The Epoxy–Polycarbonate Blends Cured with Aliphatic Amine—I. Mechanism and Kinetics

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ABSTRACT: Reaction mechanism of the PC–epoxy blends cured by aliphatic amine has been investigated by varying PC contents in the blends. The transamidation reaction tends to convert nearly all the carbonates into N-aliphatic aromatic carbamates even at ambient temperature before normal curing. The remaining amine proceeds the normal curing with epoxy at a higher temperature (80°C). For the PC–epoxy/aliphatic amine blend containing 6 wt % PC, the yielded N-aliphatic aromatic carbamate further reacts with amine to produce the urea structure. The urea undergoes substitution reaction with the hydroxyl formed from the normal curing to give the N-aliphatic aliphatic carbamate. For the blend containing 12 wt % PC, the N-aliphatic aromatic carbamate converts into the N-aliphatic aliphatic carbamate via two different routes. For the blend containing lower molecular weight of the aliphatic amine, the N-aliphatic aromatic carbamate reacts with hydroxyl to form the N-aliphatic aliphatic carbamate directly. For the blend containing higher molecular weight of aliphatic amine, the N-aliphatic aromatic carbamate decomposes into the aliphatic isocyanate accelerated by the presence of the residual oxirane. The isocyanate formed then reacts with hydroxyl to yield the N-aliphatic aliphatic carbamate. The activation energy (E_a) and preexponential factor (A) of the PC–epoxy/POPDA blends decrease with the increase of the PC content. Kinetic study by thermal analysis by the method of autocatalyzed model is able to correctly predict oxirane conversion vs. time relationship for the neat epoxy/aliphatic amine and the PC–epoxy/aromatic amine systems because the dominant reaction is the normal curing reaction between amine and oxirane. The model fails to predict the PC–epoxy/aliphatic amine system because the system is complicated by several other reactions besides the normal curing reaction. © 1997 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys **35:** 2169–2181, 1997

Keywords: epoxy; blend; polycarbonate; transesterification; transamidation; carbamate; urea

INTRODUCTION

One of the earlier studies of the PC–epoxy blend was reported by Yu and Bell in 1988.[1] During the past years, various hardners have been used to cure the PC–epoxy blend. However, PC–epoxy blends cured by aliphatic amine have been investigated recently.[2–5] One major characteristic revealed in these studies is the infrared absorption variations in the carbonyl region during the process of curing. Mera and Umetani[2] used bis(4-amino-3-methylcyclohexyl)methane to cure PC–epoxy blends, and reported the carbonyl absorption of infrared spectra shifting from 1775 cm^{-1} to 1719 cm^{-1}. Rong and Zeng[3] cured the PC–epoxy blends by tetraethylenepentamine (TEPA) and

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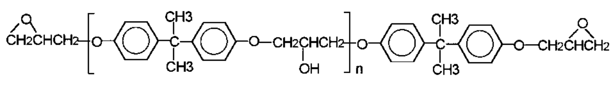
reported a shift in the position of the carbonyl group from 1776 cm^{-1} to 1725 cm^{-1}. This phenomenon was interpreted as the formation of hydrogen bonding between carbonyl groups of PC and hydroxyl groups of the cured epoxy.[3] Chen et al.[4] obtained homogeneous PC–epoxy blends cured by diethylenetriamine (DETA) and proposed the presence of hydrogen bonding, resulting in a molecular level mixing of the blend system. However, our previous studies on PC–epoxy/aliphatic amine blends revealed that the spectroscopic variations are due to the formation of carbamates rather than hydrogen bonding.[5]

In this article we will report the reaction mechanisms and kinetics of the PC–epoxy/aliphatic amine blends by varying PC contents and the molecular weights of polyoxypropylene diamines (POPDA).

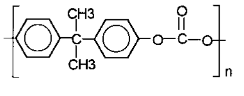
EXPERIMENTAL

Materials

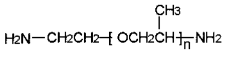
The bisphenol-A base natural grade polycarbonate with a melt flow rate of 15 (M_n = 28,000) used in this study is the Calibre 301-15 from Dow Chemical Company. The epoxy prepolymer, DER 331, used in this study was also purchased from Dow Chemical Company, which is a low molecular weight liquid diglycidyl ether of Bisphenol-A (DGEBA) with a epoxide equivalent weight of 186–192. The polyoxypropylene diamines with different molecular weights used as hardeners were obtained from Huntsman Chemical Co including Jeffamine D230 (MW = 230), D400 (MW = 400), and D2000 (MW = 2000). The chemical structures of epoxy, polycarbonate, and polyoxypropylene diamines (POPDA) are illustrated as follows:



EPOXY DER 331 n=0.1



POLYCARBONATE n=110



$H_2N-CH_2CH_2-(OCH_2CH(CH_3))_n-NH_2$

JEFFAMINE D230 n=2.6
D400 n=5.6
D2000 n=33.1

Procedures and Instrumentations

PC was dehydrated at 120°C for 24 h under vacuum before dissolving into epoxy monomer. The mixture of 30 wt % PC in epoxy was prepared by stirring the PC in the epoxy resin at 220°C under dry nitrogen gas for 1 h to give a clear, homogeneous, and viscous solution. When the mixture was cooled to room temperature, equal equivalent weight of aliphatic amine was added and mixed using a stirrer. Compositions employed in this study are listed in Table I. Typical curing was carried out by three steps: at 80°C for 2 h (primary curing), at 150°C for 2 h (secondary curing), and 180°C for 2 h (postcuring), respectively.

Infrared Spectroscopy

One drop of the mixture was placed between two sodium chloride plates and were then mounted on a sample holder in the IR instrument. The heating program was set at 80°C for 2 h, at 150°C for 2 h, and at 180°C for 2 h. Infrared spectra were obtained on a Perkin–Elmer 842 Infrared Spectrometer with a resolution of 2.4 cm^{-1}.

Differential Scanning Calorimeter

The kinetic study of the blend was carried out by a Du Pont 2100 Differential Scanning Calorimeter (DSC), with a heating rate of 10°C/min in the dynamic scan. The dynamic DSC runs were also used to determine the appropriate isothermal analysis temperature to calculate the kinetic parameters of the curing system.

RESULTS AND DISCUSSION

Infrared Spectra of PC–Epoxy/POPDA Blend

In the aliphatic amine cured PC–epoxy blend, the aliphatic amine is able to react with the carbonate group of PC to yield the N-aliphatic aromatic carbamate structure in addition to the usual ring opening with oxirane. As a result of these chemical reactions, essentially no long chain PC is left after curing when an aliphatic amine is employed.[5] The presence of PC complicates the reactions involved in the curing epoxy system. To investigate the influences of the PC presence in the PC–epoxy/POPDA blend, various ratios of the PC–epoxy blends were employed by curing with equal equivalent of polyoxypropylene diamine

Table I. The Compositions and Codes of the PC–Epoxy/POPDA Blends

Code	Epoxy (g)	Amine (g) D230/D400/D2000	PC (g)	Epo. + Am. (wt %)	PC (wt %)
A00	100	30/—/—	0.00	100	0
A03	100	30/—/—	4.02	97	3
A06	100	30/—/—	8.30	94	6
A09	100	30/—/—	12.86	91	9
A12	100	30/—/—	17.73	88	12
B00	100	—/50/—	0.00	100	0
B03	100	—/50/—	4.64	97	3
B06	100	—/50/—	9.57	94	6
B09	100	—/50/—	14.84	91	9
B12	100	—/50/—	20.45	88	12
C00	100	—/48/12.5	0.00	100	0
C03	100	—/48/12.5	4.96	97	3
C06	100	—/48/12.5	10.24	94	6
C09	100	—/48/12.5	15.87	91	9
C12	100	—/48/12.5	21.89	88	12
D00	100	—/44/25	0.00	100	0
D03	100	—/44/25	5.23	97	3
D06	100	—/44/25	10.79	94	6
D09	100	—/44/25	16.71	91	9
D12	100	—/44/25	23.05	88	12

