in the epoxy monomer that included the PC hydroly-

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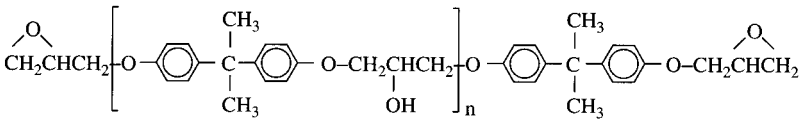
sis, transesterification and cyclization. Structural variation of the epoxy monomer can dictate the type and extent of these reactions. These reactions tend to reduce the PC molecular weight and graft certain PC segments onto the epoxy network. As the results of these reactions, the blend increases its miscibility and results in a homogeneous product.

In this paper, different epoxy monomers with known structural variations were employed to prepare PC-epoxy blends by different procedures and cured by the meta-phenylene diamine (MPDA). Both homogeneous and heterogeneous products were obtained. The reaction mechanism, viscosity change, morphologies and mechanical properties are discussed in detail.

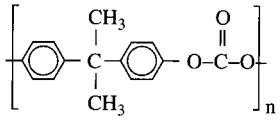
Experimental

1. Materials

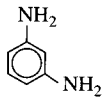
Two liquid epoxy monomers employed are the low molecular weight diglycidyl ether of bisphenol-A (DGEBA), DER331 and DER332, manufactured by the Dow Chemical Company with epoxide equivalent weight of 186 ~ 192 and 172 ~ 176 , respectively. The thermoplastic used in this study is the nature grade bisphenol-A polycarbonate (PC) with a melting flow rate of 15 which was also obtained from the Dow Chemical Company. These epoxy resins were cured by an aromatic diamine, meta-phenylene diamine (MPDA), purchased from the Aldrich Chemical Company.



Epoxy DER 331 (n = 0.10)
DER 332 (n = 0.03)



Polycarbonate



MPDA

2. PC-epoxy blends preparations

Polycarbonate pellets were dried in an oven at 120 °C for 8 hours before use. The dry PC pellets (450 g) were dissolved in the liquid epoxy (1050 g) at 200 °C by stirring under nitrogen gas for 1 hour. When the PC was dissolved completely , the solution was clear and homogeneous. After slowly cooling to room temperature, the PC-DER331 mixture remained homogeneous. While under a similar cooling procedure, the PC-DER332 solution became a wax-like inhomogeneous mixture where the PC was segregated and crystallized from the homogeneous mixture during the cooling process.

In case of the PC-DER331 system, the stoichiometric amount of the melted MPDA was added at 80 °C with vigorous stirring to the mixtures of different component ratios. After degassing under vacuum, the PC-DER331/MPDA blends were poured into a preheated steel mould for later curing.

In the case of PC-DER332 system, the wax-like heterogeneous PC-DER332 mixture was reheated to 200 °C to dissolve the PC crystals. The hot and homogeneous solution was then quenched to room temperature in an ice bath to give a clear homogeneous PC-DER332 mixture. The rest procedures of the PC-DER332/MPDA blends including stoichiometric hardner addition and sample casting was the same as the PC-DER331/MPDA blends. Compositions and codes employed in this study are listed in Table I.

All blends were cured by three stages: primary stage curing at 80 °C for 2 hours, second stage curing at 150 °C for 2 hours, and third stage post curing at 200 °C for 5 hours.

3. Characterizations

The optical micrograph of the cloudy PC-epoxy blend was taken with a polarized light to observe a spherulitic morphology. The optical microscope utilized is an Olympus BH2-UMA.

Thermal properties were investigated by a differential scanning calorimeter (TA Instruments DSC 2100). The glass transition temperature, melting temperature and reaction kinetics were determined by a DSC with a heating rate of 10 °C/min.

The dynamic mechanical analysis (TA Instruments DMA 983) with a heating rate of 5 °C/min was used to measure the loss modulus (E").

Table I. Codes and compositions of the PC-epoxy blends.

Code	Composition
R00	DER331 (100 g) + MPDA (16 g)
R03	DER331 (100 g) + MPDA (16 g) + PC (3.7 g)
R06	DER331 (100 g) + MPDA (16 g) + PC (7.4 g)
R09	DER331 (100 g) + MPDA (16 g) + PC (11.6 g)
R12	DER331 (100 g) + MPDA (16 g) + PC (15.8 g)
A00	DER332 (100 g) + MPDA (15.2 g)
A03	DER332 (100 g) + MPDA (15.2 g) + PC (3.68 g)
A06	DER332 (100 g) + MPDA (15.2 g) + PC (7.35 g)
A09	DER332 (100 g) + MPDA (15.2 g) + PC (11.53 g)
A12	DER332 (100 g) + MPDA (15.2 g) + PC (15.71 g)

Infrared (IR) spectroscopic analysis was carried out on a Perkin-Elmer 842 Infrared Spectrometer with a resolution of 2.4 cm^{-1} in the transmission mode. One drop of the blend mixture was pasted into a thin film between two sodium chloride plates and then mounted on a sample holder located in the IR instrument. The gel permeation chromatographic (GPC) study was performed on an instrument from Waters Associates equipped with a Waters-R410 refractometer. The cured PC-epoxy blends were immersed in tetrahydrofurane (THF) for a month to produce a solution. The extract obtained was injected into the GPC and the solvent utilized was THF at a flowing rate of 1.0 mL/min.

