

Fourier Transform Infrared Analysis of Polycarbonate/Epoxy Mixtures Cured with an Aromatic Amine

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ABSTRACT: In our previous article, we established that polycarbonate (PC) can react with the diglycidyl ether of bisphenol-A (DGEBA) at 200°C through transesterification and addition reactions, resulting in degraded PC chains with phenolic end groups and also in PC/DGEBA copolymers. However, these reactions can be minimized or eliminated at lower temperatures, below 160°C. In this article, Fourier transform infrared analysis (FTIR) was used to study the curing kinetics of epoxies in the presence of PC. The curing agent was an aromatic amine, diaminodiphenyl methane (DDM). FTIR results showed that the presence of a small amount of PC promoted the amine-epoxide reactions, probably due to the catalytic effect of the phenolic end groups in the PC chains. However, the PC did not alter the epoxy cure reaction mechanism. Two different blending processes were used to premix the PC and DGEBA, namely, solution-blending and melt-blending processes, in order to give different extents of prereactions. If a solution-blending process was used, PC tended to undergo crystallization during an early stage of cure. When a melt-blending process was used, no melting peak was observed in the thermograms of the differential scanning calorimeter (DSC) for the modified epoxies; PC chains bonded to DGEBA during prereaction at 200°C, thus inhibiting the crystallization of PC during cure. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2395–2407, 1998

Key words: polycarbonate; epoxy; transesterification; cure; blend; infrared analysis

INTRODUCTION

Unmodified epoxies are relatively brittle materials with poor resistance to crack propagation. Therefore, methods for increasing the fracture toughness of epoxy polymers have been the subject of studies for many years.^{1–14} Recently, there have been several articles concerning modification of epoxies with polycarbonate (PC).^{15–30} The primary object of these endeavors is to increase the fracture toughness of originally brittle epoxies, especially highly crosslinked, high glass transition temperature (T_g) epoxies. While trying to

toughen epoxies with PC, several authors suspected or found that some unexpected reactions between PC and epoxies occur; we have found that these reactions depend on the preparation methods. Chen et al.¹⁶ studied the miscibility and the fracture behavior of a diethylenetriamine (DETA)-cured epoxy resin/PC blend. Epikote® 828 was mixed with PC using methylene chloride as a cosolvent; after solvent removal, the mixture was then cured with DETA. The authors concluded that the blend was miscible and the fracture toughness, K_{IC} , was increased somewhat by the addition of the PC. In our laboratory,¹⁷ we found that aliphatic amines like DETA aggressively degrade PC through transamidation, supported by infrared analysis evidence: A shift of

the carbonyl absorption peak from 1774 cm^{-1} (aromatic–aromatic carbonate groups) to a broad peak centered at 1725 cm^{-1} (carbamate groups) was observed. Such a shift was also observed recently by Li et al.¹⁸

Bucknall et al.¹⁹ tried to enhance the ductility and, hence, the toughening ability of an epoxy matrix by forming a solid solution of the PC in the epoxy matrix. Methylene chloride was used to facilitate the dissolution of PC into two epoxy resins, MY 750 [diglycidyl ether of bisphenol-A (DGEBA)] and MY0510 (a trifunctional resin). After solvent removal, the resins were cured with diaminodiphenyl methane (DDM) at 80°C for 6 h followed by 3 h at 150°C . It was found that the fracture toughness was not improved by the addition of PC and it was suggested that some degradation of the PC had occurred. However, the nature of degradation was not specified.

In contrast, Martuscelli et al.^{20–23} found a sevenfold increase in the fracture energy of a modified epoxy containing 20 wt % of PC and produced by a melt-blending process. The possible chemical reactions during melt blending at high temperature and the fracture behavior of PC-modified epoxies were also investigated. Their results showed that during the blending of PC and a Novolac epoxy resin (DEN® 438) at high temperature, 220°C , the PC underwent chain scission through the hydrolysis of carbonate groups. Subsequently, the resulting hydroxyl groups at the PC chain ends reacted with epoxy resins, forming epoxy-terminated PC chains. Eventually, these PC chains were incorporated into the epoxy network after curing with nadic methyl anhydride (NMA) using benzyl dimethylamine (BDMA) as an accelerator. This network molecular structure then served as the explanation for the marked increase in the fracture toughness of the blend system.

Funahashi²⁴ reported that epoxide groups can react with aryl carboxylate or aryl carbonate groups in the presence of a base catalyst. A poly(ether carbonate) was prepared by the reaction of diphenyl carbonate with 1,4-bis(2,3-epoxypropoxy)-benzene catalyzed by a potassium *tert*-butoxide. Yu and Bell²⁵ studied the reactions by using model compounds, namely, diphenyl carbonate and epichlorohydrin. The reaction was believed to be of an addition-coupling type (transesterification reaction) between epoxide groups and carbonate groups. It occurred in the presence of a base catalyst such as tertiary amines, quaternary ammonium salts, and metallic alkoxides. A three-dimensional network was obtained when diepox-

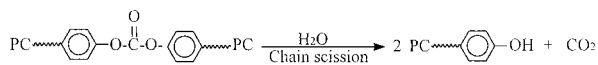
ides and PC were reacted in the presence of a benzyltrimethyl ammonium chloride (BTMAC).

Su et al.²⁶ studied the miscibility and cure kinetics of PC/TGDDM blends cured with DDS. In their study, the PC in powder form was added to the already mixed epoxy/amine resin. The cure reaction rates were higher in the PC epoxy blends and apparently obeyed an *n*-th-order reaction mechanism rather than the conventional autocatalytic mechanism for the amine-cured epoxies. A homogeneous one-phase structure was observed for all of the cured PC/epoxy blends up to 50 phr of PC. No mechanical properties were reported.