(POPDA). Figure 1(I) presents the infrared spectra of epoxy/D400 mixture (Table I B00) in the regions of oxirane. The oxirane peak (915 cm^{-1}) disappears almost completely after the secondary curing (at 150°C for 2 h), as shown in curve C of Figure 1(I). The spectrum remains unchanged after post curing at 180°C for additional 2 h by comparing curves C and D of Figure 1(I). In other words, the crosslink density is not expected to increase noticeably after further heating though postcuring. There is no absorption present in the region of carbonyl in this blending system because PC is not present in this blend. The classical amine addition curing reaction between epoxy and POPDA is shown as eq. (1).[16]

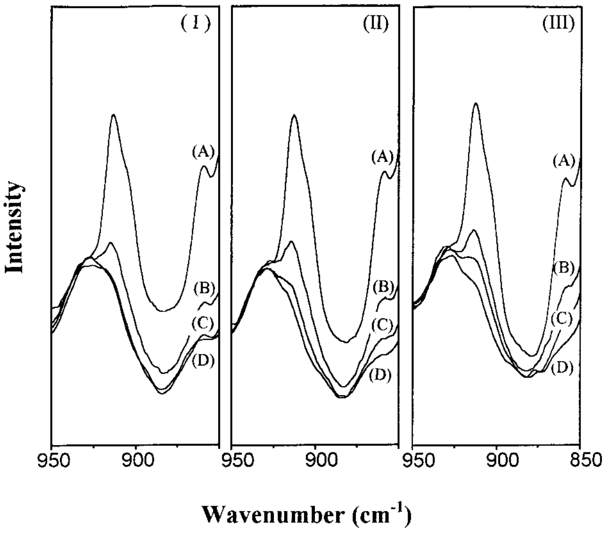
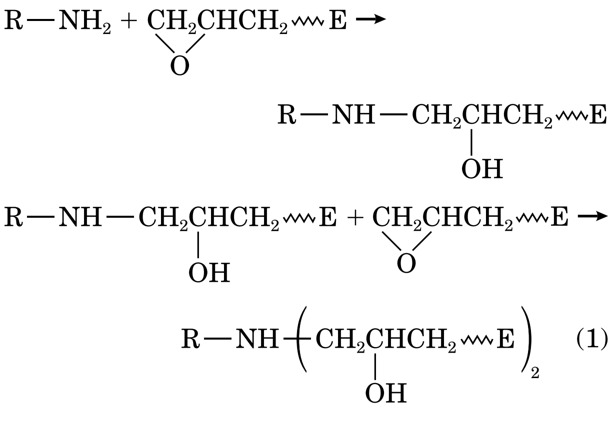


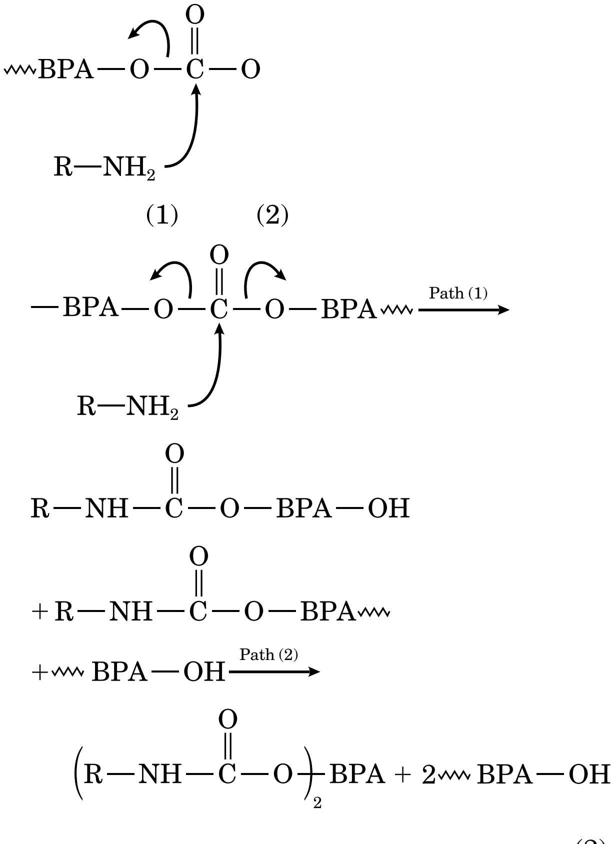
Figure 1. Infrared spectra of (I) DER 331/D400 = 100/50 (B00 of Table I), (II) DER 331/D400/PC = 100/50/9.57 (B06 of Table I), (III) DER 331/D400/PC = 100/50/20.45 (B12 of Table I) recorded in oxirane stretching region. (A) Initial, (B) 80°C for 2 h, (C) 150°C for 2 h, and (D) 180°C for 2 h.



$$R{-}NH_2 + \underset{\diagdown O \diagup}{CH_2CH}CH_2{\sim\sim}E \rightarrow R{-}NH{-}CH_2\underset{OH}{\underset{|}{C}}HCH_2{\sim\sim}E$$

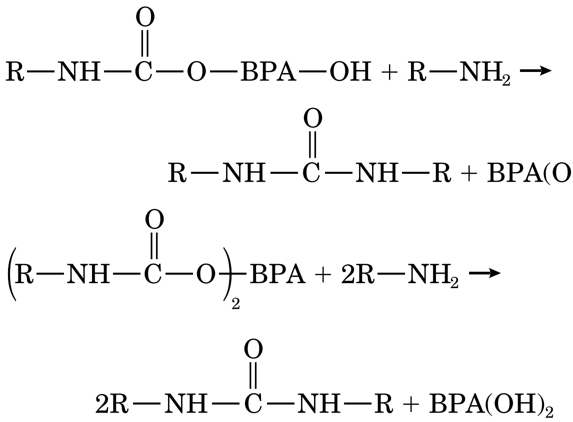
$$R{-}NH{-}CH_2\underset{OH}{\underset{|}{C}}HCH_2{\sim\sim}E + \underset{\diagdown O \diagup}{CH_2CH}CH_2{\sim\sim}E \rightarrow R{-}NH\left(CH_2\underset{OH}{\underset{|}{C}}HCH_2{\sim\sim}E\right)_2 \tag{1}$$

Figures 1(II) and 2 present the infrared spectra of the PC–epoxy/D400 blends containing PC 6 wt % (Table I B06) in the regions of oxirane and carbonyl groups, respectively. The spectrum variation in the region of oxirane of this B06 blend [Fig. 1(II)] is similar to that of the neat epoxy [B00, Fig. 1(I)]. The carbonate absorption of the original PC at 1780 cm^{-1} in the B06 blend (curve A, Fig. 2) shifts to 1740 cm^{-1} rapidly even at 25°C. This absorption band (1740 cm^{-1}) is contributed by the N-aliphatic aromatic carbamates formed immediately after mixing from the reaction between the carbonate group of PC and the aliphatic amine as shown in eq. (2).[7]