Viscosity measurements at 80 °C were performed with a Brookfield RVT viscosimeter equipped with a constant-temperature oil bath.

Flexural strength and modulus were measured by an Instron Universal Testing Machine Model 4201 using a cross-head speed of 2 mm/min as described in ASTM D-790.

Notched Izod impact strengths were measured according to the ASTM D-256 method by an impact tester (type 43-01) manufactured by the Testing Machines Inc.

A scanning electron microscope from the Jeol Company (type JSM-5300) was used to study morphologies of the fracture surfaces.

Results and Discussion

1. Phase behavior of PC-epoxy blend

Several reactions may involve during the process of dissolving PC in the epoxy monomer. The residual water present in the epoxy resin may cause hydrolysis of the epoxy and the carbonate group of PC. The aliphatic hydroxyl and the α-glycol in the epoxy resin can transesterificate and cyclize with the carbonate group of PC [15]. Transesterification reaction tends to scissor the PC chains and form the PC-epoxy copolymers that can increase the misciblity

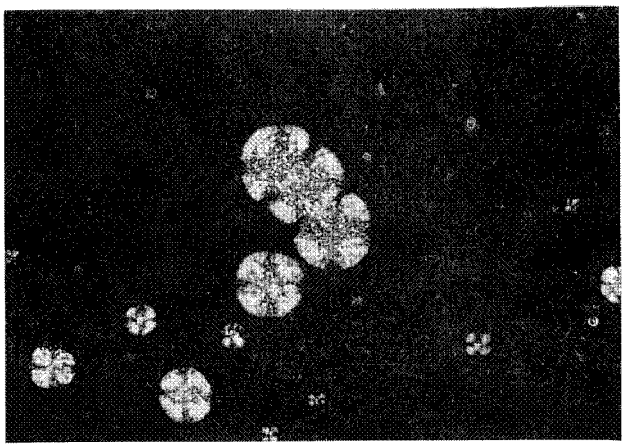


Figure 1. Optical micrograph (× 350) taken with polarized light of a 30% PC-DER332 mixture.

between PC and epoxy. Our previous report [15] investigated these reactions including hydrolyzation, transesterification and cyclization. These reactions indeed occur in the PC-DER331system because of higher content of water, aliphatic hydroxyls and α-glycol than that of the PC-DER332 system. PC molecular weight reduction caused by transesterification is considered more substantial in the PC-DER331 system than that in the PC-DER332 blend system. The high molecular weight PC in the PC-DER332 blend tends to separate and crystallizes from the epoxy monomer to form spherulites during the slow cooling process. Figure 1 shows the photograph of PC spherulites separated from the epoxy monomer as a well-developed Maltese Crosse pattern taken by a polarized light.

Don and Bell [14] reported that the PC can be dissolved in the epoxy resins at high temperatures or both of them can be dissolved in dichloromethane, CH_2Cl_2 at ambient conditions. These two different dissolution processes result in different morphologies of the finally cured PC-epoxy products. The former procedure yielded a homogeneous product while the latter resulted in a heterogeneous product. The DGEBA type epoxy resin that Don et al. employed (Epon 828, manufactured by Shell Corp. U.S.A. with Mn 386) is equivalent to the DER331 employed in our previous study (DER331, manufactured by Dow Chemical Co. U.S.A.) [16]. We expect that many aliphatic hydroxyls contained in both epoxy resins. The melt blending of PC-epoxy at 200 °C should result in transesterification and yields the PC-epoxy copolymers with PC chains bonded to the epoxy network. The solution blending process is carried out at a substantially lower temperature, therefore, these reactions between PC and epoxy do not occur or occur insignificantly. The result from Don and Bell investigation [14] coincides with our

previous study [15].

If the heterogeneous PC-DER332 mixture is reheated to 200 °C to dissolve the PC crystals and then quenched to room temperature by an ice bath, the blend remains homogeneous and transparent. Phase separation and crystallization of PC can not proceed kinetically due to rapid increase in viscosity of mixture after quenching to lower temperatures. In other words, the tendency of forming a phase separated morphology of the PC-DER332 blend during slow cooling is driven by the thermodynamical immisciblity between PC and epoxy while the formation of a homogeneous PC-DER332 blend is a kinetically-controlled process.

2. Viscosity variations during curing

Figures 2 presents the viscosity versus time for PC-DER331/MPDA and PC-DER332/MPDA blends cured isothermally with stoichiomatric amount of MPDA at 80 °C. The observed gel times decrease with the presence of PC 12 wt% in blends. Higher reactivity of curing reaction results in shorter gel time. Comparing gel times from these two blending systems, the PC-DER332/MPDA blends have relatively longer gel time than the PC-DER331/MPDA blends.

Another important observation in these figures is different types of viscosity changes from these two blend systems. Curve B of Figure 2(II) gives the viscosity versus time change of the PC-DER332/MPDA homogeneous blend containing 12 wt% PC. This blend shows a gradual viscosity increase with a plateau at 20 ~ 30 minutes instead of a sudden viscosity rise observed for other blends. This observed plateau can be explained as the result of PC phase separation during the process of curing. Our previous study [5] provided the evidence that the carbonate group of PC does not transesterificate with the hydroxyl group generated from the epoxy curing reaction at 80 °C. Therefore, the PC molecular weight should remain essentially unchanged at 80 °C in this homogeneous PC-DER332/MPDA blend. Flory-Huggins equation [17] is able to predict PC phase separation from the blend because the epoxy molecular weight increases with the progress of the curing reaction while the PC molecular weight remains constant. These phenomena cause the decrease of the entropy of mixing (ΔS_{mix}) and induce the phase separation of this blending system. The viscosity of the blend tends to decrease with the increasing extent of PC phase separation and less PC dissolved in epoxy, while the viscosity tends to increase with the increase of the epoxy molecular weight. These two opposite effects on viscosity lead to a viscosity balance in this "plateau zone" as shown in Curve B of Figure 2(II). The homogeneous PC-DER331/MPDA blends give the typical epoxy curing curves as shown in Figure 2(I).

