

Structures and Properties of Polycarbonate-Modified Epoxies from Two Different Blending Processes

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Received 13 November 1998; accepted 20 April 1999

ABSTRACT: It has been proved in our previous study that during the melt-blending of an epoxy oligomer based on the diglycidyl ether of bisphenol-A (DGEBA) with polycarbonate (PC) at 200°C, the secondary hydroxyl groups in the DGEBA react with the carbonate groups in PC through transesterification, resulting in degraded PC chains with phenolic end groups and also in PC/DGEBA copolymers. Yet, in the same study, it was found that the prereactions between DGEBA and PC can be minimized or eliminated if a solution-blending process was used. Therefore, it was expected that, after being cured with a curing agent, different epoxy-network structures should result as a consequence of the two different premixing processes of DGEBA and PC. In addition, we also expect that in the melt-blending process, the fracture toughness of epoxies should be increased due to the incorporation of ductile PC chains into the epoxy network. In this study, therefore, we attempted to examine and compare the structures and properties of PC-modified epoxies through these two different blending processes. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2510–2521, 1999

Key words: polycarbonate; epoxy; solution-blending process; melt-blending process; fracture toughness

INTRODUCTION

Unmodified epoxies are relatively brittle materials with poor resistance to crack propagation. Therefore, methods to increase the fracture toughness of epoxy polymers have been the subject of studies for many years.^{1–6} Generally, rubbers are used to increase the fracture toughness of brittle epoxies and, in some instances, the fracture toughness can be increased by an order of magnitude through rubber cavitation and shear yielding in the epoxy matrix.^{7–10} However, this method generally does not provide substantial improvements in toughness for highly cross-

linked, high glass transition temperature (T_g) epoxies.⁵ Also, in many instances both tensile modulus and yield strength are reduced due to the addition of soft inclusions into a stiff matrix.^{6–7} Therefore, alternative methods of toughening epoxy resins based on the incorporation of rigid thermoplastics have emerged.^{11–21} The engineering thermoplastics typically incorporated into epoxy resins to enhance toughness include poly(ether sulfone),^{11–13} hydroxyl-terminated bisphenol-A polysulfone,^{14–17} amino-terminated polysulfone,^{18–19} amino-terminated poly(ether ketone),²⁰ and poly(ether imide).^{18,21} Polycarbonate (PC) is an engineering thermoplastic with high fracture toughness. However, there are only a few studies concerning PC-modified epoxy systems and most of them have been published recently.^{22–33}

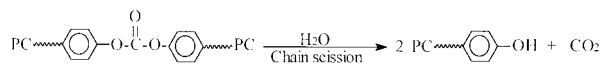
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Journal of Applied Polymer Science, Vol. 74, 2510–2521 (1999)

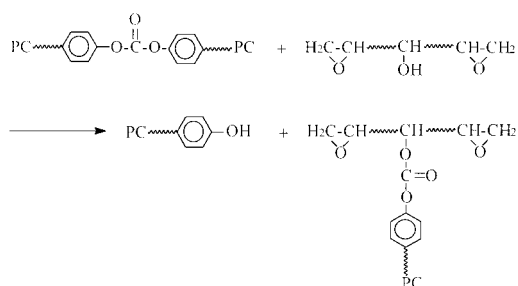
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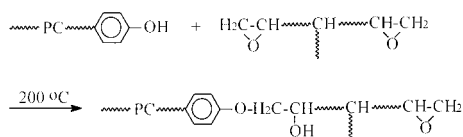
I. Hydrolysis of polycarbonate



II. Transesterification between secondary hydroxyl groups and carbonate groups



III. Reaction between an epoxide group and a phenolic group



Scheme 1 The proposed reactions in the DGEBA/PC blend at 200°C.³²

In our previous studies^{32,33} about the reactions between an epoxy oligomer based on the diglycidyl ether of bisphenol-A (DGEBA) and PC prior to cure, we have demonstrated that at 200°C the secondary hydroxyl groups in the DGEBA react with the carbonate groups in PC through transesterification, resulting in degraded PC chains with phenolic end groups and also in PC/DGEBA copolymers (see Scheme 1). The secondary hydroxyl groups are regenerated by the addition reaction between the epoxide groups and the phenolic end groups that are formed from the transesterification and the hydrolysis of PC. Therefore, by melt-blending DGEBA and PC at 200°C, an epoxy-network structure with bonded PC chains was expected after cure, due to the prereactions of DGEBA and PC in the melt-blending process. Yet, after adding a curing agent, the basic cure mechanism was not altered by the presence of a small amount of PC.³³ As a result, the fracture toughness of epoxies should be increased due to the incorporation of ductile PC chains into the epoxy network. For comparison, a solution-blending method was also used, in which DGEBA oligomer and PC were dissolved into a cosolvent before adding curing agent. Therefore, the prereactions between DGEBA and PC were minimized or eliminated deliberately. In this study, we report the

structures and properties of PC-modified epoxies cured with the diaminodiphenyl methane (DDM) by these two blending methods.

EXPERIMENTAL

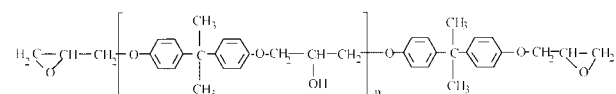
Materials

The poly(bisphenol-A carbonate) (PC) Lexan[®] 181 was supplied by General Electric Company (Pittsfield, MA). The \bar{M}_w and \bar{M}_n of this PC were 35,300 and 18,610, respectively, and the T_g was found at 152°C by differential scanning calorimetry (DSC). EPON[®] 828, an epoxy resin based on the diglycidyl ether of bisphenol-A (DGEBA), was supplied by Shell Chemical Company (Houston, TX). The \bar{M}_n of this DGEBA was 386.³⁴ This epoxy resin is composed principally of two homologues: $n = 0$ ($M_w = 340$) and $n = 1$ ($M_w = 624$) (see Scheme 2 for the structure). It is noticed that the $n = 1$ homologue has secondary hydroxyl groups. The DSC thermogram shows that the T_g of EPON[®] 828 is -12°C. The curing agent used was diaminodiphenyl methane (DDM) from Eastman Kodak Company (Rochester, NY). The melting point of this DDM is 92°C. It was used as received without further purification. Methylene chloride (CH_2Cl_2) from Aldrich Chemical Company (Milwaukee, WI) was used as a solvent for PC and EPON[®] 828.