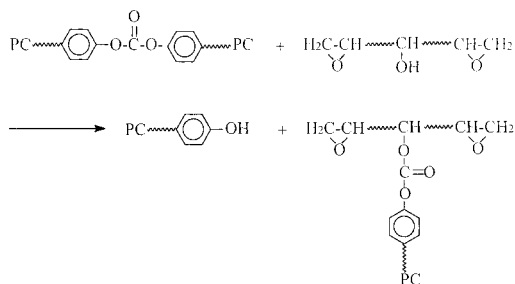
Li et al.²⁷ studied the chemical reactions in the epoxy/PC blends with a tertiary amine catalyst. They found, in addition to a transesterification reaction between epoxides and carbonate groups which produced aromatic–aliphatic and aliphatic–aliphatic carbonates, a cyclic carbonate was formed during the reaction. Two sequential mechanisms were proposed to explain the formation of the cyclic carbonate by proceeding through a zwitterion followed by a nucleophile attack at the aromatic–aliphatic or the aliphatic–aliphatic carbonate group. However, Don²⁸ proposed a more simple mechanism to explain the formation of cyclic carbonates: They are formed directly through the reaction of the epoxide groups with carbon dioxide (CO_2) which is produced internally through the hydrolysis of PC. It is well known that CO_2 can react with epoxide groups in the presence of tertiary amines and thus form cyclic carbonates.^{28,31,32}

Lee et al.²⁹ investigated the thermal stability and compatibility of tetrafunctional epoxy resin/PC blends cured with an aromatic diamine. They found that epoxy underwent thermal degradation when the cure temperature was high, 230°C . The thermal degradation was induced by the etherification, subsequently proceeded via dehydration and thermal oxidation, and finally resulted in the scission of network chains. As a result, the T_g of the epoxy increased during cure and reached a maximum and then began to decrease due to the degradation. The addition of tetramethyl polycarbonate enhanced the thermal stability of the epoxy. However, with the bisphenol-A type PC, the added PC was hydrolyzed by the H_2O produced in the dehydration step of the epoxy thermal degradation. Prateepasane³⁰ studied the chemical reactions in a DGEBA/PC system as well as several model compounds in the presence of quaternary ammonium salts. It was concluded that the salt catalyzed the hydrolysis of PC first, and, subse-

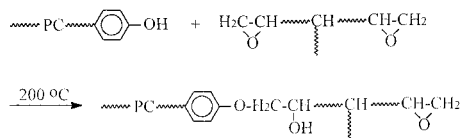
I. Hydrolysis of polycarbonate



II. Transesterification between secondary hydroxyl groups and carbonate groups



III. Reaction between an epoxide group and a phenolic group



Scheme 1 Proposed reactions in the DGEBA/PC blend at 200°C.¹⁵

quently, the produced hydroxyl groups at the PC chain ends reacted with the epoxide groups.

In our previous article¹⁵ about the reactions between an epoxy oligomer based upon the DGEBA and PC prior to cure, we 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 which 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 pre-reactions of DGEBA and PC. As a result, the fracture toughness of the cured 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 the DGEBA oligomer and PC were dissolved into a cosolvent before adding a curing agent. Therefore, the pre-reactions between DGEBA and PC were minimized or eliminated deliberately. In this study, we investigated the effects of PC and also the different blending methods on the curing reac-

tion mechanism of epoxies and the final formed structures of PC-modified epoxies.

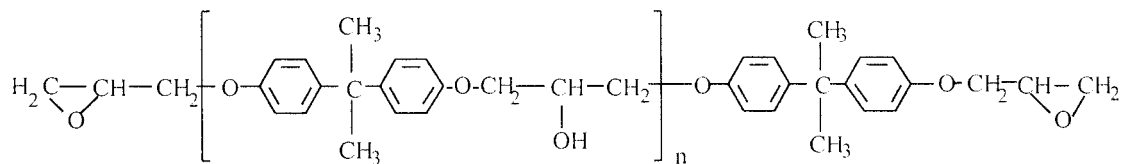
EXPERIMENTAL

Materials

The poly(bisphenol-A carbonate) (PC), Lexan® 181, was supplied by General Electric Co. The \overline{M}_w and \overline{M}_n measured by the gel permeation chromatography (GPC) method were 35,300 and 18,610, respectively. The glass transition temperature of PC was found at 152°C by differential scanning calorimetry (DSC). An epoxy resin, EPON® 828, based upon DGEBA was supplied by Shell Chemical Co. The \overline{M}_n of this DGEBA was 386, as measured by a titration method.³³ This epoxy resin is composed principally of two homologs: $n = 0$ (MW = 340) and $n = 1$ (MW = 624); see Scheme 2 for the structure. It is noticed that the $n = 1$ homolog 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 Co. 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 Co. was used as a solvent for PC and EPON® 828.

Procedures and Instrumentation

Since PC and EPON® 828 have very close solubility parameters (δ)^{15,34}: 20.7 (MJ/m^3)^{1/2} for PC and 20.9 (MJ/m^3)^{1/2} for EPON® 828 due to their similar chemical structures, they are expected to be miscible in the amorphous state. It was 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. The former is called a solution-blending (SB) method, and the latter, a melt-blending (MB) method. Therefore, samples were made from these two processes. Before blending, both the PC and epoxy resin were dried at 130°C in a vacuum oven overnight. In the SB method, 30 parts of PC was dissolved into CH_2Cl_2 in a distillation flask and then mixed with 100 parts of EPON® 828 with a magnetic stirrer at room temperature. The solvent was removed by distillation using a silicon oil bath; the boiling point of CH_2Cl_2 is 42°C. The solution was stirred to prevent the crystallization of PC during the evapora-



Scheme 2 Structure of EPON 828: $X_n = 0.163$ and $M_n = 384$. (composed principally of two homologs $n = 0$ and $n = 1$).

tion of the solvent. At the final stage of distillation, the bath temperature was increased to 90°C to remove as much of the solvent as possible. Any residual solvent has a pronounced effect on the morphologies of the final cured products. In the MB method, 30 parts of PC pellets was mixed into 100 parts of EPON® 828 at 200°C. After continuously stirring for 3–5 h at 200°C, a clear homogeneous solution was obtained. Chemical reactions occurred at this high temperature as demonstrated in the previous article¹⁵ (Scheme 1). Following mixing, the temperature of the mixture was allowed to decrease to 90°C.

After a clear solution of PC/EPON® 828 was obtained either by an SB or an MB method, 27 parts of DDM, previously melted at 90–100°C, was added to the solution. Fourier transform infrared (FTIR) spectroscopy was used for the isothermal kinetic measurements at 90°C. From the above solution, samples were prepared by casting a thin film of $12 \pm 4\text{-}\mu\text{m}$ thickness on a sodium 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. The heated cell was driven by an Omega CN 7100 model temperature controller to an accuracy of $\pm 1^\circ\text{C}$. In addition to the dry air in the surroundings, dry nitrogen gas was purged into the chamber, both to keep the chamber as dry as possible and to eliminate CO_2 . 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. A commercial software "Spectra Calc" from Galactic Industries Corp. was used to process and calculate all the data from the spectra.