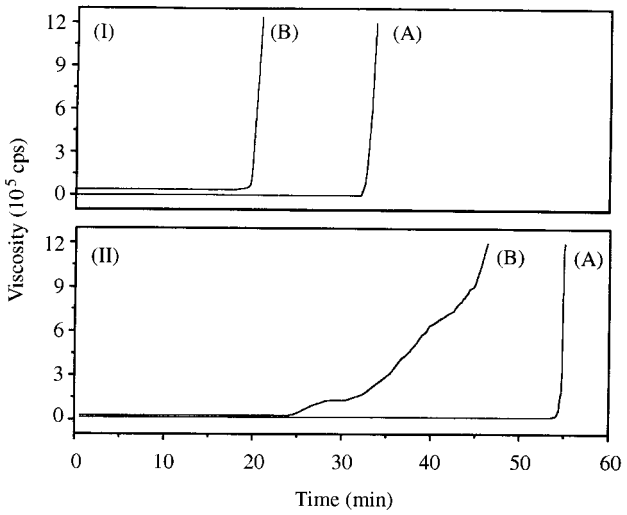


Figure 2. Plots of the viscosity versus time: (I) PC-DER 331/MPDA blends at 80 °C (A) PC 0 wt%, (B) PC 12 wt%, and (II) PC-DER332/MPDA blends at 80 °C (A) PC 0 wt% and (B) PC 12 wt%.

3. Kinetic studies of PC-epoxy blends

Our previous study [5] using DSC technique demonstrated that the curing of the PC-DER331/MPDA blend follows the autocatalyzed model as below:

$$d\alpha/dt = k\alpha^m(1 - \alpha)^n$$

where n and m are reaction orders, α is the fractional conversion measured by the partial heat of the reaction. ΔH_p obtained from the isothermal analysis divided by the total heat of the reaction obtained from the dynamic DSC run (ΔH_o), k is reaction rate constant that obeys the Arrhenious expression:

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

where A = pre-exponential factor (1/sec)
E_a = activation energy (J/mole)
R = 8.314 (J/mole K)
T = temperature (K)

Our another report [18] investigated the epoxy curing kinetics by DSC autocatalytic methods but the results did not agree with those from the infrared spectroscopic measurements. Many side reactions take place during the curing of a PC-epoxy (DER331) but their individual heat of reactions are not expected to be equal during that interval [18]. This phenomenon should also be considered in the PC-DER332/MPDA blend where fraction of the PC

Table II. Kinetic parameters of the PC-epoxy/MPDA blends.

	m	n	log A	E_a (J/mol)
PC-DER331/MPDA				
R00	0.45	1.45	4.3	37.9
R06	0.38	1.53	2.95	28.8
R12	0.25	1.94	1.12	16.3
PC-DER332/MPDA				
A00	0.70	1.98	6.25	51.6
A06	0.74	2.19	5.29	47.9
A12	0.71	1.90	4.63	39.1

is separated from the blend during curing. Relatively, the exotherm associated with PC crystallization from the homogeneous blend [19] is significantly smaller than the heat released from the epoxy curing. Therefore, it is reasonable to assume that all the heat produced from the DSC thermogram is come from the normal curing between DER332 epoxy resin and MPDA by neglecting contribution from the PC phase transformation. The obtained kinetic parameters of PC-DER332/MPDA and PC-DER331/MPDA blends such as reaction orders (m and n), activation energies (E_a) and pre-exponential factors (A) are listed in Table II. These calculated kinetic parameters (m, n, E_a and A) can be substituted into the integrated autocatalytic model to estimate the epoxy reaction rate as a function of conversion and the results are given in Figure 3. As shown in the Table II, the activation energies of the DER331/MPDA system are substantially lower than those of the DER332/MPDA system, and therefore the reaction rates ($d\alpha/dt$) of former are higher than those of latter (Figure 3). This result can be attributed to the aliphatic hydroxyls present in the DER331 epoxy resin that can catalyze the reaction between oxirane and amine [20]. The curing acceleration induced by hydroxyls is considered to be insignificant in the DER332/MPDA system since the hydroxyl content is very small and almost can be neglected. Figure 3 also clearly illustrates that the reaction rate increases with PC content increasing. Our previous study [5] interpreted that this phenomenon was caused by the presence of phenolic-OH in the blend. The phenolic-OH chain end of PC has higher acidity than that of the aliphatic hydroxyl and can serve as a more effective catalyst to accelerate the epoxy/amine curing reaction. Polycarbonates manufactured from most Japanese producers and Dow use the *tert*-butyl phenol as the chain terminator while PC from General Electric and Mobay use phenol as terminator. The amount of the phenolic-OH end group in most commerical PC products is minimum and can be ignored. In other word, the phenolic-OH chain ends of PC are essentially come from the hot melt procedure during the process of dissolving PC into the