Synthesis of PC-Modified Epoxies

Blending of PC and EPON[®] 828

It has been found that PC and EPON[®] 828 can be dissolved into a common solvent such as CH_2Cl_2 , or PC can be directly dissolved into the EPON[®] 828 at high temperatures.^{32,33} The former is called a solution-blending method (SB); and the latter, a melt-blending method (MB). Therefore, samples were made from these two processes, and properties of cured epoxies were compared. Before blending, PC and epoxy resin were dried at 130°C in a vacuum oven overnight. In the SB method, 5 to 20 parts of PC was dissolved in CH_2Cl_2 in a distillation flask and then mixed with 100 parts of EPON[®] 828 with a magnetic stirrer. The solvent



Scheme 2 The structure of EPON[®] 828: $\bar{X}_n = 0.163$ and $\bar{M}_n = 384$.

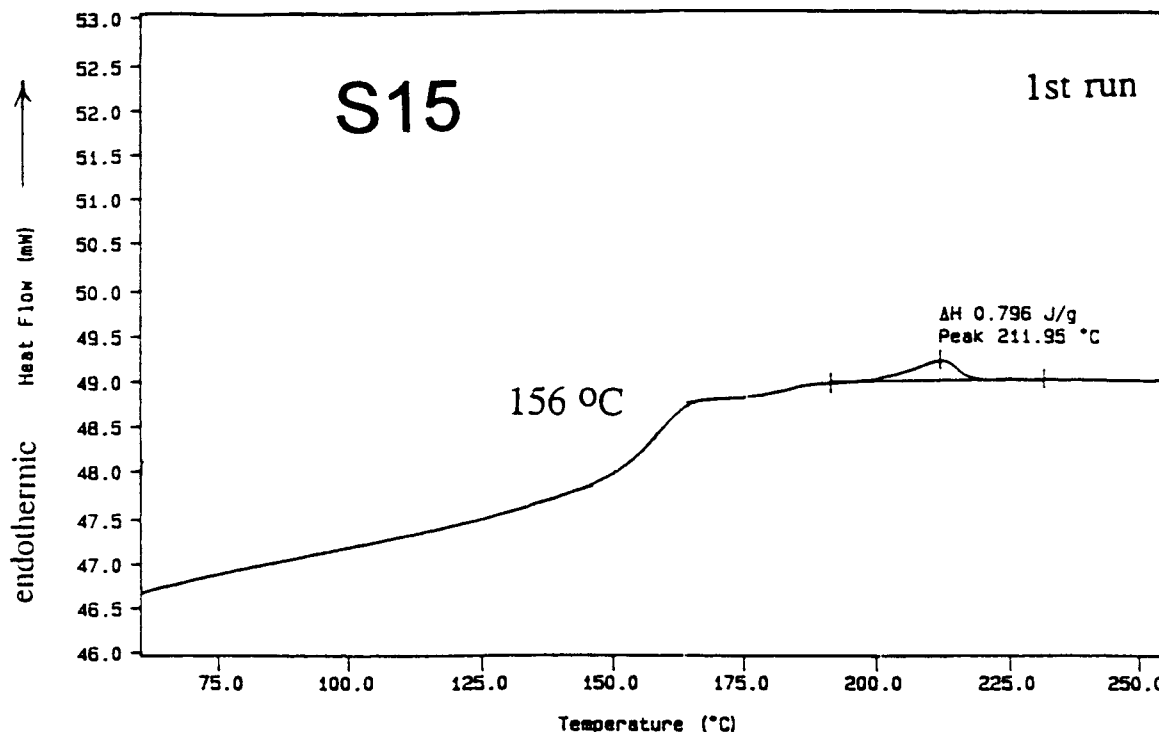


Figure 1 The DSC thermogram of a modified epoxy with 15 phr PC by a solution-blending method. The curing agent was DDM.

was removed by distillation using a silicon oil bath. The solution was stirred to prevent crystallization of PC during the evaporation of solvent. At the final stage of distillation, the bath temperature was increased to 100°C to remove as much of the solvent as possible. Any residual solvent has a pronounced effect on morphologies of the final cured products. In the MB method, 5 to 20 parts of PC pellets was mixed into 100 parts of EPON[®] 828 at 200°C. After continuously stirring for 3 to 5 h at 200°C, a clear homogeneous solution was obtained. Chemical reactions occurred at this high temperature as demonstrated in the previous studies.^{32,33} Following mixing, the temperature of the mixture was allowed to decrease to 100°C.

Curing of PC-Modified Epoxies

After a clear solution of PC/EPON[®] 828 was obtained, 27 parts of DDM, previously melted at 100°C, were added to the solution either by a SB or a MB method. The mixture was then degassed in a preheated mold in vacuum at 75–80°C for 30 min to 1 h, depending on the viscosity of the solution, and then cured at 90°C for 1 h, followed by 4 h at 160°C. The designations of the cured

epoxies are S05–S20 and M05–M20, where S and M stand for the solution- and the melt-blending process, respectively, and the number represents the parts of PC based on 100 parts of EPON[®] 828.