For cured epoxies, samples were cured at 90°C for 1 h followed by 4 h at 160°C. A Perkin–Elmer DSC 7 with a Model 7700 data station was used to observe the thermograms of the cured epoxies. The instrument was first calibrated with indium

followed by baseline adjustment. Nitrogen gas was purged into the cell. Approximately 10–12-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 .

RESULTS AND DISCUSSION

Neat Epoxy

A detailed review and discussion of amine–epoxide reactions has been given in several books and articles.^{31,35–44} In principle, primary amines react with epoxide groups, producing secondary amines. Subsequently, secondary amines react with epoxide groups and produce tertiary amines. In the DGEBA/DDM system, the side reactions, etherification and homopolymerization, can be neglected for the present cure conditions.^{33,44–53} The isothermal cure of epoxies was monitored at 90°C by an FTIR technique *in situ*, since in the preparation of all epoxy sheets, the resins were cured with DDM at 90°C for 1 h and then postcured at 160°C for 4 h. Figure 1 shows the FTIR spectra of a DGEBA/DDM film at 90°C *in situ* for various times. The assignment of various peaks of DGEBA are available in the literature^{22,31,54}; of these peaks, the most important absorption is the epoxide group at 914 cm^{-1} . The addition of diamines (DDM) results in the absorption of primary amines at 3454 and 1624 cm^{-1} as well as the secondary amines at 3367 cm^{-1} . It is obvious that the primary amine peak at 1624 cm^{-1} and the epoxide-group peak at 914 cm^{-1} both decreased in size with time. By calculating the area under these peaks, the conversion of these functional groups at different times can be determined. It is relatively easy to calculate the conversion of epoxide groups since the peak is well separated from the other peaks. However, for primary amines, the absorption peak at 3454 cm^{-1} cannot be used for quantitative analysis due to the severe overlapping with secondary amines and hydroxyl

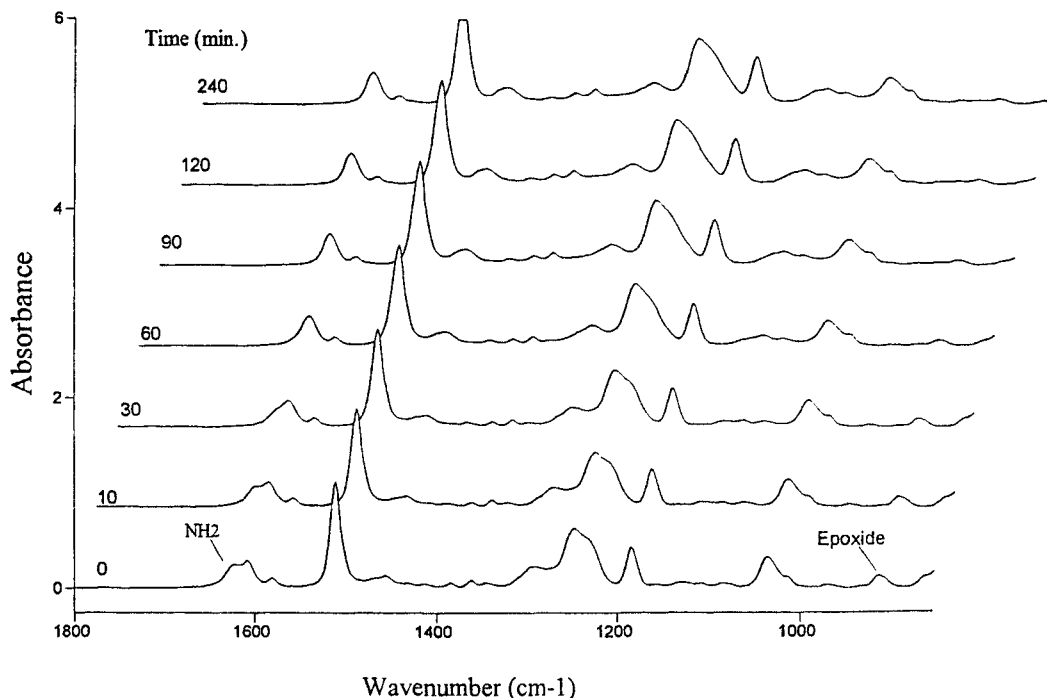


Figure 1 FTIR spectra of a DGEBA/DDM (100/27) film *in situ* at 90°C.

groups produced during cure. Fortunately, it is feasible to use the peak at 1624 cm^{-1} , since it is only overlapped with the phenyl ring at 1607 cm^{-1} and the two can be separated by using a least-square curve-fitting program. The adopted half-widths, $\omega_{1/2}$, for resolving the overlapped peak are $22 \pm 1\text{ cm}^{-1}$ for the primary amines and $17 \pm 1\text{ cm}^{-1}$ for the phenyl absorption peak. After carefully setting the baselines, we curve-resolved the experimental spectra, and a typical curve-fitting result is shown in Figure 2. Therefore, conversions of epoxide groups and primary amines were calculated as shown in Figure 3. It was found that after 2 h the reaction was almost complete for the primary amines but only reached about 65% for the epoxide groups. The incomplete conversion of epoxide groups was due to the vitrification of the epoxy resin, in which the T_g of the sample reached the cure temperature. In addition, the results indicate an unequal reactivity of primary amines and secondary amines in this bulk system; the primary amines have a higher reactivity than that of the secondary amines.

A generalized form of the kinetic equation to describe the kinetics of amine/epoxide reactions originally derived by Horie⁴⁴ is shown below as

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (1)$$

where α is the conversion of epoxide and k_1 and k_2 are the specific rate constants related to the noncatalytic and catalytic rate constants, respectively. The reaction orders m and n are adjustable parameters and the sum $m + n = 2$ has been adopted in most literature reports.^{51,55} Here, we are most concerned about the effects of the PC modifier on the amines/epoxide reactions. Therefore, $m = n = 1$ was adopted for the kinetic analysis, which favors the condition of an autocatalyzed reaction, as in the studies of Golub and Lerner⁵¹ and Barton.⁵⁵ Figure 4 shows the linear plot of $(d\alpha/dt)(1/1 - \alpha)$ versus α . The rate constants k_1 and k_2 obtained from the intercept and slope are 7.36×10^{-3} and $1.77 \times 10^{-2}\text{ min}^{-1}$, respectively. The fit failed at the latter stage of cure, because the reactions were no longer controlled by the kinetics; instead, slow diffusion, because of the approach of vitrification, became limiting.