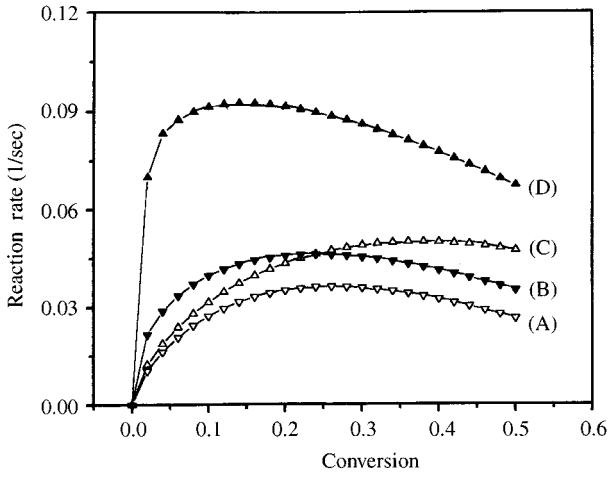


Figure 3. Plots of the reaction rate *vs.* conversion: (A) DER332/MPDA (PC 0 wt%), (B) DER331/MPDA (PC 0 wt%), (C) PC-DER332/MPDA (PC 12 wt%) and (D) PC-DER331/MPDA (PC 12 wt%).

epoxy monomer. Relative to the DER332, the DER331 epoxy resin has greater amounts of alcoholic hydroxyls available to transesterificate and scissor the PC molecular chains and yield greater numbers of phenolic chain ends [15].

Another characteristic revealed in this PC-DER332/MPDA blend is the gradual PC phase separation from the epoxy matrix during the progress of curing (at about 30% conversion). PC separated from the epoxy matrix in the PC-DER332/MPDA blend implies less quantity of the dissolved phenolic-OH chain ends available to accelerate the epoxy curing reaction than that of the homogeneous PC-DER331/MPDA blend. Table II clearly shows that the activation energies of curing PC-DER331/MPDA blends are substantially lower than the corresponding PC-DER332/MPDA blends. Higher pre-exponential factors (A) are obtained from the PC-DER332/MPDA blends than those of the PC-DER331/MPDA blends. The presence of the dissolved PC molecular chains in the epoxy matrix tends to dilute the concentrations of epoxy and amine in the system and thus decreases the chance of collision between them. Compromising the activation energy and effective collision influenced by the presence of the PC, the observed reaction rate increases with the increase of the PC content as shown in Figure 3.

4. Thermal properties of PC-epoxy blend

The glass transition temperatures (T_g's) of various PC-epoxy/MPDA blends after second stage curing and third stage post curing, determined by DSC scans are tabulated in Table III. Except for the blend containing 12 wt% PC, T_g's of the PC-DER

Table III. Glass transition temperatures (T_g's, °C) of the PC-epoxy/MPDA blends after second stage curing (80 °C / 2 hr + 150 °C / 2 hr) and third stage post curing (80 °C / 2 hr + 150 °C / 2 hr + 200 °C / 5 hr) determined with DSC.

PC	Second stage curing		Third stage post curing	
(wt%)	PC-DER331 /MPDA (R)	PC-DER332 /MPDA (A)	PC-DER331 /MPDA (R)	PC-DER332 /MPDA (A)
0	143.3	153.1	177.5	178.7
3	152.2	159.4	166.5	177.1
6	155.6	157.2	159.2	176.7
9	143.6	159.1	155.3	172.3
12	136.1	156.4	146.6	171.1

331/MPDA blends are higher than those of the unmodified DER331/MPDA blends after the second stage curing (80 °C for 2 hours and 150 °C for 2 hours) while T_g's of PC-DER332/MPDA blends are higher than that of the unmodified DER332/MPDA blend. This result can be attributed to different extents of epoxy conversions influenced by the presence of different PC contents in these blends. As mentioned earlier, the presence of the phenolic-OH chain ends is able to accelerate the cure reaction and results in higher epoxy conversion. Therefore, those PC-modified blends have higher T_g's than that of the neat system which is expected. However, the transesterification between PC and epoxy for those PC-DER331/MPDA blends results in carbonate groups of PC crosslinking or grafting PC segments onto the epoxy network. These reactions release the bisphenol-A monomer or PC oligomers in the same time that tend to plasticize the epoxy network and decrease T_g's of the cured products. Compromising these two adverse effects, T_g increases with increasing PC content when the PC content is below 6 wt%. When the PC content is higher than 6 wt%, T_g decrease due to plasticizing of the network is more than the T_g increase resulting from the higher conversion. Table III shows the T_g of the PC-DER 331/MPDA blend containing 12 wt% PC has a lower T_g than the unmodified blend (DER331/MPDA).

Third stage post curing of the blend at 200 °C for 5 hours should result in near maximum achievable epoxy conversion but also the greatest extent of transesterification. After post curing, T_g of the PC-DER331/MPDA blend decreases substantially with the increase of the PC content as shown in Table III. Since the epoxy conversion plays relatively less role now, greater extent of transesterification reaction implies more of the bisphenol-A monomer or PC oligomers present in the system to plasticize the blend and results in lower T_g of the cured product.