Instrumental Procedures

Thermal Properties

A Perkin–Elmer DSC 7 with a model 7700 data station was used to observe the thermograms of the samples. The instrument was first calibrated with indium followed by baseline adjustment. Nitrogen gas was purged into the cell. Approximately 10 to 12 mg samples were placed in aluminum pans and were scanned from 50 to 300°C at a heating rate 20°C/min for PC-modified epoxies. A midpoint method was employed to estimate the T_g .

Structure Identification

Fourier transform infrared (FTIR) spectroscopy was used to identify the chemical structures of PC/DGEBA blends and cured epoxies. Samples for PC/DGEBA blends were prepared by casting a thin film of $8 \pm 4 \mu\text{m}$ thickness on a sodium

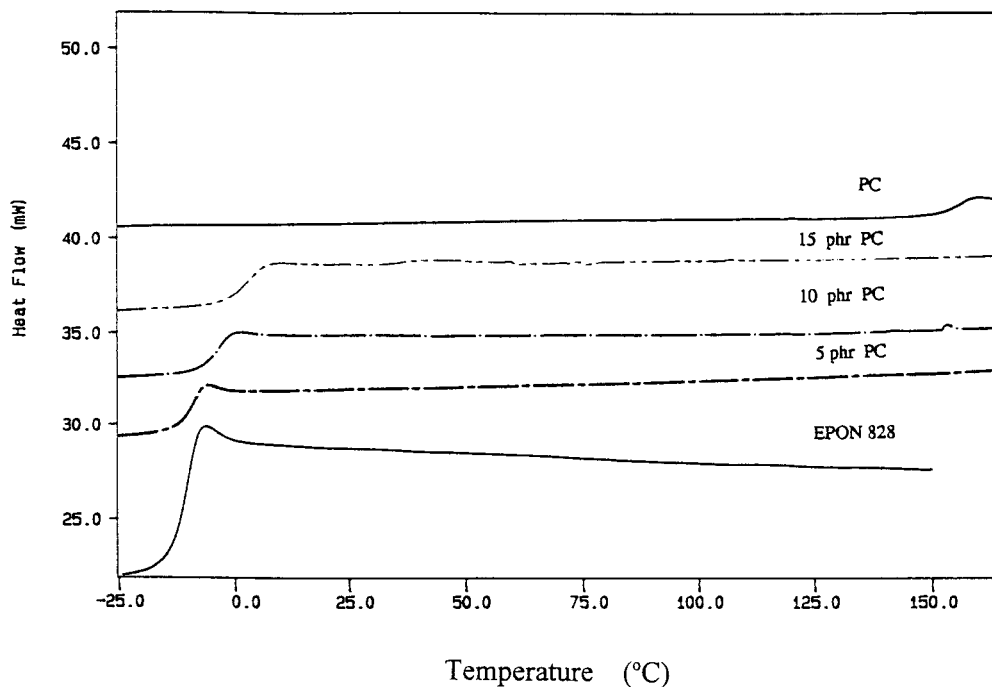


Figure 2 The DSC thermograms of PC/DGEBA blends, DGEBA, and PC.

chloride plate and followed by covering with another plate. The sandwichlike salt plate was placed in a heated cell, which was then mounted

in the spectrometer to carry out the *in situ* reactions. In addition to the dry air in the surroundings, dry nitrogen gas was purged into the cham-

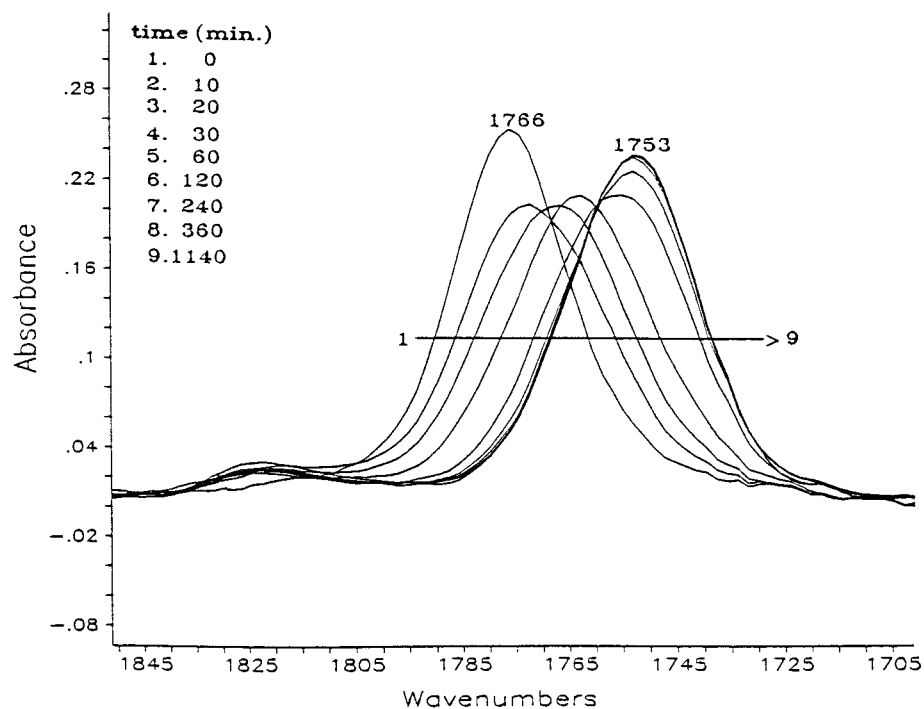


Figure 3 The FTIR carbonyl absorption peaks of a PC/DGEBA (16.5/100) film heated at 200°C for various times.