PC-modified Epoxies

SB Samples

The curing reactions of PC-modified epoxies were also studied by the FTIR technique. In the SB method, PC and DGEBA were both dissolved in CH_2Cl_2 at room temperature. Figure 5 shows the FTIR spectra of a PC/DGEBA/DDM (30/100/27)

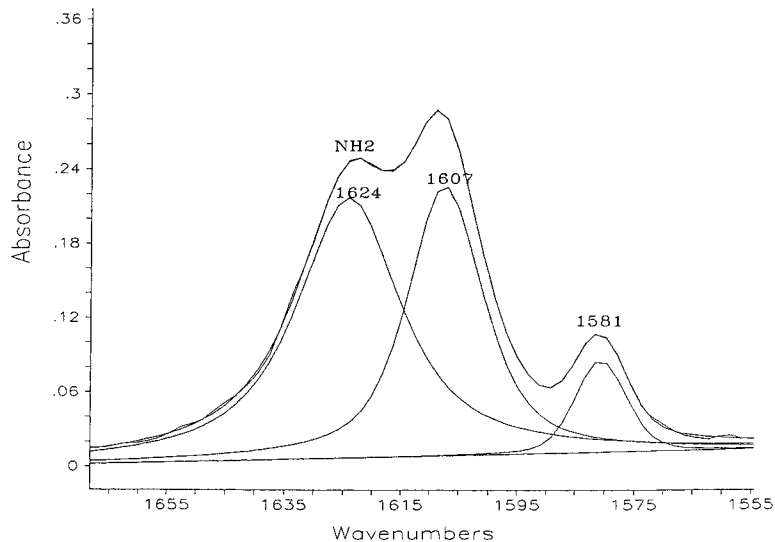


Figure 2 Resolved peaks of primary amines and a phenyl ring using a least-square curve-fitting program.

film by the SB method at 90°C *in situ*. From the peak area change, the conversions of primary amines and epoxide groups were calculated as shown in Figure 6. By comparison with Figure 2, it can be seen that the reaction mechanism basically was not altered. However, the effort to calculate the kinetic constants by using eq. (1) with $m = n = 1$ was not successful. Since it is possible that the parameters were no longer realistic for

the SB samples, we tried to fit the data with $m = 1$ and $n = 2$ (ref. 44), but still failed. It was found that the FTIR spectra shifted upward (decreasing transmittance) as reactions proceeded, in agreement with the observation that the transparency of the film decreased. It was presumably assumed that the PC underwent crystallization during the early stage of cure, which will be explained and more evidence will be provided in the

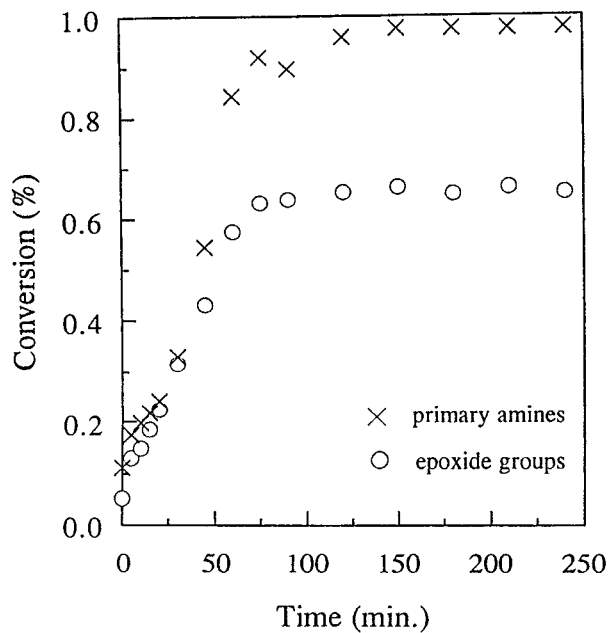


Figure 3 Conversion of primary amines and epoxide groups in a DGEBA/DDM film *in situ* at 90°C.

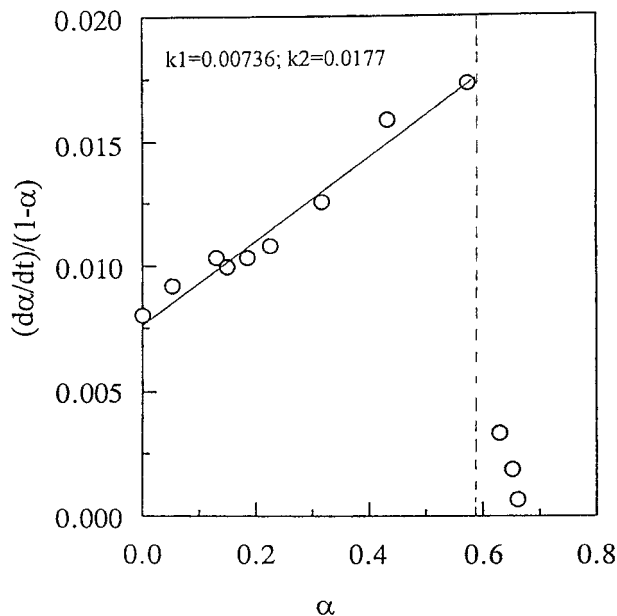


Figure 4 Kinetic plot for the DGEBA/DDM (100/27) reaction at 90°C.