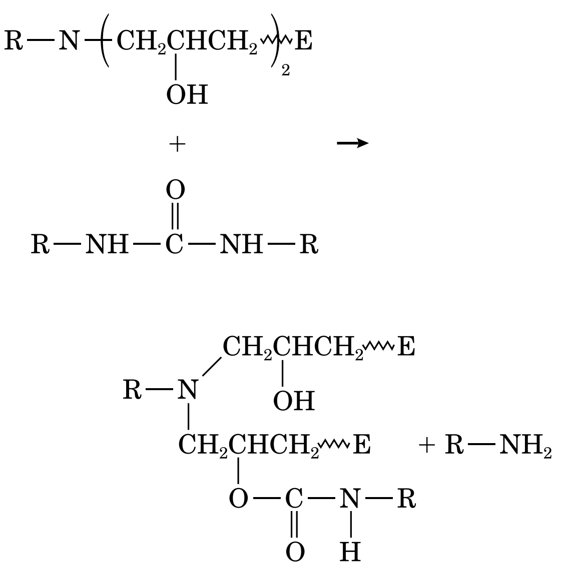
$$\sim\mathrm{BPA{-}O{-}\overset{O}{\overset{\|}{C}}{-}O} \qquad \mathrm{R{-}NH_2}$$
$$(1)\qquad(2)$$
$$\mathrm{{-}BPA{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}BPA}\sim \qquad \mathrm{R{-}NH_2} \xrightarrow{\text{Path (1)}}$$
$$\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}BPA{-}OH}$$
$$+\,\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}BPA}\sim$$
$$+\sim\mathrm{BPA{-}OH} \xrightarrow{\text{Path (2)}}$$
$$\left(\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O}\right)_2\mathrm{BPA} + 2\sim\mathrm{BPA{-}OH} \tag{2}$$

During the stage of primary curing at 80°C for 2 h, the remaining aliphatic amine undergoes the usual ring opening reaction with oxirane [eq. (1)] and the substitution reaction with N-aliphatic aromatic carbamate to form the urea structure. Curve B of Figure 2 shows that the IR absorption of the N-aliphatic aromatic carbamate at 1740 cm^{-1} (curve A) is converted completely to the urea at 1650 cm^{-1}, as shown in eq. (3).[8]



$$\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}BPA{-}OH} + \mathrm{R{-}NH_2} \rightarrow \mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R} + \mathrm{BPA(OH)_2}$$
$$\left(\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O}\right)_2\mathrm{BPA} + 2\mathrm{R{-}NH_2} \rightarrow 2\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R} + \mathrm{BPA(OH)_2} \tag{3}$$

Curve C of Figure 2 gives the IR spectrum of the same blend in the carbonyl region after secondary curing (at 150°C for 2 h). The band at 1700–1725 cm^{-1} appears, while the intensity of the urea band at 1650 cm^{-1} decreases substantially. The absorption band at 1700–1725 cm^{-1} can be attributed to the formation of the N-aliphatic aliphatic carbamates through the substitution reaction between the urea and the hydroxyl group of the epoxy, as shown in eq. (4).[9]



$$\mathrm{R{-}N}\left(\mathrm{CH_2\underset{\underset{OH}{|}}{C}HCH_2}\sim\mathrm{E}\right)_2 + \mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R} \rightarrow \mathrm{R{-}N}\begin{cases}\mathrm{CH_2\underset{\underset{OH}{|}}{C}HCH_2}\sim\mathrm{E}\\ \mathrm{CH_2\underset{\underset{O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{H}{|}}{N}{-}R}{|}}{C}HCH_2}\sim\mathrm{E}\end{cases} + \mathrm{R{-}NH_2} \tag{4}$$

Comparing the N-aliphatic aliphatic carbamate with the N-aliphatic aromatic carbamate, the substitute groups of the former have lower inductive effects than those of the latter and, therefore, cause the absorption of the N-aliphatic aliphatic carbamate lower (at 1700–1725 cm^{-1}) than that of the N-aliphatic aromatic carbamate (at 1740 cm^{-1}). The intensity of the N-aliphatic aliphatic absorption at 1700–1725 cm^{-1} further increases after postcuring

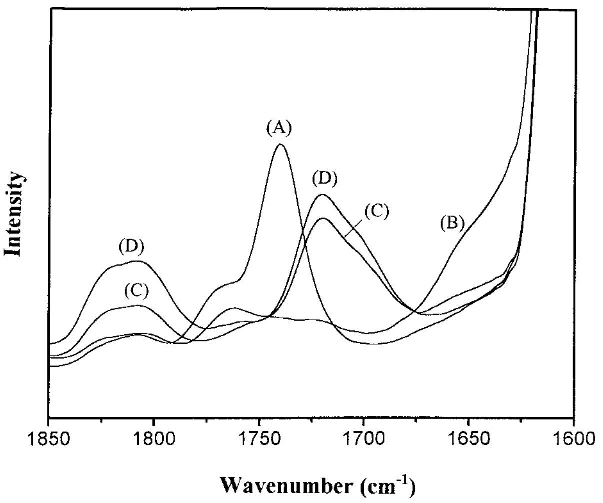
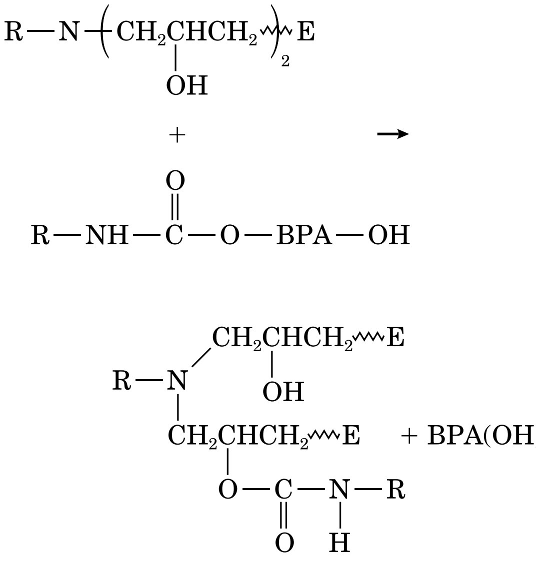


Figure 2. Infrared spectra of the DER 331/D400/PC = 100/50/9.57 blend (B06 of Table I) recorded in the carbonyl stretching region. (A) 25°C for 3 min, (B) 80°C for 2 h, (C) 150°C for 2 h, and (D) 180°C for 2 h.

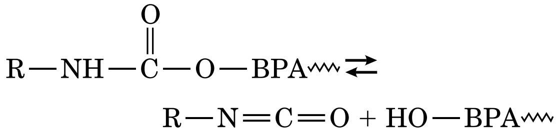
at 180°C for 2 h (curve D of Fig. 2) as would be expected.

It is interesting to note that the intensity of oxirane absorbed at 915 cm^{-1} further decreases after postcuring compare curves C and D of Figure 1(II). The substitution reaction between urea and hydroxyl groups of the epoxy network releases amine [eq. (4)] that can further react with the residual epoxide ring. Consequently, the cross-linking density of blend is expected to be increased after postcuring.