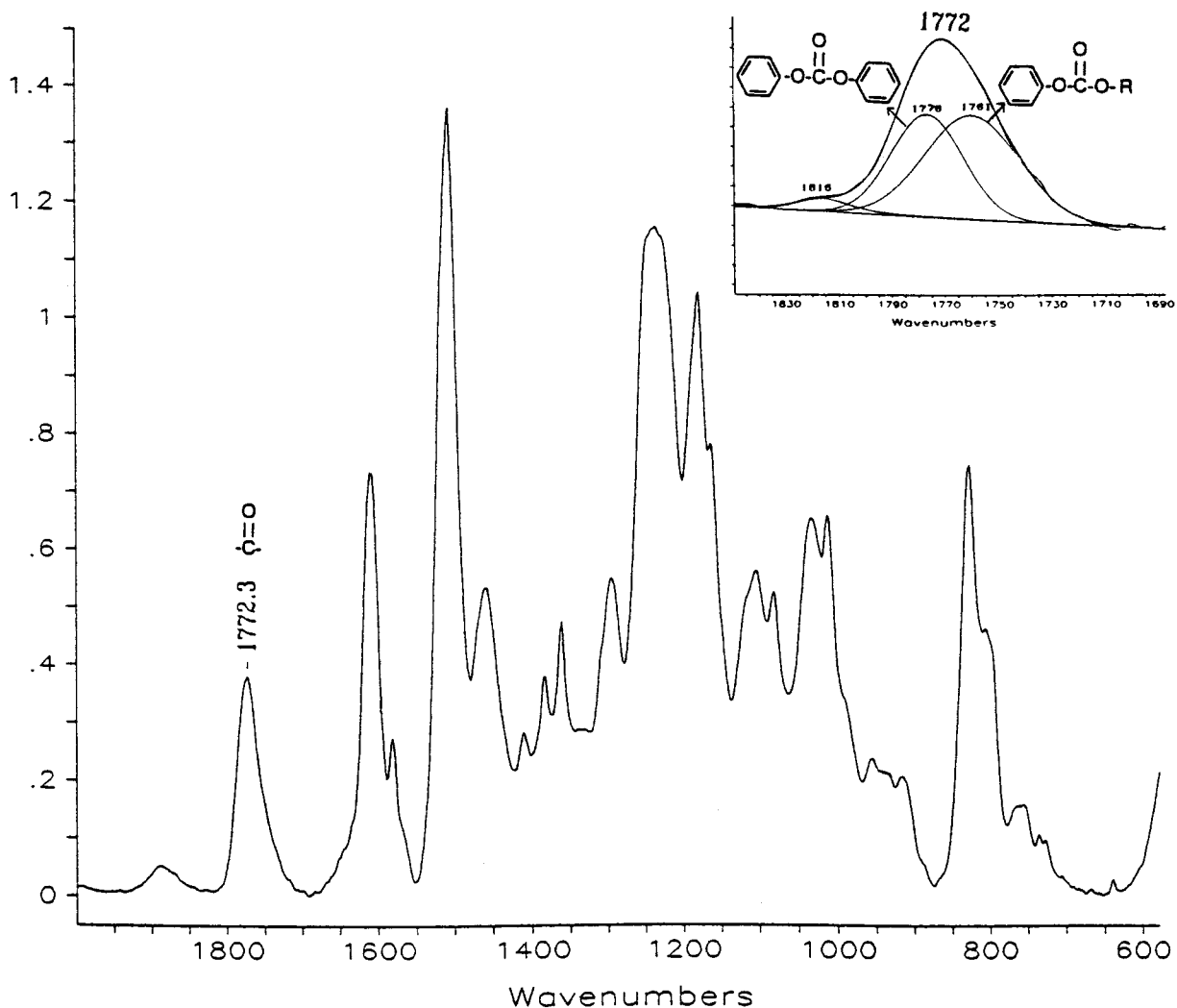


Figure 4 The FTIR spectrum of a modified epoxy with 15 phr PC by a melt-blending process and the resolved carbonyl peaks (upper right).

ber, both to keep the chamber as dry as possible and to eliminate CO_2 . For cured epoxies, samples were prepared by a standard KBr pellet procedure. FTIR spectra were obtained by use of a Nicolet 60 SX system at 4 cm^{-1} resolution with a deuterated triglycine sulfate detector (DTGS) and a germanium/KBr beam splitter. The recorded wavenumber range was from 600 to 4000 cm^{-1} and 32 spectra were averaged to reduce the noise.

Mechanical Properties

The tensile properties—initial modulus, ultimate tensile strength, and elongation at break—were evaluated using an Instron® Testing Machine, with type V specimens according to ASTM D-638. All the specimens were prepared from machine

operation from material in sheet. The thickness of the samples was 0.32 cm. The specimens were tested at room temperature at a cross-head speed of 0.1 cm/min and a gauge length of 1.27 cm. Approximately seven specimens were tested for each condition and the results were averaged.

The dynamic mechanical properties were measured using a dynamic mechanical thermal analyzer (Polymer Laboratories, DMTA Mk II). Samples of 0.1-cm thickness and 1.0-cm width were run in a single-cantilever bending mode at 1 Hz frequency. The temperature range was from -130 to 220°C with a heating rate of $2^\circ\text{C}/\text{min}$.