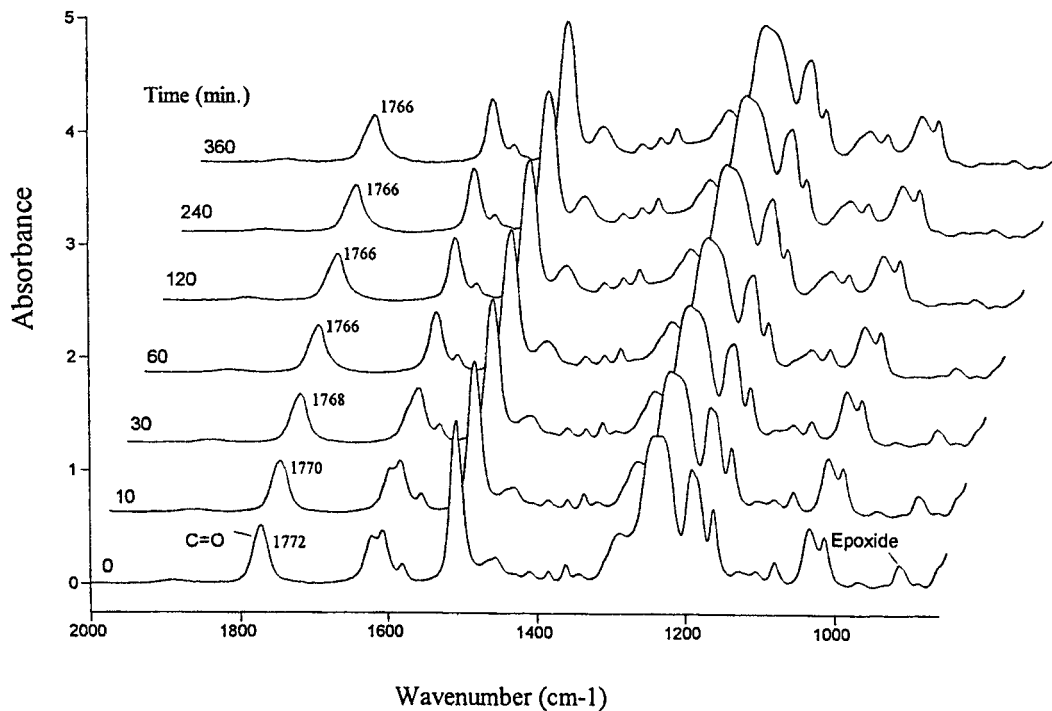


Figure 5 FTIR spectra of a PC/DGEBA/DDM (30/100/27) film *in situ* at 90°C. PC and DGEBA were first dissolved in CH_2Cl_2 .

following paragraph. The change of morphology gave some variations of the local environment of the absorbing groups and subsequently affected the optical extinction coefficient of these groups. As a result, the data are more scattered and the validity of calculated kinetic constants cannot be assured.

In Figure 5, it was found that the absorption peak of carbonyl groups in the PC shifted from 1772 cm^{-1} at the beginning to 1766 cm^{-1} after 1 h at 90°C. It was established in our previous article¹⁵ that the 1766 cm^{-1} peak is the carbonyl absorption in the PC crystalline region. PC is well known as an amorphous polymer when it is processed under ordinary conditions, because thermal crystallization of PC occurs at a very slow rate due to the rigid molecular backbone. Still, PC is capable of crystallization when annealed at temperatures between the T_g and T_m , although at a strikingly slow rate.⁵⁶ It has been reported⁵⁷ that the annealing of very thin films ($100\text{ }\mu\text{m}$) required 8 days at 190°C for the first crystallites to appear. The induction time for nucleation is strongly dependent upon the specimen thickness. For 1-mm-thick PC specimens, 76 days was required to develop 12% crystallinity at 190°C.⁵⁸ The time for crystallization can be greatly reduced through the addition of either a solvent or a plasti-

cizer.^{56,58} When immersed in acetone, PC crystallizes at room temperature up to a 24% crystallinity in only 24 h. In the present case, residual methylene chloride and the epoxy oligomer both facilitate the crystallization of PC. The plasticization of PC by the DGEBA oligomer can be understood by using Fox's equation, where the calculated T_g of the mixture PC/DGEBA (30/100) is only 14°C. Thus, the plasticized PC chain segments have much mobility at 90°C. Yet, the rapid increase of the molecular weight of the epoxy resin and therefore viscosity during cure could retard the further crystallization of PC.

Figure 7 shows a typical DSC thermogram of a modified epoxy with 15 parts PC, which was cured for 1 h at 90°C followed by 4 h at 160°C. In addition to the T_g at 156°C, a small melting peak at 212°C was observed, a little lower than that of pure PC, 235°C.⁵⁸ The presence of epoxy resin and the rapid increase of viscosity during cure resulted in the imperfection and smallness of PC crystallites, depressing the melting point of PC and giving a low crystallinity. The other reason for the observed small melting peak in the DSC thermograms was because only a small amount of PC was in the system. In principle, crystallization depends on three characteristic temperatures: (1) the cure temperature (same as the crystallization

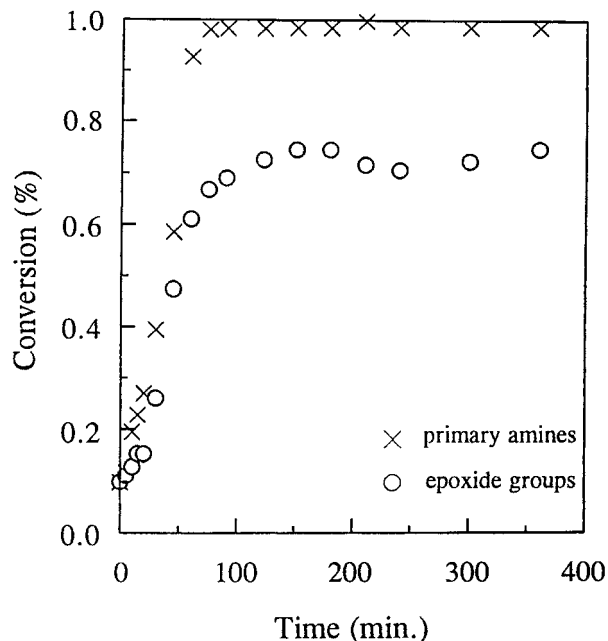


Figure 6 Conversion of primary amines and epoxide groups in a PC/DGEBA/DDM (30/100/27) film *in situ* at 90°C. PC and DGEBA were first dissolved in CH_2Cl_2 .

temperature in this case), (2) melting temperature (T_m) of PC, and (3) the glass transition temperature (T_g) of the epoxy matrix, which increases with the extent of cure.

By using a least-square curve-fitting program

with the band parameters described in the previous article,¹⁵ that is, a bandwidth ($\omega_{1/2}$) of $26 \pm 1 \text{ cm}^{-1}$ and a 0.6 Gaussian shape for the peak 1776 cm^{-1} and a $13.0 \pm 0.5 \text{ cm}^{-1}$ bandwidth with a Lorentzian shape for the peak 1766 cm^{-1} , the carbonyl peak was resolved into two peaks, corresponding to the carbonyl vibration in the amorphous and crystalline regions. The results are shown in Figure 8. It can be seen that the crystallinity increased rapidly during the first 0.5 h and then increased more slowly. The appearance and growth of spherulites in the epoxy matrix would be expected to affect the mechanical properties of the cured epoxies.²⁸ In addition, it was also found from the DSC thermograms (not shown here) that there was no change of the T_g of the cured epoxies with PC up to 30 parts as compared with the neat epoxy. Basically, the reason to use PC, in addition to its ductility, is its relatively high T_g at 152°C , close to the T_g of the DDM-cured epoxy (156°C). With the close T_g values of these two components and with only a small amount of the PC modifier, the predicted T_g values by using Fox's equation show excellent agreement with the experimental results. This agreement 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.