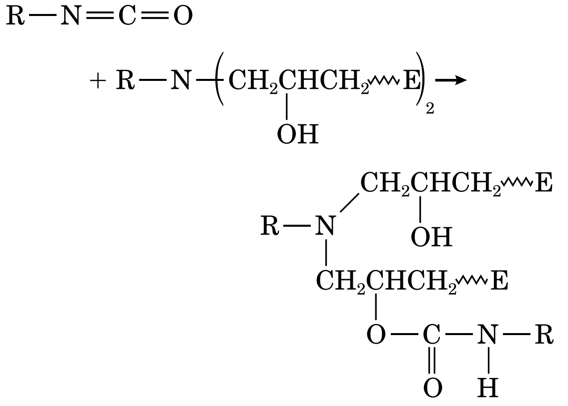
Figures 1(III) and 3 present the infrared spectra of PC–epoxy/D400 blend containing 12 wt % PC (B12, Table I) in the regions of oxirane and carbonyl group, respectively. Again, the IR absorption of the carbonate group of PC at 1780 cm^{-1} shifts to 1740 cm^{-1} instantly (curve A, Fig. 3) due to fast transamidation reaction. However, curve B of Figure 3 shows that absorption band of the N-aliphatic aromatic carbamate at 1740 cm^{-1} is unchanged after primary curing (80°C for 2 h) but its intensity is substantially reduced and the appearance of the urea absorption at 1650 cm^{-1}. The major spectroscopic difference between the B12 system and that of the B06 system is the greater PC content in the B12 system than that of the B06 system (12 wt % vs. 6 wt %). The relative amount of aliphatic amine available for substituting the N-aliphatic aromatic carbamate into the urea structure is considerably less in the B12 system than that of the B06 system. Additionally, there is a shoulder peak corresponding to the N-aliphatic aliphatic carbamate appeared in the lower frequency at 1720 cm^{-1} after 80°C for 2 h. However, there is only small absorption corresponding to the isocyanate group that can be found in the IR spectrum (curve B of Fig. 4). The N-aliphatic aliphatic carbamate formed (at 1720 cm^{-1}) can proceed further substitution reaction by reacting with the hydroxyl group of epoxy [eq. (5)].[9] There is another process to obtain the N-aliphatic aliphatic carbamate from N-aliphatic aromatic carbamate. The N-aliphatic aromatic carbamate decomposes into the aliphatic isocyanate and phenol [eq. (6)].[10] The aliphatic isocyanate can react with the hydroxyl group of epoxy to yield the N-aliphatic aliphatic carbamates [eq. (7)].[11] The decomposition reaction of the N-aliphatic aromatic carbamate at 80°C is accelerated by the presence of oxirane as shown in eq. (8).[12]



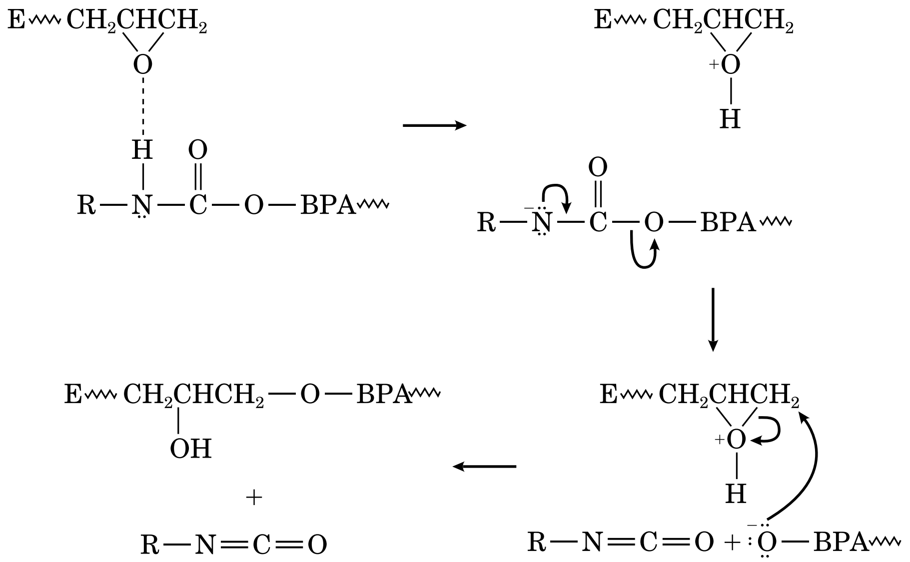
$$\mathrm{R{-}N\left(CH_2\underset{OH}{\underset{|}{C}}HCH_2{\sim}E\right)_2 + R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}BPA{-}OH \longrightarrow R{-}N\begin{cases}CH_2\underset{OH}{\underset{|}{C}}HCH_2{\sim}E\\ CH_2\underset{O-\underset{O}{\underset{\|}{C}}-\underset{H}{\underset{|}{N}}-R}{\underset{|}{C}}HCH_2{\sim}E\end{cases} + BPA(OH)_2} \quad (5)$$



$$\mathrm{R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}BPA{\sim} \rightleftarrows R{-}N{=}C{=}O + HO{-}BPA{\sim}} \quad (6)$$



$$\mathrm{R{-}N{=}C{=}O + R{-}N\left(CH_2\underset{OH}{\underset{|}{C}}HCH_2{\sim}E\right)_2 \longrightarrow R{-}N\begin{cases}CH_2\underset{OH}{\underset{|}{C}}HCH_2{\sim}E\\ CH_2\underset{O-\underset{O}{\underset{\|}{C}}-\underset{H}{\underset{|}{N}}-R}{\underset{|}{C}}HCH_2{\sim}E\end{cases}} \quad (7)$$



(8)

Curves A, B, C, and D of Figure 4 present the infrared spectra recorded in the isocyanate stretching region of the mixtures A12, B12, C12, and D12 (Table I) after 2 h at 80°C. The isocyanate absorption appears on the PC–epoxy blend cured by the highest molecular weight of POPDA (D12) but such absorption is considerably reduced or absent on those blends cured by those lower molecular weight of POPDAs (A12, B12, and C12) under the same curing conditions. Increasing quantity of the PC in the blend reduces the ratio of (amine–carbonate)/oxirane. At a fixed PC content, the PC–epoxy blend cured by a higher molecular weight of POPDA, the (amine–carbonate)/oxirane ratio tends to be less. In other words, more residual oxirane is available to accelerate the decomposition of the N-aliphatic aromatic carbamate [eq. (8)] if the higher molecular weight POPDA is employed. As mentioned above, the N-aliphatic aliphatic carbamate can be produced from two different routes via eqs. (5) and (7). However, the reaction via eq. (5) is more preferable than that of eq. (7) because the latter mechanism does not occur in some blending systems.

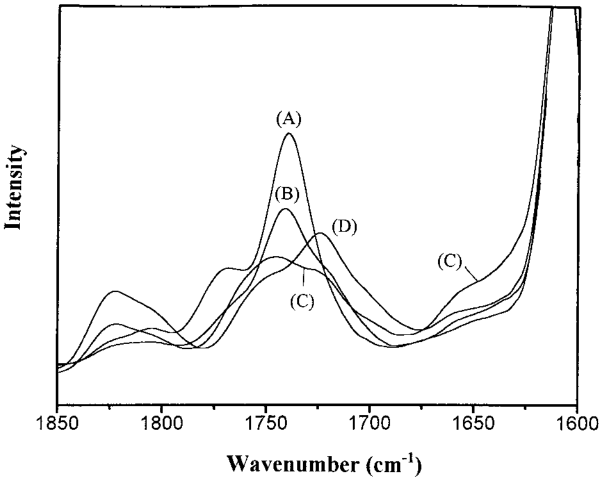


Figure 3. Infrared spectra of the DER 331/D400/PC = 100/50/20.45 blend (B12 of Table I) recorded in the carbonyl stretching region. (A) 25°C for 3 min, (B) 80°C for 2 h, (C) 150°C for 2 h, and (D) 180°C for 2 h.

Curves C to D of Figure 3 show that most of the N-aliphatic aromatic carbamate at absorption 1740 cm^{-1} converts to the N-aliphatic aliphatic carbamate (1725 cm^{-1}). Although the infrared spectra of the final products of B06 system (6 wt % PC, curve D of Fig. 2) is similar with that of the B12 system (12 wt % PC, curve D of Fig. 3); however, the reaction mechanisms involved are different as described above.