The plane strain fracture toughness values K_{IC} were determined using single-edge notched bending (SENB) type specimens in a three-point bend-

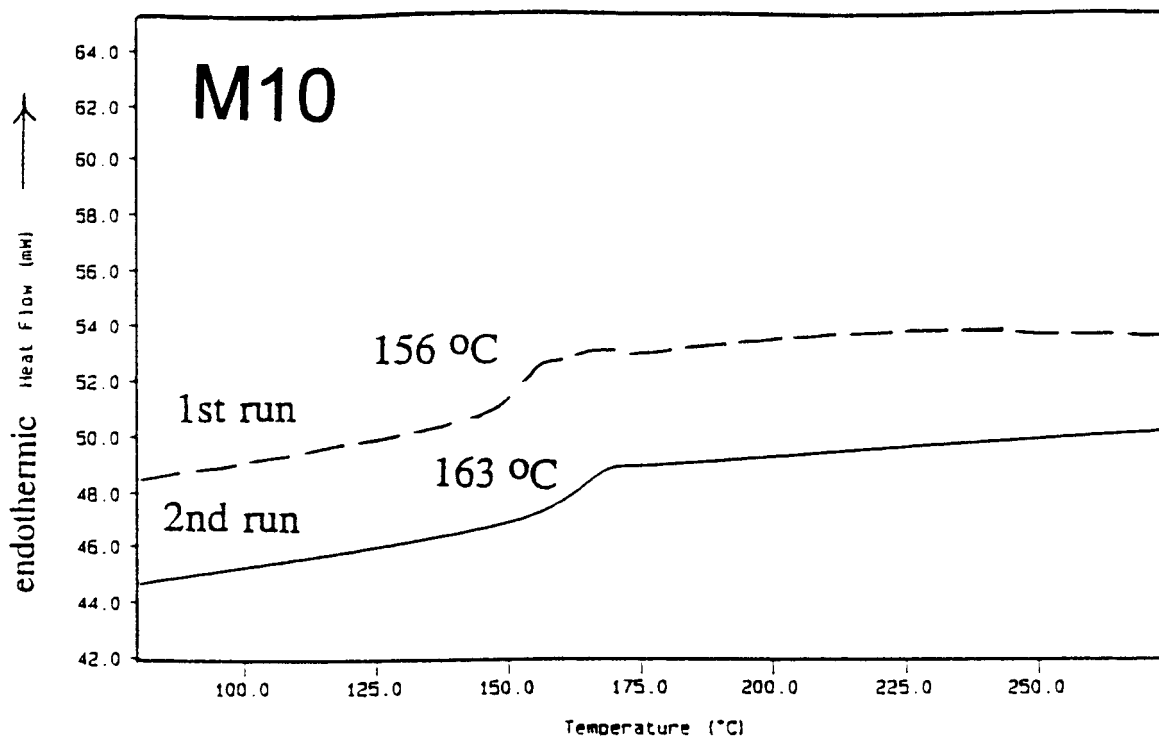


Figure 5 The DSC thermogram of a modified epoxy with 10 phr PC by a melt-blending method.

ing geometry according to ASTM D5045-91a. These SENB specimens had the dimensions of $0.96 \times 0.48 \times 6.25$ cm (a span of 3.84 cm was used). Sharp cracks were initiated by tapping with a hammer on a razor blade. A screw-driven Instron[®] testing machine, model 1011, was used with a cross-head speed of 1.0 cm/min. Five specimens were averaged to determine the K_{IC} value.

Morphology

A scanning electron microscope, model AMR 1200B SEM, was used to observe the sample fracture surfaces. The fractured or etched surfaces were coated with gold using a Polaron sputter coater. For etched samples, the specimens were fractured and then immersed in a 5% ethanolic potassium hydroxide solution for 4 h.

RESULTS AND DISCUSSION

Structures and Thermal Properties

SB Samples

The reason to use PC, in addition to its ductility, is its relatively high T_g at 152°C, close to the T_g

(156°C) of the DDM-cured epoxy. For SB samples, we found that there was no change of T_g of the modified epoxies up to 20 phr PC as compared with the neat epoxy. This indicates that the presence of PC did not decrease the final cure conversion or the crosslink density of the epoxy. Otherwise, the T_g of the epoxy matrix should decrease, subsequently decreasing the T_g 's of the resulting PC-modified epoxies. In addition to the T_g , a small melting peak at 212°C was observed for all the modified epoxies, except the sample with the least amount of PC, 5 phr. A typical DSC thermogram is shown in Figure 1 for a modified epoxy with 15 phr PC. This melting peak indicates PC crystallized during cure, which agrees with the findings from the FTIR analysis in the previous study³³: an absorption peak at 1766 cm^{-1} , corresponding to the carbonyl vibration in the PC crystalline region, was found during the cure.

MB Samples

In the melt-blending method, PC was directly dissolved into DGEBA resin at 200°C first, before adding the curing agent. Figure 2 shows the DSC thermograms of these PC/DGEBA blends after 3–5 h at 200°C; only one T_g was observed for each

Table I Mechanical Properties of PC-Modified Epoxies from the Solution-Blending Method

Content (phr)	Neat	S05	S10	S15	S20
Initial modulus (GPa)	2.46 ± 0.12 ^a	2.66 ± 0.10	2.82 ± 0.13	2.78 ± 0.05	2.83 ± 0.13
Tensile strength (MPa)	79.9 ± 1.93	78.9 ± 2.51	77.9 ± 1.78	76.5 ± 1.99	74.2 ± 3.89
Elongation at break (%)	6.36 ± 0.22	6.85 ± 0.28	6.19 ± 0.16	5.77 ± 0.11	5.63 ± 0.30

^a Standard deviation.