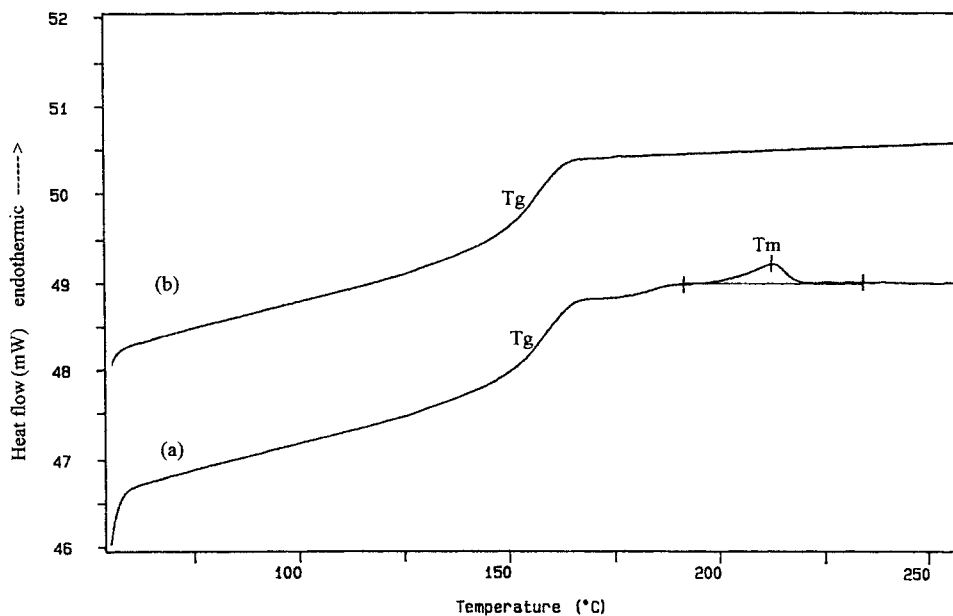


Figure 7 DSC thermograms of (a) a modified epoxy with 15 phr PC by an SB method and (b) a neat epoxy.

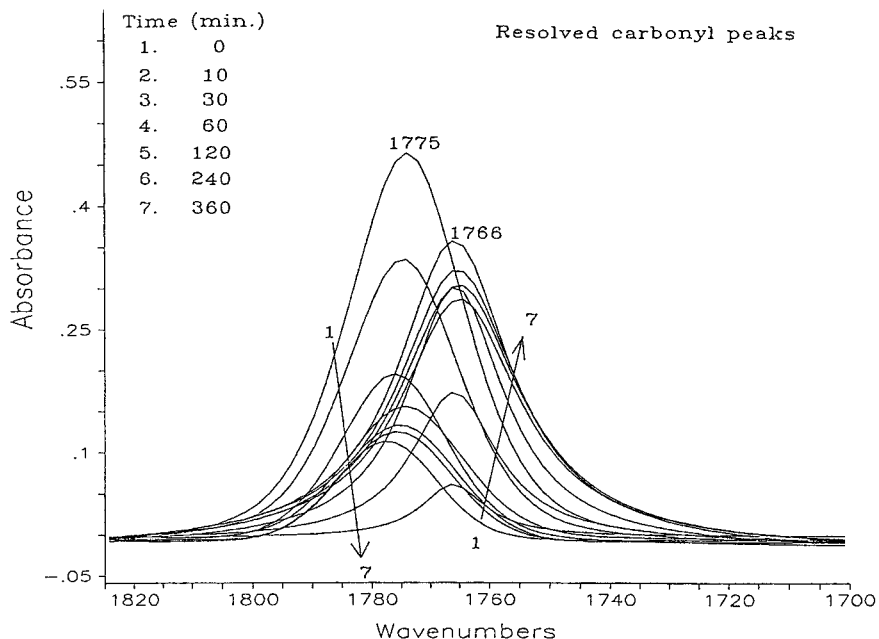


Figure 8 Resolved carbonyl peaks of a PC/DGEBA/DDM film *in situ* at 90°C. PC and DGEBA were first dissolved in CH₂Cl₂.

MB Samples

It has been shown that during blending at high temperatures, for example, 200°C, PC can react with DGEBA through the transesterification and epoxide-phenolic hydroxyl addition (Scheme 1). The effect of this prereaction on the cure reactions and structures in the final epoxy resin was therefore of interest. PC pellets (30 phr) were directly dissolved into the DGEBA resin prior to cure at 200°C for 3 h. FTIR analysis showed that epoxide conversion from this prereaction was only 5 (± 2)%. Compared to the previous study,¹⁵ in which a solution-cast film was kept at 200°C and used for the kinetic study, this extent of reaction was low. The epoxide conversion reached 16% when a solution-cast film was heated at 200°C for 3 h. The difference is obviously due to the different sample preparation methods. A much lower reaction extent in the mixture by directly blending pellets into another polymer, compared with the method using a solution-cast film and then subjected to the same heating period, was explained by Yang et al.⁵⁹ When the two components are dissolved in a cosolvent and subsequently a film is cast, the two components exist in a single phase or a well-mixed two-phase system, which facilitates the chemical reaction. In an MB process, one tries to dissolve polymer pellets with high melt viscosity into another polymer component. This

physical mixing is unlikely to lead to materials that are as intimately mixed as their solution-cast counterparts. Thus, the extent of reaction in a practical MB process should not be as high as that in the solution-cast film with the same heating period. Nevertheless, from the FTIR data and the decrease of molecular weight of the PC chains, the transesterification indeed occurred to some extent in the MB of PC and DGEBA, resulting in PC-DGEBA copolymers. Details of these reaction mechanisms were explained in the previous article.¹⁵