Curing Kinetics

Dynamic DSC

Figure 5(I) and (II) shows the DSC heating thermograms ranging from 0–300°C of neat epoxy/POPDA blends and the corresponding blends con-

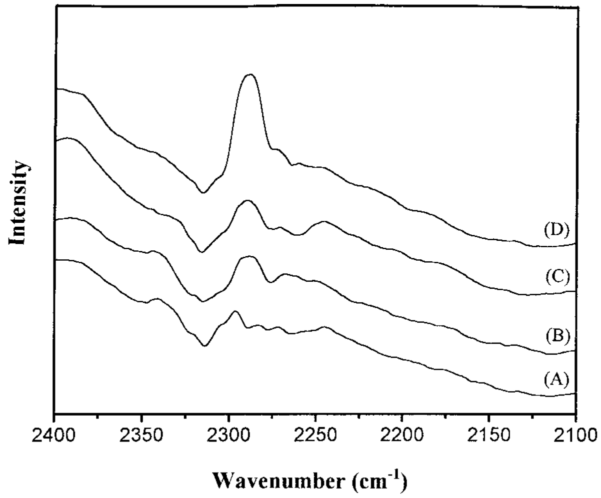


Figure 4. Infrared spectra of PC–epoxy/POPDA blends with 12 wt % PC in the isocyanate stretching region after 80°C for 2 h. (A) A12, (B) B12, (C) C12, (D) D12.

taining 12 wt % PC. Curves A, B, and C of these figures represent the increase of POPDA molecular weight, as shown in Table I. The observed exothermic peak temperature (T_p) decreases with the decrease of the POPDA molecular weight while the heat of reaction (ΔH_o) reverses the trend. The exothermic peak temperatures of epoxy cured with POPDAs in the blends of A00, B00, and D00 are 122.6, 130.7, and 136.2°C, respectively. The heat of reaction (ΔH) of A00, B00, and D00 blends are 390.5 J/g, 326.7, and 270.7 J/g, respectively. This obtained result is reasonable because the blend containing higher molecular weight of POPDA has less absolute amine functional groups for the curing reaction based on equal weight of sample.

Another characteristic revealed in these DSC scans of the PC–epoxy/POPDA systems [Fig. 5(II)] is the presence of two distinct exothermic peaks. The first peak is mainly contributed by the heat generated via normal curing reaction between POPDA and epoxide. The substitution reaction occurring at a higher temperature contributes the second minor exothermic peak. The substitution reactions between N-aliphatic aromatic carbamate or urea with hydroxyl group have been identified by spectroscopy previously. The presence of 12 wt % PC in these blends results in substantial reduction of peak temperature and ΔH of the first exothermic peak. Comparing curve A of Figure 5(II) (A12) with curve A of Figure 5(I) (A00), the peak temperature decreases by 18.2°C and the ΔH_o is only 69.8% of the virgin system. Lower peak temperature indicates higher reaction rate of the A12 blend relative to that of the virgin system. The reasons for the observed lower ΔH_o of the A12 system than that of A00 system are very complex that should include: (1) the effect of concentration: the amounts of oxirane and amine are only 88% of the virgin system; (2) the effect of transamidation: the reaction [eq. (2)] between amine and carbonate proceeds at a much high rate at room temperature (curve A of Figs. 2 and 3), the exotherm of this reaction is not included in these thermograms; (3) the effect of nonstoichiometry: the ratio of amine participating in the transamidation reaction does not react with

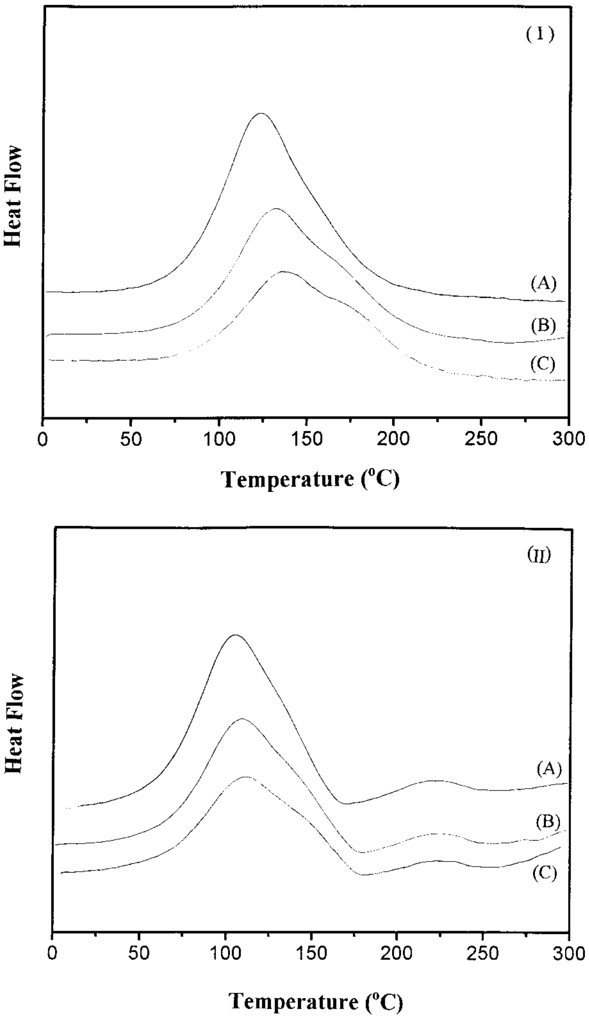


Figure 5. DSC dynamic runs in the temperature range between 30°C and 300°C (I): (A) A00, (B) B00, and (C) D00, (II) (A) A12, (B) B12, and (C) D12.

oxirane, causing nonstoichiometry between oxirane and amine; and (4) the effect of substitution: reaction heat of these reactions [eqs. (4) and (5)] may be substantially lower than that of the normal curing reaction [eq. (1)].

Comprising these effects, the observed reaction heat (ΔH) by DSC scans decreases significantly as PC content increases.

Kinetics by Borchardt and Daniels Method

The dynamic DSC runs shown in Figures 5(I) and (II) have been used to calculate the kinetic parameters according to the Borchardt and Daniels (B & D) method.[13] The method assumes that the reaction follows *n*th order kinetics as below:

$$d\alpha/dt = k(1 - \alpha)^n \tag{9}$$

The reaction rate ($d\alpha/dt$) is obtained by dividing the peak height (dH/dt) at temperature T by the total heat of the reaction (ΔH_o) [eq. (10)], and the fractional conversion (α) is decided by measuring the ratio of the partial area, ΔH_p, at temperature T to the total peak area [eq. (11)].

$$d\alpha/dt = (dH/dt)/\Delta H_o \tag{10}$$

$$\alpha = \Delta H_p/\Delta H_o \tag{11}$$

Borchardt and Daniels's technique also assumes the reaction rate constant (k) obeys the Arrhenius expression:

$$k = A\exp(-E_a/RT) \tag{12}$$

Where A = preexponential factor (1/s); E_a = activation energy (J/mol); R = 8.314 (J/mol K); and T = absolute temperature (K).

Substituting eq. (12) into eq. (9) and taking logarithms produce eq. (13), as follows:

$$\begin{aligned}\ln(d\alpha/dt) &= \ln k + n\ln(1 - \alpha)\\ &= \ln A - E_a/RT + n\ln(1 - \alpha)\end{aligned} \tag{13}$$

The reaction rate and the fractional conversion from eqs. (10) and (11) are required in order to solve eq. (13) with a multiple linear regression.