blend. This indicates that the components were miscible. From the previous results,^{32,33} we know PC chains can react with DGEBA through transesterification and phenolic-epoxide addition reactions at 200°C (see Scheme 1). A secondary hydroxyl group in the DGEBA reacted with an aromatic–aromatic carbonate group of PC to form a graft copolymer, containing an aromatic–aliphatic carbonate branching point, as well as a scission of PC chain with one phenolic end group. Each time this reaction occurred, the molecular weight of PC decreased and so did the numbers of aromatic–aromatic carbonate groups. This has been proved by the GPC and FTIR studies in the previous study.³² The aromatic–aliphatic carbonate groups could further react with the secondary hydroxyl groups to form the aliphatic–aliphatic carbonate groups. As a result, the carbonate infrared absorption peak would shift to lower wavenumbers as the reactions proceeded, since the aromatic–aromatic, aromatic–aliphatic, and aliphatic–aliphatic carbonate absorption peaks are at 1774, 1761, and 1746 cm⁻¹, respectively.³² Indeed this is shown in Figure 3, in which a PC/DGEBA film was heated *in situ* at 200°C. After premixing of PC and DGEBA at 200°C, the temperature was decreased to 100°C and the curing agent was added. It was then degassed, cured at

90°C for 1 h, followed by 4 h at 160°C. Figure 4 shows the FTIR spectrum of a modified epoxy with 15 phr PC. By using FTIR analysis with the help of the curve-fitting program and band parameters mentioned in the study by Don and Bell,³² an aromatic–aliphatic carbonate absorption peak at 1761 cm⁻¹ thus can be resolved.

Compared with the SB samples, these modified epoxies do not show any melting peak up to 20 phr PC in the DSC thermograms. A typical thermogram is shown in Figure 5. Therefore, PC did not crystallize in the MB samples, presumably due to the chemical bonding of PC onto the epoxy network. The DSC thermograms also show that the T_g of MB samples did not change.

Tensile Mechanical Properties

SB Samples

The tensile properties were measured by Instron[®] according to ASTM D638 using dog-bone specimens. Table I shows the initial modulus, tensile strength, and elongation at break of PC-modified epoxies from the SB method. Basically, there were no obvious changes in the tensile properties of these samples relative to neat epoxy controls. The slight increase of modulus (~10%) could be explained by the presence of PC crystallites. In

Table II Mechanical Properties of PC-Modified Epoxies from the Melt-Blending Method

Sample	Neat	M05	M10	M12	M15	M20
Initial modulus (GPa)	2.46 ± 0.12 ^a	2.63 ± 0.02	2.83 ± 0.09	2.60 ± 0.02	2.54 ± 0.08	2.48 ± 0.09
Tensile strength (MPa)	79.9 ± 1.93	74.3 ± 1.24	88.0 ± 2.44	84.4 ± 1.41	78.4 ± 1.41	73.6 ± 1.02
Elongation at break (%)	6.36 ± 0.22	5.20 ± 0.21	5.30 ± 0.80	8.68 ± 0.91	6.08 ± 0.31	6.36 ± 0.28

^a Standard deviation.

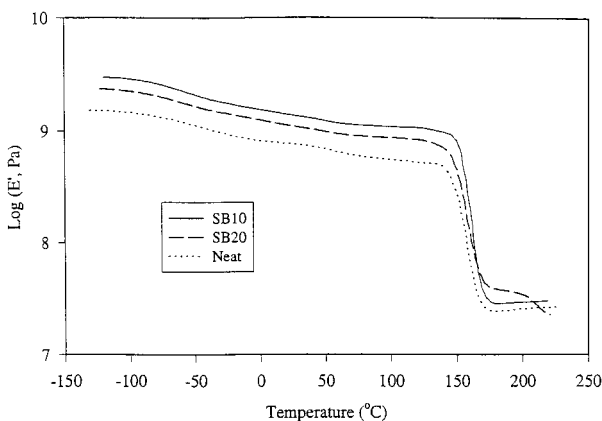


Figure 6 The dynamic modulus of modified epoxies with 10 and 20 phr PC by a solution-blending method compared with the neat epoxy.

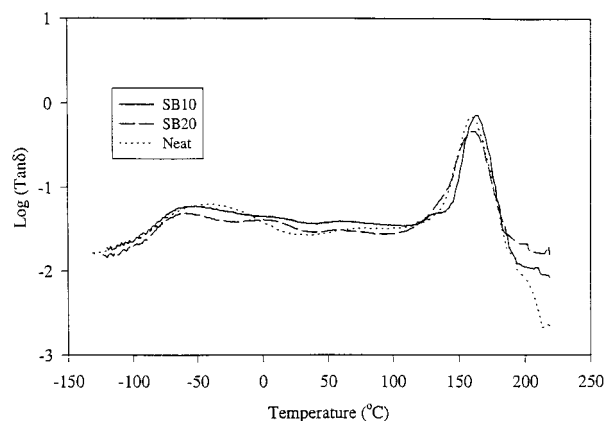


Figure 7 The loss $\tan \delta$ curves of modified epoxies with 10 and 20 phr PC by a solution-blending method compared with the neat epoxy.

order to transfer the load to the crystallites, there must be a good interfacial bonding between the PC chains and epoxy molecules. Indeed, the interfacial bonding was provided by hydrogen bonding between the PC carbonyl groups and the hydroxyl groups in the epoxy, which can be seen by the shift and broadening of the carbonyl absorption peak.³⁵ It must be pointed out that, in some circumstances, a strong hydrogen bonding between the additives and matrix is enough to cause a slight increase in modulus. This phenomenon is called antiplasticization behavior.^{36–39}

MB Samples

The tensile properties of MB samples are shown in Table II. The room temperature tensile strength and elongation at break did not change significantly, but there was again a slight increase in the initial modulus, demonstrating that the hydrogen bonding between PC and epoxy is one reason for the increase in modulus in both SB and MB samples. The data were more scattered than those in the SB samples, mainly because of the sample preparation method. In the SB method, the solvent helped reduce the viscosity of the resins, which resulted in easy processing, making the samples more homogeneous.