After a homogeneous solution of PC/DGEBA was obtained by MB, the solution was cooled to 90°C and then the curing agent, DDM, was added. A film was cast onto a NaCl plate. Figure 9 shows the FTIR spectra of this PC/DGEBA/DDM (30/100/27) film at 90°C. The peak position of the carbonyl absorption remained the same at 1772 cm⁻¹ for 4 h without any sign of the 1766 cm⁻¹ peak. This indicates that there was no crystallization of PC during cure in the MB samples. A typical thermogram of a cured epoxy is shown in Figure 10, which does not show any melting peaks such as were observed for the SB samples. Therefore, PC did not crystallize in the MB samples, which was believed due to the chemical bonding of PC onto DGEBA through the transesterification in the premixing at 200°C. In addition, the IR

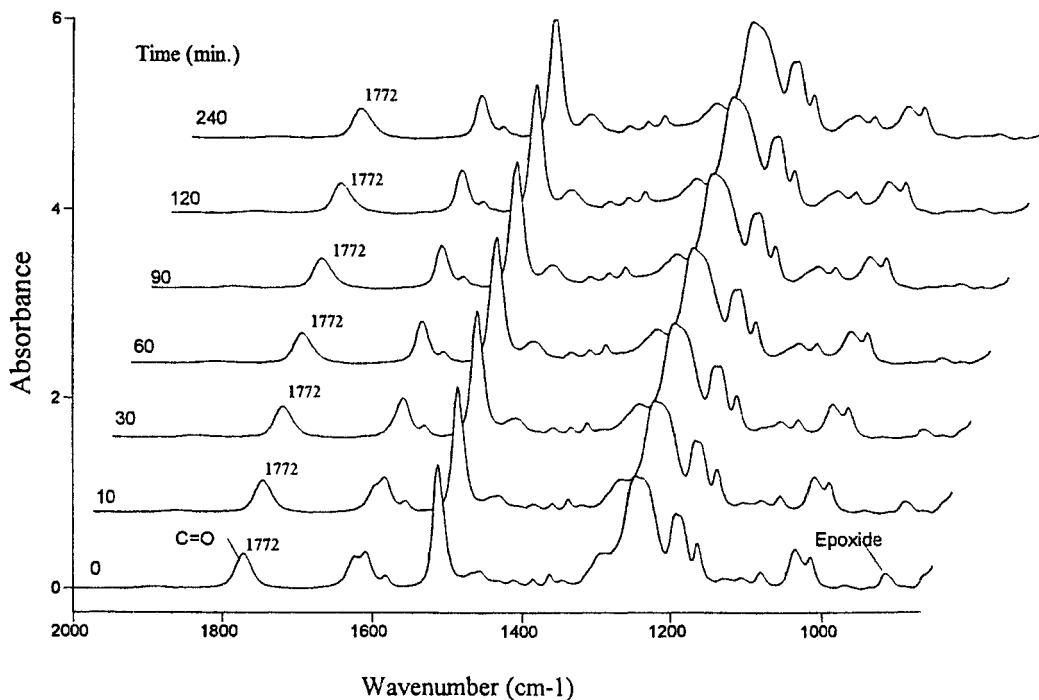


Figure 9 FTIR spectra of a PC/DGEBA/DDM (30/100/27) film *in situ* at 90°C. PC was first dissolved into DGEBA at 200°C.

spectra also indicates that there were no further reactions of carbonate groups in the PC/epoxy system during cure, that is, transesterification (Scheme 1) and transamidation (Scheme 3). In general, the carbonates can react with both hy-

droxyl groups (transesterification) and amino groups (transamidation), but the reactivity is much higher with the hydroxyl groups.^{17,60} If either reaction occurs, the carbonyl peak would shift to lower wavenumbers such as 1761 cm^{-1}

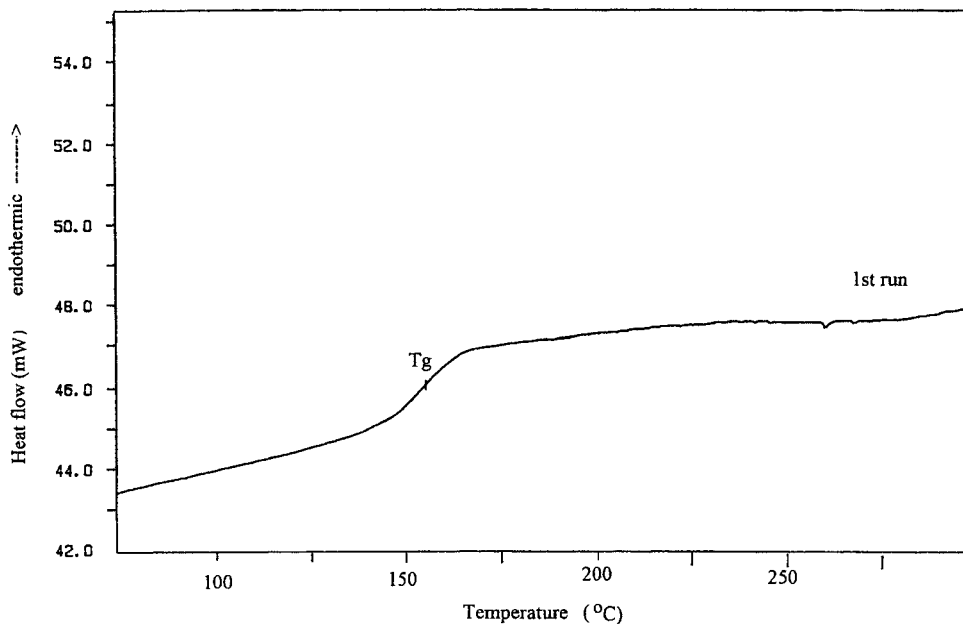
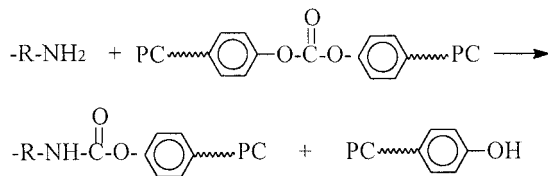


Figure 10 DSC thermogram of a modified epoxy with 15 phr PC by an MB method.



Scheme 3 Transamidation.

from aromatic-aliphatic carbonates, 1746 cm^{-1} from aliphatic-aliphatic carbonates, or 1725 cm^{-1} from carbamate groups. Previously, in the Introduction, we stated that if aliphatic amines were used to cure epoxies in the presence of PC, transamidation occurs between aliphatic amines and carbonates. However, the FTIR spectra shown here indicate that if aromatic amines were used instead of aliphatic amines, the transamidation did not occur to an appreciable extent. This is because most of the amino groups were reacted with epoxide groups before they could react with carbonates. The higher reactivity of aromatic amines with epoxide groups in comparison with carbonates has been confirmed by the experiments using model compounds.^{30,60} In conclusion, in an aromatic amine-cured system (without catalyst), no significant shift of the carbonyl band was observed, indicating that the PC did not take part in the curing.