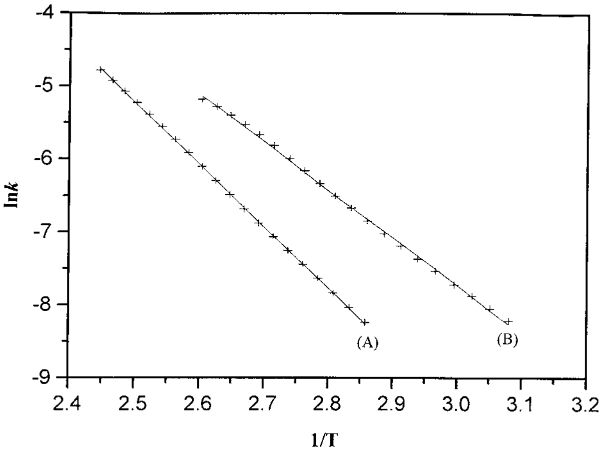
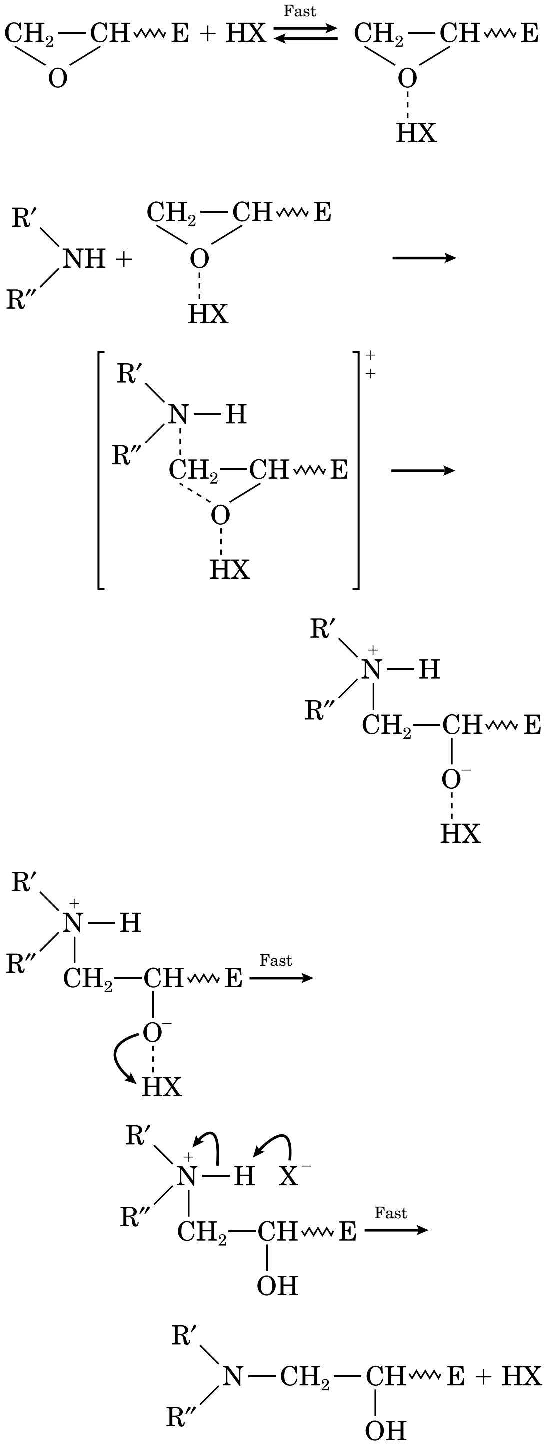


Figure 6. Plots of log k vs. $1/T$ for (A) DER 331/D400 = 100/50 blend (B00 of Table I), and (B) DER 331/D400/PC = 100/50/20.45 blend (B12 of Table I).

Figure 6 shows an Arrhenius plot of ln k vs. $1/T$ for the virgin (B00) and the PC-containing blend (B12) over the region from 10% peak height to 50% peak area of the DSC exotherm. Both plots of ln k against $1/T$ show fairly good straight lines. These obtained results imply that these systems follow the *n*th order kinetics and the Arrhenius expression when the conversion of reaction is less than 50%.

Table II summarizes the obtained reaction order (n), activation energy (E_a) and preexponential factor (A) of various epoxy/POPDA and PC–epoxy/POPDA blends. As shown in this table, the presence of PC decreases the activation energy of the reaction between oxirane and amine. The transamidation reaction [eqs. (2) and (3)] produces the phenolic–OH chain ends that can act as a catalyst for the epoxy/amine curing reaction. However, dilution by the PC presence results in lower concentrations of epoxy and amine in the PC–epoxy/POPDA blends are than those of the virgin epoxy/POPDA blends. Additionally, the transamidation reaction would further reduce the concentrations of amine in the blend and causes those blends less than stiochiometric. These phenomena would decrease the effective collisions between epoxy and amine and cause lower of the preexponential factor (A). Compromising these effects, the presence of PC in the epoxy/POPDA still results in higher curing rate between epoxy and aliphatic amine. The activation energies of epoxy/POPDA systems obtained from the Borchardt and Daniels analysis are 60–70 KJ/mol, which are higher than the similar values from other epoxy/aliphatic amine systems previously reported in the literature.[13–15] This may be due to certain autocatalyzing behavior by the hydroxyl-containing intermediates produced from the curing reaction. The autocatalyzed mechanism of epoxy/amine system is expressed as following[16]:



(14)

Knowing the kinetic parameters n, E_a, and A, we should be able to estimate the conversion as a function of time and temperature. However, results from Figures 8 and 9 show that the experimental values deviate substantially from the predicted values.

Kinetics by Autocatalytic Method

The dynamic DSC runs [Fig. 5(I) and (II)] are also used to determine the appropriate isothermal analysis temperature to calculate the kinetic parameters of the autocatalytic model. In this case, the isothermal temperatures are selected between the onset of curve and a point midway to the peak maximum at 80, 90, and 100°C, respectively. The autocatalytic model is expressed by eq. (13), where the fractional conversion (α) is measured by the partial heat of reaction (ΔH_p) obtained from the isothermal analysis divided by the total heat of the reaction obtained from the dynamic DSC run (ΔH_o).

$$d\alpha/dt = K\alpha^m(1-\alpha)^n \tag{15}$$

Taking logarithms of eq. (15) yields eq. (16) as follows:

$$\begin{aligned}\log(d\alpha/dt) &= \log K + \log[\alpha^m(1-\alpha)^n] \\ &= \log K + n[\log \alpha^{m/n}(1-\alpha)] \end{aligned}\tag{16}$$

Polts of $\log(d\alpha/dt)$ vs. $[\log \alpha^{m/n}(1-\alpha)]$ of virgin and blend systems (Fig. 7) at various temperatures result in good linear relationship up to 68–74% conversion. The observed linear relationship indicates that these systems follow the autocatalytic model. If we assume the reaction rate constant (k) obeys the Arrhenius expression as eq. (12), the reaction order (m and n), activation energy (E_a), and preexponential factor (A) can be determined and the results are tabulated in Table II. The observed trend in kinetic parameters by this autocatalytic method is similar to that of the Borchardt and Daniels method. The presence of PC reduces activation energy (E_a) and preexponential factor (A) of the blend. Another characteristic revealed in this model is that the reaction order (m) representing the autocatalyzed effect is very small in these PC–epoxy/POPDA blends. This result is reasonable because the phenol has been found to be a more powerful proton donor in the epoxy curing than that of the aliphatic alco-

Table II. The Kinetic Parameter of PC–Epoxy/POPDA Blend Calculated by (I) B&D Method and (II) Autocatalyzed Method

	I B&D Method				
	n	E_a (KJ/mol)	log A (min^{-1})	Std Error (s^{-1})	Conversion Range (%)
A00	1.86	76.9	9.85	0.012	2.1–49.7
A12	1.35	60.1	7.92	0.023	2.8–52.7
B00	1.92	73.3	9.14	0.015	1.8–48.9
B12	1.17	55.6	7.14	0.031	2.9–49.5
D00	2.16	72.3	8.86	0.018	2.2–47.2
D12	0.97	48.7	6.09	0.039	2.6–53.5

n represents the reaction order.
E_a represents the activation energy.
A represents the preexponential factor.