Relative to the T_g changes of the PC-DER331/MPDA blends, T_g reductions for the post cured PC-DER332/MPDA blends are less substantial (Table III). Since most of the originally dissolved PC is already phase separated from the epoxy matrix before curing in the PC-DER332/MPDA system, only smaller fraction of the originally dissolved PC in the epoxy matrix is available to proceed the expected transesterification reaction. Figure 4 presents the DSC scans of two post cured blends. Both PC-epoxy/MPDA blends exhibit a single T_g while there is an endothermic peak at higher temperature appearing in the PC-DER332/MPDA blend (Curve 4(B)). This characteristic peak at 215 ~ 220 °C is come from the melting of the dispersed PC crystals in the cured blends. It is worthy to mention here that no T_g of PC can be detected from the PC-DER332/MPDA blends (Curve 4(B)) even though the PC phase separation is evident. The appearace of the melting peak of PC crystals at 220 °C reveals that the phase separated PC is in crystalline form.

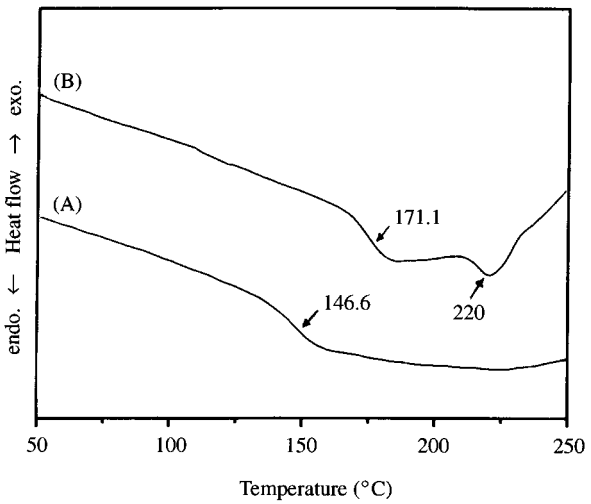


Figure 4. DSC scans of various post cured blends: (A) PC-DER 331/MPDA (PC 12 wt%) and (B) PC-DER332/MPDA (PC 12 wt%).

Figure 5 compares the loss moduli (E") of the post cured PC-DER332/MPDA blends by varying PC contents. This figure presents only a single peak of alpha transition (T_g) in the blending system, the existence of amorphous and crystallized PC in the second phase can not be detected by this thermal analysis technique. The T_g decreases with the increase of PC content, similar to that obtained by DSC (Table III).

5. Infrared spectra and gel permeation chromatography

Figure 6 shows the IR spectra of the PC-DER331/MPDA (PC 12 wt%) blend in the carbonyl region after various stages of curing. Curve 6(A) presents the initial carbonyl absorption of the blend.

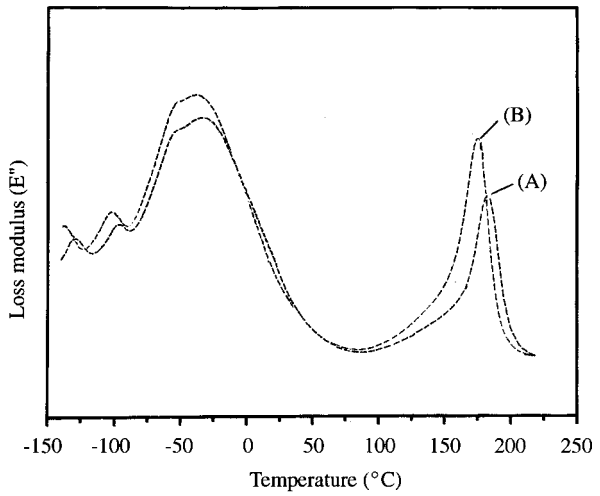


Figure 5. Dynamic mechanical analyses for PC-DER332/MPDA blends: (A) PC 0 wt% and (B) PC 12 wt%.

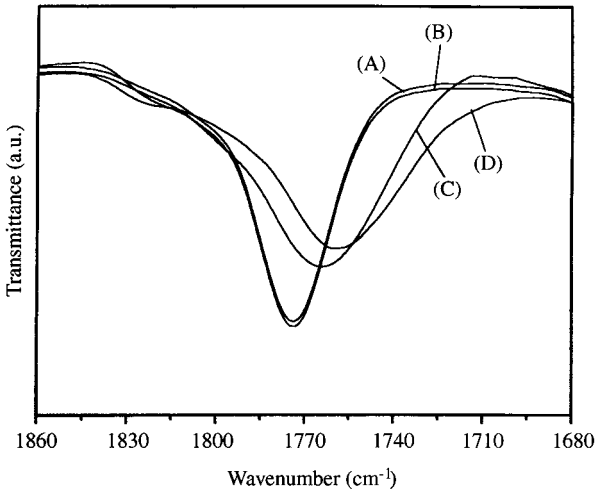


Figure 6. IR spectra of PC-DER 331/MPDA (PC 12 wt%) in the carbonyl stretching region: (A) initial, (B) at 80 °C for 2 hrs, (C) at 150 °C for 2 hrs, and (D) at 200 °C for 5 hrs.