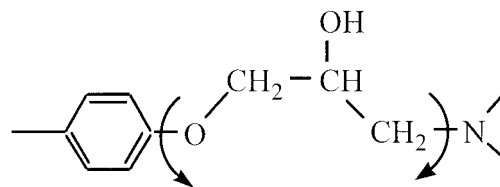
Dynamic Mechanical Properties

SB Samples

Figure 6 shows the dynamic modulus of modified epoxies with 10 and 20 phr PC from the SB method as compared with a neat epoxy. The modulus of modified epoxies was higher than that of

the neat epoxy over the entire temperature region, including the rubbery region. In the glassy region, the increase can be explained by both the presence of PC crystallites and the hydrogen bonding, as mentioned previously. However, the modulus increase in the rubbery plateau region can be explained only by the presence of tiny PC crystallites (which have a melting point at about 212°C, almost 50°C above the T_g of modified epoxies), because at this high temperature region, there should be only a little intermolecular hydrogen bonding left in the system.

The $\tan \delta$ curves of these SB samples are shown in Figure 7. The presence of PC modifier did not result in a change of the glass transition temperatures such as was found in the DSC results. However, the presence of PC slightly suppressed the β -relaxation peak at about -51°C . Most authors^{40–50} assign this low-temperature secondary transition to the motions of the 2-hydroxypropyl ether sequence. Scheme 3 shows a crankshaft motion of the glycidyl amine linkage in the amine-cured resin, which is most probable for this 2-hydroxypropyl ether motion.⁴¹ Since the hydroxyl group is involved in the motion, the β



Scheme 3 Proposed crankshaft motion of the 2-hydroxypropyl ether moiety.⁴¹

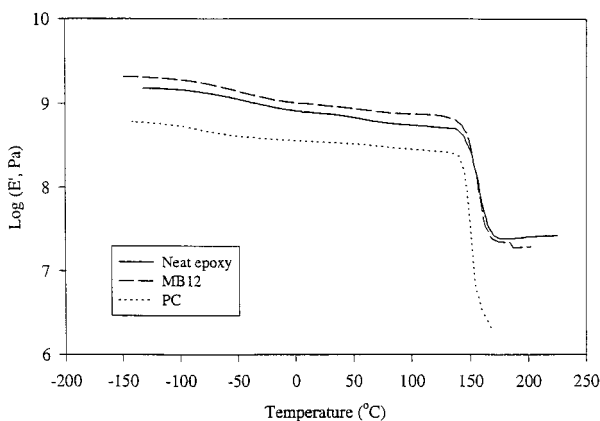


Figure 8 The dynamic modulus of a modified epoxy with 12 phr PC by a melt-blending method compared with the PC and neat epoxy.

relaxation can be suppressed by the formation of hydrogen bonds to other groups.^{41,42,46} Indeed, in the present system the carbonate group of PC chains can form the hydrogen bonding with this 2-hydroxypropyl ether. Therefore, strong hydrogen bonding as well as the PC crystallites restricted the segmental motion and depressed the β -relaxation peak.

MB Samples

In the case of MB samples, the dynamic modulus for PC-modified epoxies was also higher than that in the neat epoxy but only in the glassy region, as shown in Figure 8. The rubbery modulus became a little lower than that in the neat epoxy, in contrast to the findings in the SB samples. Possible reasons for this are: (1) there was no crystallization of PC in the MB samples; (2) the unbonded PC chains acted as a plasticizer at this high-temperature region (above PC's T_g); and (3) the bonding of PC chains to epoxy decreased the effective crosslink density. In order to calculate the crosslink density in both SB and MB samples by using classical rubber elasticity theory, a

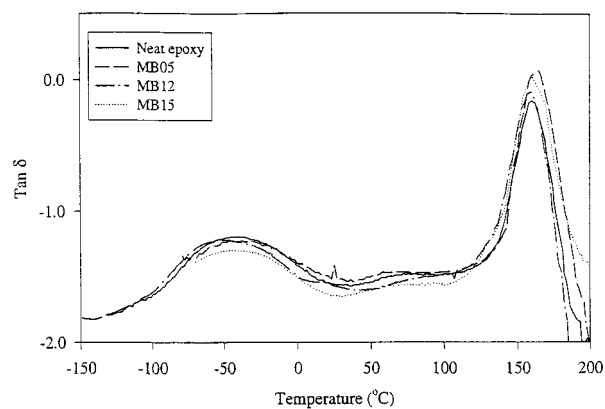


Figure 9 The loss tan δ curves of modified epoxies by a melt-blending method compared with the neat epoxy

knowledge of rubbery modulus exerted only by the epoxy network is required. Efforts to subtract the contribution of PC modifier from the experimental rubbery modulus values failed. This is because of the unknown fraction and unknown modulus of each PC form in the epoxy rubbery region; the PC modifier could be in the form of crystallites (as in the SB samples), plasticizer (as in both the SB and MB samples), or flexibilizer (as in the MB samples). Figure 9 shows tan δ curves of PC-modified epoxies by a MB method. The β -relaxation peak was depressed and shifted to a lower-temperature region. They were attributed to the bonding of PC chains onto the epoxy network and hydrogen bonding between PC and epoxy.

Fracture Toughness

Table III shows the fracture toughness (K_{IC}) of SB samples measured by a three-point-bending method with single-edge notched samples. There was no significant increase in fracture toughness with the addition of PC modifier. However, in samples from the MB method, the fracture tough-

Table III Fracture Toughness (K_{IC}) and Fracture Energy (G_{IC}) of PC-Modified Epoxies from the Solution-Blending Method

Sample	Neat	S05	S10	S15	S20
K_{IC} (MPa m ⁻²)	0.720 ± 0.048 ^a	0.794 ± 0.025	0.925 ± 0.016	0.849 ± 0.025	0.794 ± 0.028
G_{IC} ^b (kJ/m ²)	0.187 ± 0.022	0.211 ± 0.014	0.270 ± 0.016	0.230 ± 0.012	0.198 ± 0.015

^a Standard deviation.