	II Autocatalyzed Method				
	n	m	E_a (KJ/mol)	log A (min^{-1})	Conversion Range (%)
A00	1.76 ± 0.05	0.25 ± 0.02	48.9 ± 1.0	6.13 ± 0.14	5.1–70.0
A12	1.70 ± 0.07	0.10 ± 0.03	46.1 ± 1.4	6.04 ± 0.21	5.2–74.2
B00	1.73 ± 0.05	0.18 ± 0.03	45.8 ± 1.1	5.53 ± 0.16	5.5–72.5
B12	1.73 ± 0.10	0.07 ± 0.05	38.1 ± 2.3	4.85 ± 0.32	5.9–73.4
D00	1.91 ± 0.05	0.18 ± 0.03	42.2 ± 1.8	4.91 ± 0.25	4.9–68.1
D12	1.89 ± 0.07	0.04 ± 0.03	39.7 ± 1.4	4.86 ± 0.21	5.0–68.3

m and n represent the reaction order.
E_a represents the activation energy.
A represents the preexponential factor.

hol.[17] Cure acceleration due to the alcoholic hydroxyl formed during process of epoxy curing has not been positively identified in these PC–epoxy/POPDA blends.

The calculated kinetic parameters, m, n, E_a, and A can be substituted into the integrated autocatalytic model to estimate the epoxy conversion as a function of time and temperature, and the results are given in Figures 8 and 9.

The results of these kinetic analyses by Borchardt and Daniels method and the autocatalytic method (curves A and B of Figs. 8 and 9) can be verified by partially reacting the blend and then comparing its residual reactivity to that by the calculated values. In this experiment, the uncured blend is held isothermally at 80°C and a time that is partially cured. The sample is then dynamically heated and compared the remaining heat of curing to the ΔH_o of the blend to yield a % conversion. Figures 8 and 9 compare the actual (by DSC) and model predicted values, the isothermal method appears more accurate than the B&D method in predicting the result of the PC–epoxy POPDA blends.

The results of these kinetic analyses can also be verified using the infrared spectroscopic technology. The conversion of the epoxy curing is determined directly by the heat changes of DSC and by the infrared absorption of the oxirane band. Figure 8 shows that both experimental conversions vs. time of the neat epoxy/D400 blend (B00) at 80°C are in good agreement with the predicted curve by the autocatalyzed method. Figure 9 presents the conversion vs. time of the PC–epoxy/D400 blend (B12) at 80°C. It shows that the experimental results obtained by DSC method is in good agreement with the predicted curve by the autocatalyzed method (square symbol and curve B, Fig. 9). However, Figure 9 also shows that the oxirane conversion vs. time of this PC–epoxy/D400 blend by the IR spectroscopic method is deviated substantially from the autocatalytic model predicted value (triangle symbol and curve B, Fig. 9). In other words, the autocatalytic model can successfully predict the cure kinetics of the neat PC–epoxy system but fails to predict the PC–epoxy/POPDA blend. The failure to model the PC-containing systems is due to that the heat evolved by the thermal analysis in a small time interval is assumed to be directly proportional to the number of moles reacted during that time interval.[13] As mentioned earlier, various reactions take place during the curing of the PC–epoxy/POPDA blend and their individual heat of reactions are not expected to be the same. It is difficult or nearly impossible to resolve the heat produced by each reaction. The model based on the thermal analysis is improper by assuming that all the heat produced has come from the normal curing between amine and oxirane and by neglecting contributions from other reactions. This is why the model can successfully predict the neat epoxy/POPDA system because only the normal curing is involved. In addition, transamidation reaction causes reduction of the amine, and the remaining oxirane in the blend can be quantified by the infrared spectroscopy. In the thermal analysis approach, excess of the oxirane due to transamidation has not been taken into consideration. This is why the conversion represented by the spectroscopic technology (triangle symbol of Fig. 9) is substantially lower than that by the thermal analysis (curve B of Fig. 9).

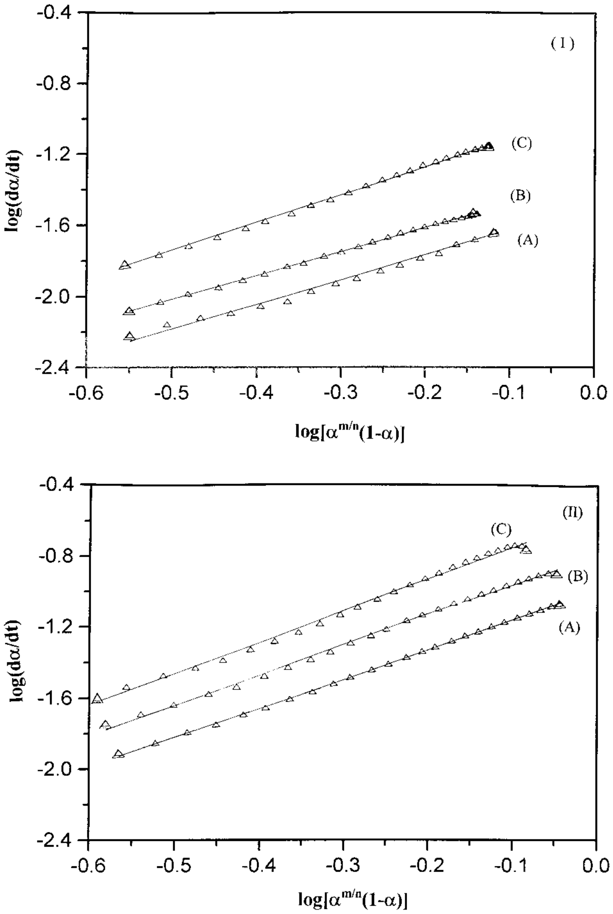


Figure 7. Plots of $\log(d\alpha/dt)$ vs. $\log[\alpha^{m/n}(1-\alpha)]$ (I) DER 331/D400 = 100/50 blend (B00 of Table I). (A) at 80°C, (B) at 90°C, and (C) at 100°C and (II) DER 331/D400/PC = 100/50/20.45 blend (B12 of Table I): (A) at 80°C, (B) at 90°C, and (C) at 100°C.

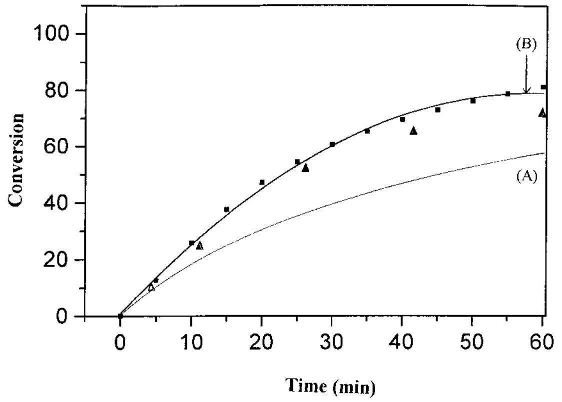


Figure 8. Plots of conversion vs. time at 80°C for (A) B00 system modeled by the B&D method, (B) modeled by the autocatalytic method, (■) found by dynamic DSC after isothermal holding and (▲) found by the infrared spectroscopic analysis.