The major component is the aromatic-aromatic carbonate absorption at 1776 cm^{-1}. The absorption of two other components are the aromatic-aliphatic carbonate and the cyclic carbonate at 1762 and 1804 cm^{-1}, respectively [15]. The aromatic-aromatic carbonate is the original PC structure while the aromatic-aliphatic carbonate is come from the transesterification reaction by grafting PC onto the epoxy network. The cyclic carbonate is the product by reacting α-glycol with PC during the preparation of the PC-DER331 melt blend [15]. Curve 6(B) presents the spectrum of the PC-DER331/MPDA blend after primary stage of curing at 80 °C for 2 hours. The carbonate structure is virtually unchanged at this stage of curing with 70% epoxide conversion, most of the PC molecular chains interpenetrate within the epoxy network. Curves 6(C) and 6(D) show the spectra of the blend after second stage of curing at 150 °C for 2 hours and after third stage post curing at 200 °C for 5 hours, respectively. The absorption bands of the carbonate group shift to lower frequencies (1780 and 1750 cm^{-1}). This phenomenon is mainly due to the transesterification reaction occuring between the carbonate groups of PC and the hydroxyl groups produced in the cured epoxy [5]. Transesterification reaction scissors the PC long molecular chains into short segments by grafting or crosslinking these segments with epoxy network and releases the bisphenol-A monomers or PC oligomers at the same time. In other words, the semi-IPN's structure formed of the PC-DER331/MPDA blend during the primary stage of curing has been destroyed after the second stage of curing and the third stage post curing.

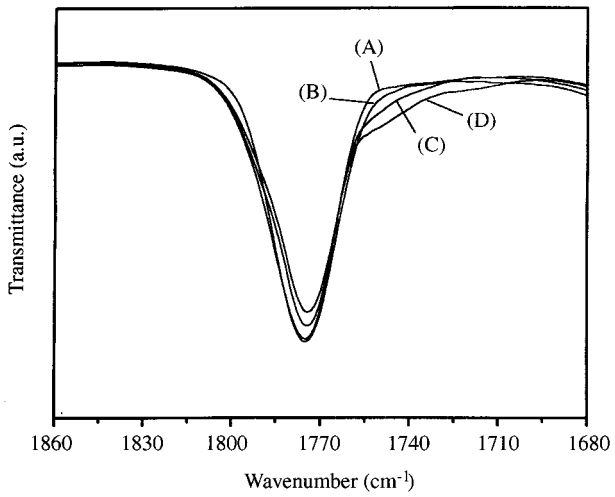


Figure 7. IR spectra of PC-DER332/MPDA (PC 12 wt%) in the carbonyl stretching region: (A) initial, (B) at 80 °C for 2 hrs, (C) at 150 °C for 2 hrs, and (D) at 200 °C for 5 hrs.

Figure 7 shows the IR spectra in the carbonyl region of the PC-DER332/MPDA (PC 12 wt%) blend at various stages of curing. Curve 7(A) represents the absorption of the blend at the beginning of curing. Curve 7(B) shows the spectrum of the blend after primary stage of curing at 80 °C for 2 hours. Comparing curves 7(A) and 7(B), the absorption peaks of the carbonate group are essentically unchanged. This blend is homogeneous at the begining of curing reaction but most of the PC is gradually separated from the epoxy matrix during the primary stage of curing at 80 °C for 2 hours. Curves 7(C) and 7(D) give the absorptions of the blend after second stage and the third stage post curing, respectively. Curve 7(C) shows the intensity of carbonate absorption decreasing slightly to 1775 cm^{-1} and the

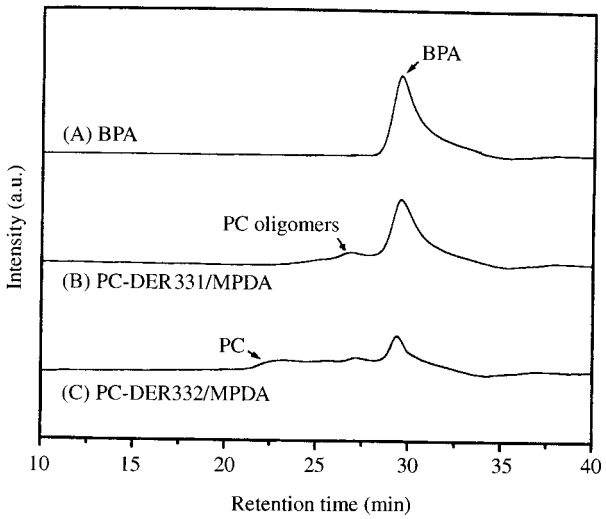


Figure 8. The GPC chromatograms of: (A) bisphenol-A, (B) extract from the PC-DER331/MPDA (12 wt%), and (C) extract from the PC-DER332/MPDA (12 wt%).

appearance of a shoulder at 1755 cm^{-1}. This absorption at 1755 cm^{-1} is a characteristic band of the aliphatic-aliphatic carbonate (Al-O-CO-O-Al). Although most of the PC is separated from the epoxy matrix at the primary stage of curing, small fraction of the PC is expected to be still dissolved in the cured network for thermodynamic or kinetic reasons. Those PC molecular chains trapped within the epoxy matrix in molecular level are able to transesterificate with the hydroxyl group of the epoxy network. Insignificant absorption of the Ar-O-CO-O-Al (1760 cm^{-1}) is detected, because the numbers of these trapped PC chains in matrix are substantially smaller than those of the PC-DER331/MPDA system with the same PC content. Thus, the transesterification reaction tends to convert essentially all of the dissolved aromatic-aromatic carbonate (Ar-O-CO-O-Ar) into the aliphatic-aliphatic carbonate (Al-O-CO-O-Al).