Figure 11 shows the conversion of primary

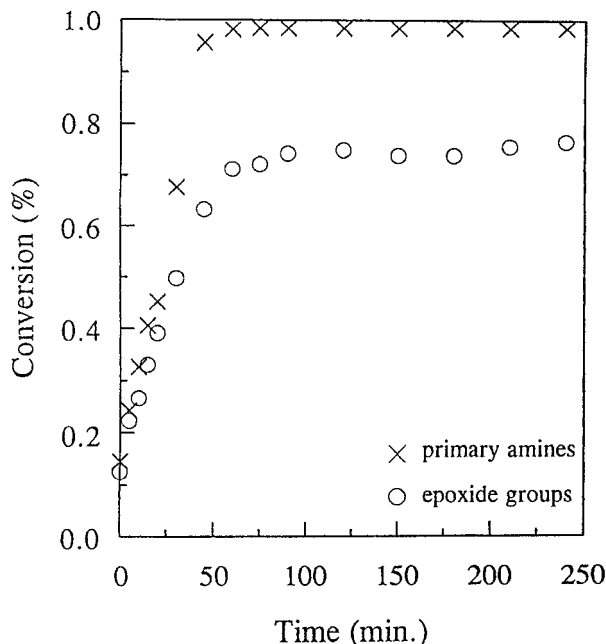


Figure 11 Conversion of primary amines and epoxide groups in a PC/DGEBA/DDM (30/100/27) film *in situ* at 90°C . PC was first dissolved into DGEBA at 200°C .

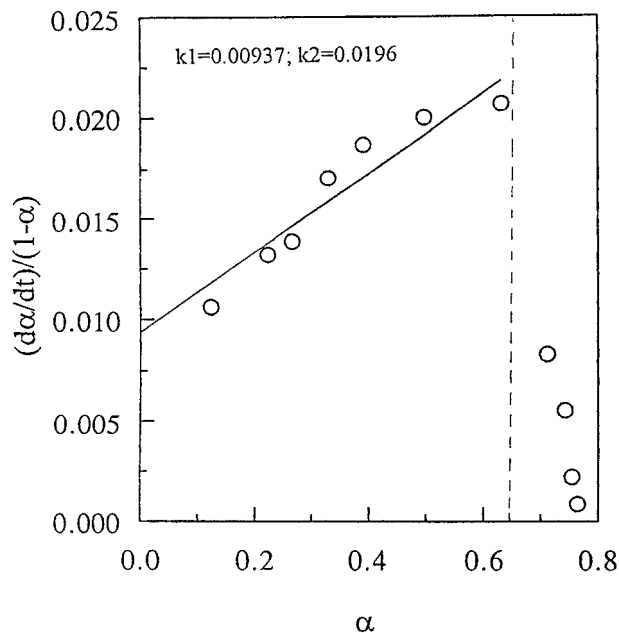
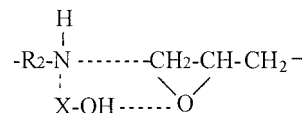


Figure 12 Kinetic plot for the PC/DGEBA/DDM (30/100/27) film at 90°C . PC was first dissolved into DGEBA at 200°C .

amines and epoxide groups of this blend during cure. The primary amines completely reacted with epoxide groups after 1 h. The amine-epoxide reaction rate was faster than that found for the neat epoxy. Figure 12 shows the kinetic plot of $(d\alpha/dt)/(1-\alpha)$ versus α ; the rate constants k_1 and k_2 are 9.37×10^{-3} and $1.96 \times 10^{-2}\text{ min}^{-1}$, respectively. These values are larger than that in the neat epoxy, which indicates that the presence of PC promoted the amine-epoxide reactions. This is in contrast to what was found by Martuscelli et al.^{22,23} who used an anhydride curing agent instead of the amines used in this study. They found that the presence of PC lowered the initial curing rate and the final conversion, although it did not alter the overall reaction mechanism. It has been proven⁶¹⁻⁶³ that hydroxyl groups can promote the amine-epoxide reaction through hydrogen bonding and facilitating the opening of the epoxide groups. Scheme 4 shows the formation of an intermediate complex of the reactants with



Scheme 4 The formation of a ternary intermediate complex of the reactants with hydroxyl-containing compound.

compounds containing hydroxyl groups.⁶³ Therefore, we assume in the present case that the hydroxyl end groups of the PC chains interacted with the epoxide groups and promoted the amine-epoxide reactions. In principle, the use of an MB process of DGEBA and PC results in a PC-epoxy copolymer network structure after cure without inducing crystallization of PC. As a result, the fracture toughness of PC-modified epoxies is expected to be increased through the incorporation of PC ductile chains into the epoxy network. The mechanical properties and fracture behavior of this PC-modified epoxy system will be reported in the next article.⁶⁴

CONCLUSIONS

An epoxy resin based upon the diglycidyl ether of bisphenol-A (DGEBA) was modified with polycarbonate (PC). After the blending of DGEBA resin and PC, the curing agent, diaminodiphenyl methane (DDM), was added into the mixture. It was found that the presence of a small amount of PC promoted the amine-epoxide reactions. This is probably due to the catalytic effect of the phenolic hydroxyl end groups of the PC chains. However, the PC did not alter the reaction mechanism of the epoxy cure. If a solution-blending (SB) process was used, PC was able to undergo crystallization during the early stage of curing. A small melting peak at 212°C was observed in DSC thermograms for the modified epoxies. It is suggested that the residual solvent and the DGEBA resin plasticized PC and induced PC crystallization during the cure before the matrix became too viscous. However, there was no melting peak observed in the DSC scans for the modified epoxies when a melt-blending (MB) process was used. This is because of the bonding of PC chains onto DGEBA from the prereaction at 200°C (MB) before cure, thus inhibiting the crystallization of PC during cure. The glass transition temperatures (T_g 's) of PC-modified epoxies were not decreased because the T_g of PC (152°C) is very close to the T_g of DDM-cured epoxy (156°C) and also because the final extent of epoxy cure was not decreased by the addition of PC.

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