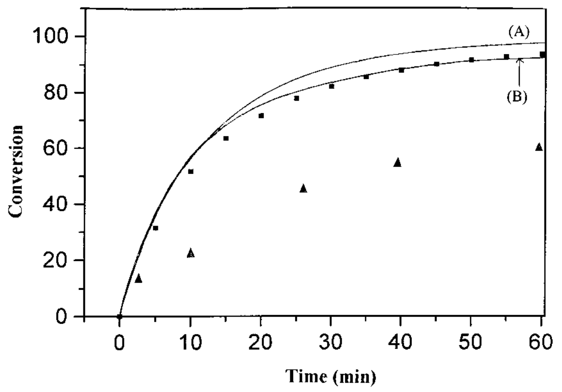


Figure 9. Plots of conversion versus time at 80°C for (A) B12 system modeled by the B&D method, (B) modeled by the autocatalytic method, (■) found by dynamic DSC after isothermal holding, and (▲) found by the infrared spectroscopic analysis.

Comparison of the PC–Epoxy Blend Cured by Aliphatic and Aromatic Amine

As revealed in Figures 2 and 3, the transamidation reaction takes place rapidly in the PC–epoxy/aliphatic amine blend. The inductive effect of this aromatic structure of the substitute group makes the carbonate carbon highly electrophilic, which can be easily attacked by a nucleophilic reagent. The aliphatic amines in the PC–epoxy blend act as a nucleophile that can attack the oxirane and the carbonate at the same time. This study has shown that the reaction rate of aliphatic amines (POPDAs) with carbonate is significantly higher than that with oxirane. However, when an aromatic amine is used to cure the blend, the situation is quite different. An aromatic amine, metaphenylene diamine (MPDA), was utilized to cure the PC–epoxy blend to study the reaction between carbonate and aromatic amine.[18] Curves A, B, and C of Figure 10 are the spectra of initial, 2 h at 80°C, and 2 h at 150°C, respectively. There is little spectroscopic variation in the carbonate group of PC (compare curves A and B) even after 2 h at 150°C. Lower nucleophility of the aromatic amine due to electron attraction by the benzene ring requires more stringent conditions to react with the carbonate of PC. In other words, an aromatic amine can only proceed by normal curing reaction with oxirane in the PC–epoxy/aromatic amine blend at 80°C or below. Curve C of Figure 10 shows the carbonyl absorption peak at 1760 cm^{-1} that is lower than that of the original carbonate absorption at 1780 cm^{-1} due to the transesterification reaction. The carbonate of PC transesterificates with the hydroxyl group formed from the curing of oxirane with amine at higher temperature. Therefore, the transesterification should not influence the kinetic results of the normal curing carried out at 80–100°C.

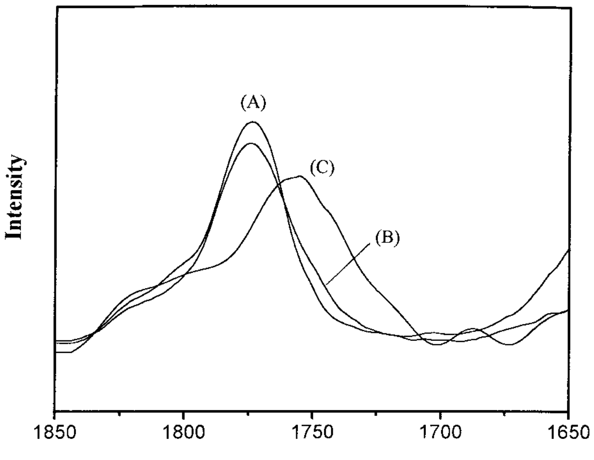


Figure 10. Infrared spectra of the DER 331/MPDA/PC = 100/16/15.8 blend recorded in the carbonyl stretching region: (A) initial, (B) 80°C for 2 h, and (C) 150°C for 2 h.

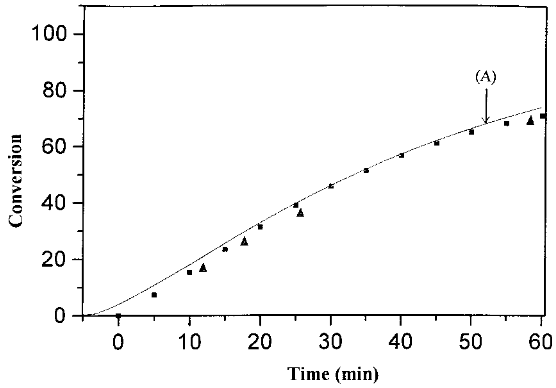


Figure 11. Plots of conversion vs. time at 80°C for the DER 331/MPDA/PC = 100/16/15.8 blend: (A) predicted by autocatalytic method, (■) found by dynamic DSC after isothermal holding, and (▲) found by the infrared spectroscopic analysis.

The autocatalytic model [eq. (14)] was also used to calculate the kinetic parameters m, n, E_a, and A.[18] There data were substituted into the integrated autocatalytic model to estimate conversion as a function of time and temperature (curve A, Fig. 11). The verification of the kinetic results using DSC autocatalytic methods and infrared spectroscopic measurements are illustrated in Figure 11. Comparing these curves, the experimental obtained DSC and IR results are in good agreement with the predicted conversion. Thus, the autocatalytic model and the associated kinetic parameters can also successfully describe the kinetics of the neat and the PC–epoxy/aromatic amine systems.

CONCLUSION

The reaction mechanisms of the PC–epoxy blend cured by aliphatic amine are influenced by the amount of PC presence in the blend. For the blends containing lower PC content (PC 6 wt %), the transamidation reaction converts nearly all the carbonate and fraction of the amine into N-aliphatic aromatic carbamate immediately after mixing at an ambient condition. Further amine substitution of this carbamates into ureas takes place at the high temperature of 80°C. The remaining amine precedes the normal curing reaction with oxirane and produces the hydroxyl at the same time. The produced hydroxyl is able react with urea to yield the N-aliphatic aliphatic carbamate at 150°C. For the blend containing higher PC content (PC 12 wt %), the transamidation reaction takes place first. Then, most of the produced N-aliphatic aromatic carbamate converts into N-aliphatic aliphatic carbamates at 80°C via two routes: (1) by reacting N-aliphatic aromatic carbamate with the hydroxyl formed from the normal curing directly, and (2) decomposition of the N-aliphatic aromatic carbamate into the aliphatic isocyanate followed by reacting with the hydroxyl to yield the N-aliphatic aliphatic carbamates. The latter route occurs more significantly in the PC–epoxy blend cured by the higher molecular weight of aliphatic amine because more residual oxirane is available to accelerate the decomposition of the N-aliphatic aromatic carbamates. The activation energy (E_a) and preexponential factor (A) of the PC–epoxy/POPDA blends decrease with increasing the PC content. However, the kinetic study using the autocatalyzed model is able to predict only the oxirane conversion vs. time from DSC thermal analysis, and IR spectroscopic results for the neat epoxy/POPDA and the PC–epoxy/aromatic amine systems at 80°C because only the normal curing reaction is involved. DSC has often been applied in the analysis of simple reactive systems but it is unable to apply to the system where many different reactions are involved. The IR method has the advantage of direct determination of certain particular types of functional groups and their concentrations relative to a known standard. Any reactive system can be monitored by the absorption changes of these groups with time. Further study by FTIR, which will appear later, is in progress to determine the kinetics of the PC–epoxy/aliphatic amine blends.

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