^b G_{IC} is equal to $K_{IC}^2 (1 - \nu^2)/E$. The Poisson's ratio ν of epoxy was taken as 1/3.

Table IV Fracture Toughness (K_{IC}) and Fracture Energy (G_{IC}) of PC-Modified Epoxies from the Melt-Blending Method

Sample	Neat	M05	M10	M12	M15	M20
K_{IC} (MPa m ⁻²)	0.720 ± 0.048 ^a	0.912 ± 0.016	1.006 ± 0.042	1.167 ± 0.061	0.770 ± 0.007	0.614 ± 0.027
G_{IC} ^b (kJ/m ²)	0.187 ± 0.022	0.281 ± 0.008	0.307 ± 0.023	0.466 ± 0.039	0.207 ± 0.008	0.135 ± 0.011

^a Standard deviation.

^b G_{IC} is equal to $K_{IC}^2 (1 - \nu^2)/E$. The Poisson's ratio ν of epoxy was taken as 1/3.

ness increased from 0.72 MPa m⁻² for the neat epoxy to 1.17 MPa m⁻² for the modified epoxy with 12 phr PC (see Table IV). In terms of the fracture energy (G_{IC}), the increase was about 2.5 times. It must be emphasized that this increase of toughness was by a change of molecular structure, in which the ductile PC chains were bonded to the epoxy network. Therefore, the capability for plastic deformation was increased. This is unlike other thermoplastic-modified epoxies, in which the increase in the fracture toughness is by triggering some damage processes such as particle bridging and tearing, microcracking, crack bifurcation, and crack pinning.^{14-19,51,52}

Morphology

Figure 10 shows a SEM micrograph of the fracture surface of a neat epoxy. The surface is basically featureless due to the intrinsic brittleness of this epoxy system. By etching the samples with 5% ethanolic potassium hydroxide, PC was etched away from the fracture surface leaving puddles and troughs in SB samples, but not in MB sam-

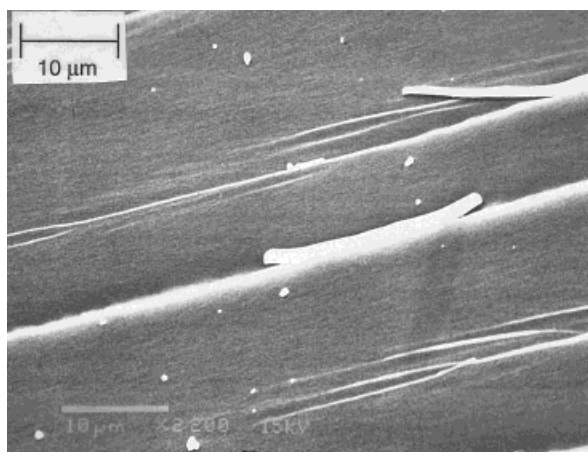


Figure 10 A SEM micrograph of the fracture surface of a neat epoxy.

ples. This validated that PC chains were bonded on epoxy network in MB samples. Figure 11 shows the fracture surface of a MB sample. Apparently the capability for plastic deformation was increased in this sample as compared with the neat epoxy.

CONCLUSIONS

An epoxy resin based on the DGEBA was modified with PC. After the blending of DGEBA resin and PC, the curing agent was added into the mixture. The glass transition temperatures of modified epoxies were not decreased by the PC presence, which further confirmed the previous findings in the FTIR studies³³ that PC did not alter the reaction mechanism of epoxy cure. If a solution-blending process was used, PC could undergo crystallization during the earlier stage of cure. A small melting peak at 212°C was observed. It was thought the residual solvent and

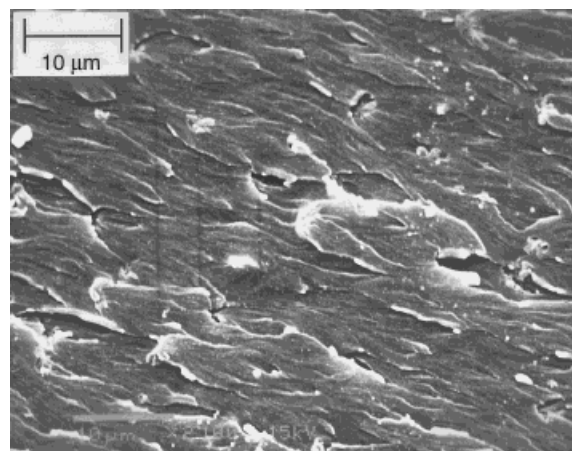


Figure 11 A SEM micrograph of the fracture surface of a modified epoxy with 12 phr PC by a melt-blending method.

the DGEBA resin plasticized PC and induced PC crystallization during cure before the matrix became too viscous. However, there was no melting peak observed in DSC scans for the modified epoxies when a melt-blending process was used. This is because of the bonding of PC chains onto DGEBA from the prereaction at 200°C (melt-blending) before cure, thus inhibiting the crystallization of PC during cure.

The tensile mechanical properties were basically maintained in the PC-modified epoxies from both the solution- and melt-blending processes. There was a slight increase in initial modulus compared to the neat epoxy, probably due to the PC crystallites as in the SB samples and hydrogen bonding between PC and epoxies both in the SB and MB samples. There was no significant increase in fracture toughness with the addition of PC modifier if a solution-blending process was used. However, by a melt-blending process, the fracture toughness was increased from 0.72 for the neat epoxy to 1.17 MPa m⁻² for the modified epoxy with 12 phr PC. The increase of toughness was due to the bonding of ductile PC chains onto the epoxy network through the melt-blending. Therefore, the capability for plastic deformation was increased.

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