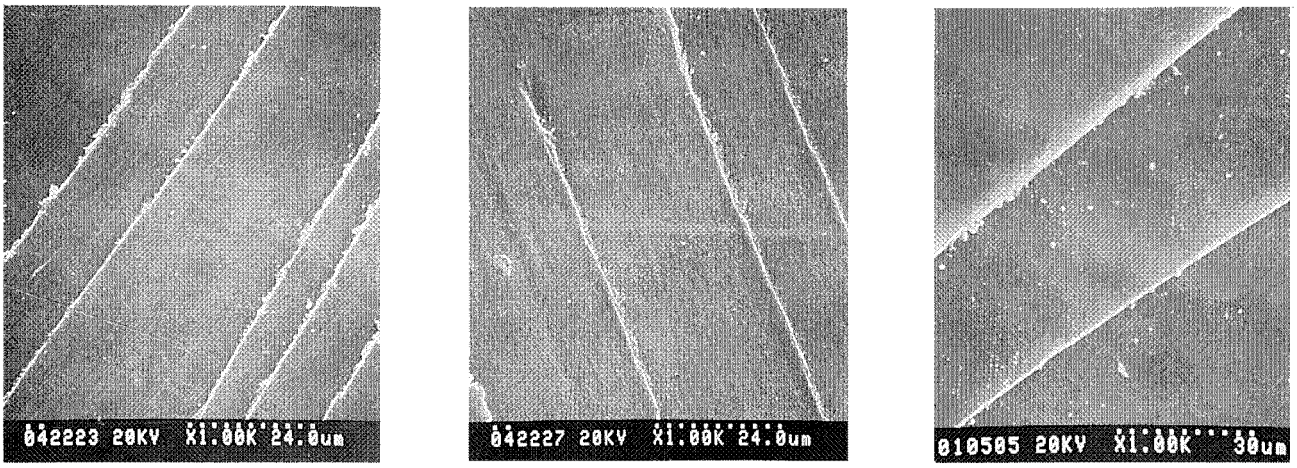
Figure 8 shows the GPC results of the PC-epoxy/MPDA blends. Curve 8(A) is the chromatogram of the bisphenol A (BPA) monomer. Curve B represents the chromatogram of the extract from the cured PC-DER331/MPDA blend (PC 12 wt%). Comparing these two curves it indicates that the extract from the blend was made up mostly of the BPA monomer and small amount of PC oligomer yielded from the transesterification reaction. The GPC chromatogram of the extract from the cured PC-DER332/MPDA blend (PC 12 wt%) is illustrated as curve 8(C) where the component with lower retention time is attributed to the PC phase separated from the epoxy matrix. These observed chromatographic phenomena are coincident with the results by the IR analysis mentioned previously.

Table IV. Flexural moduli (E), flexural strengths (σ) and notched Izod impact strengths (I.S.) of the postcured PC-epoxy/MPDA blends.

PC content (wt%)	E (GPa)	σ (MPa)	I.S. (J/m)
PC-DER331/MPDA (R)			
0	2.56	72.1	23.5
3	2.81	75.8	20.9
6	2.92	100.2	22.1
9	3.30	92.5	21.4
12	3.35	64.5	18.0
PC-DER332/MPDA (A)			
0	2.57	81.8	24.1
3	2.74	69.3	23.5
6	2.86	57.5	18.7
9	2.94	56.6	14.5
12	3.03	54.0	13.6

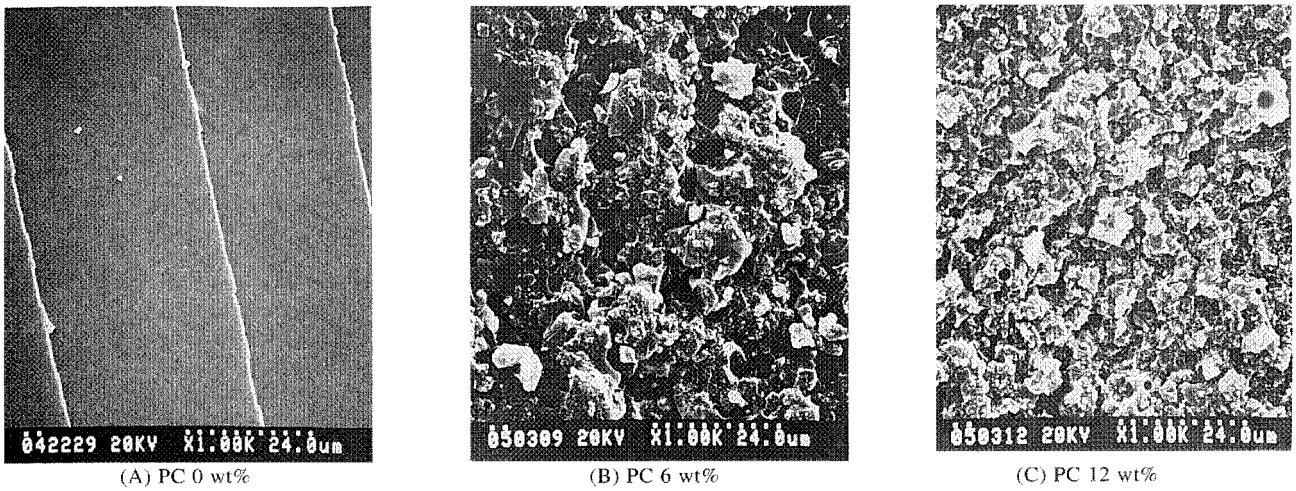
6. Mechanical properties and morphologies

Mechanical properties of various post cured PC-epoxy/MPDA blends are summarized in Table IV. Flexural modulus (E) of the PC-DER331/MPDA blend increases with increasing PC content that can be attributed to the hydrogen-bonding formation between carbonate groups and hydroxyl groups of the epoxy network [21]. The hydrogen-bonding acts as a physical crosslinking and causes a higher packing density of the cured product. The intermolecular attraction is probably responsible for the observed higher flexural modulus. For the PC-DER332/MPDA blends, most of the originally dissolved PC is separated from the blend and only a small fraction of the carbonate group is expected to be dissolved in the cured network. This is the reason why the flexural modulus of the PC-DER332/MPDA blend is lower than the corresponding PC-DER331/MPDA blend as shown in Table IV. This hydrogen-bonding effect also tends to give higher flexural strength of the PC-DER331/MPDA blends relative to those of the PC-DER332/MPDA blends. However, those bisphenol-A monomers and/or the PC oligomers produced from the transesterification reaction tend to reduce the flexural strength of the cured products due to plasticizing effect. Compromising these two effects, the maximum flexural strength is the homogeneous PC-DER331/MPDA blend containing 6 wt% of PC. For the heterogeneous PC-DER332/MPDA blends, the decreasing trend on flexural strength probably comes from the internal stress created by the PC crystals formation in the matrix. The internal stress at the interface between PC crystals and the cured epoxy matrix is induced after cooling because the thermal expansion coefficients of PC and epoxy matrix are different. The impact strength of both PC-DER331/MPDA and PC-DER332/MPDA blends decreases with increasing PC content as



(A) PC 0 wt% (B) PC 6 wt% (C) PC 12 wt%

Figure 9. SEM micrographs (× 1000) of fracture surfaces of PC-DER331/MPDA blends: (A) PC 0 wt%, (B) PC 6 wt%, and (C) PC 12 wt%.



(A) PC 0 wt% (B) PC 6 wt% (C) PC 12 wt%

Figure 10. SEM micrographs (× 1000) of fracture surfaces of PC-DER332/MPDA blends: (A) PC 0 wt%, (B) PC 6 wt%, and (C) PC 12 wt%.

shown in Table IV. These results are reasonable since the hydrogen-bonding between carbonate and hydroxyl is able to act as a physical crosslinking and increases the packing density that tend to decrease the chain flexibility and mobility of network structure during fracture. Furthermore, the PC crystals may also function as stress concentrators in the matrix and cause earlier fracture of the test specimen. Both of the factors, internal stress at the interface and stress concentrators cause the toughness reduction by incorporating PC within epoxy. Figures 9 and 10 show scanning electron micrographs of the fracture surfaces of the post cured epoxy resins. In the case of PC-DER331/MPDA homogeneous blends (Figures 9(A), 9(B) and 9(C)) and the unmodified DER332/MPDA blend (Figure 10(A)), the fracture surfaces show a characteristic single-phase brittle fracture morphology with some river patterns following the direction of crack propagation. In the case of inhomogeneous PC-DER332/MPDA blends (Figures 10(B) and 10(C)), the SEM micrographs present a rough fractured surface and the crack propagation direction is not clearly defined. This phenomena can be interpreted as the easier crack initiated at the high internal stress region, the interface between the epoxy matrix and the PC. The schematic diagram showing the fracture mechanism of the inhomogeneous blend is given in Figure 11.

Conclusion

Chemical reactions between PC and different

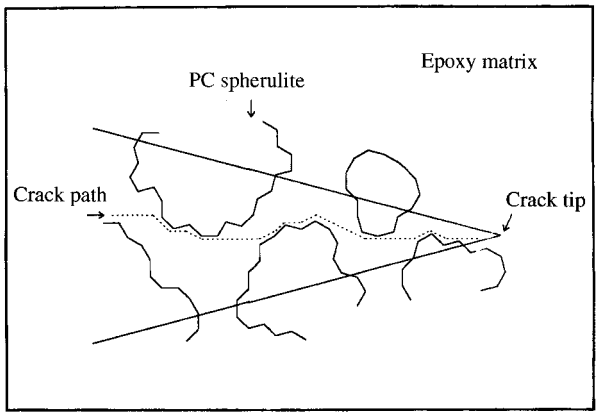


Figure 11. Schematic diagram of the formation mechanism and the fracture pattern of heterogeneous PC-DER332/MPDA blend.

epoxies during hot melting process control the phase separation behavior, curing kinetics, curing mechanism, mechanical and morphological properties after curing. The presence of PC reduces the activation energy and accelerates the curing reaction evidently. PC-DER331/MPDA system remains homogeneous before and after curing and its cure rate is faster than that of PC-DER332/MPDA. For PC-DER331/MPDA blends, some small molecules generated from the transesterification reaction during curing reaction plasticize the network and reduce the glass transition temperature. In the case of PC-DER332/MPDA blends, PC disperses in the matrix in the form of spherulites with a melting point about 217 °C. The flexural modulus increases with the increase of the PC content while the notched Izod impact strength decreases with the increase of the PC content for all the blending systems. SEM fracture surfaces show a single phase morphology for the PC-DER331/MPDA blends while a rough and heterogeneous morphology for the PC-DER332/MPDA blends.

Acknowledgments

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