

Kinetic Study on Simultaneous Interpenetrating Polymer Network Formation of Epoxy Resin and Unsaturated Polyester

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SYNOPSIS

Simultaneous interpenetrating polymer networks (SIN) based on diglycidyl ether of bisphenol-A (DGEBA) and unsaturated polyester (UP) in weight ratios of 100/0, 50/50, and 0/100 were blended and cured simultaneously by using cumene hydroperoxide (CHP) and *m*-xylenediamine (MXDA) as curing agents. A kinetic study during SIN formation was carried out at 43, 53, 58, and 64°C. Concentration changes for both epoxide and C=C bond were monitored with Fourier transform infrared (FTIR). Rate expressions for epoxide polymerization were established with model reactions for phenyl glycidyl ether (PGE) and benzylamine in dichloroethane containing benzyl alcohol. Experimental results revealed that a lower cure rate constant for the C=C bond during SIN formation was found, compared with pure UP network formation. A model of network interlock is proposed to account for this phenomenon. During simultaneous cure of DGEBA and UP, the network interlock should provide a sterically hindered environment, which subsequently retards cure rate for UP. On the other hand, epoxide cure during SIN formation indicates higher rate constants for both uncatalyzed and catalyzed reactions, compared with those of pure DGEBA cure. Presumably the catalytic effect of hydroxyl end groups in UP overcomes the effect of network interlock. Kinetic parameters were calculated and are discussed.

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INTRODUCTION

In our previous article on the chemorheology of the simultaneous interpenetrating polymer network (SIN) formation of epoxy resin and unsaturated polyester (UP),¹ we reported on various intermolecular interactions on the curing behavior such as changes of viscosity and gelation time. It was noted that the unusual increase in viscosity and decrease in gelation time for the SIN formation of diglycidyl ether of bisphenol-A (DGEBA)/UP can be interpreted as resulting from the extensive H-bonding in systems like DGEBA/UP, DGEBA/diamine, and UP/diamine.¹ On the other hand, we also reported that possible network interlock between DGEBA

and UP networks should provide additional steric hindrance and therefore retard curing reactions.¹ In order to understand the net effect of such factors on the kinetics of SIN formation, we further analyzed the kinetic data for this SIN system.

Jin and Meyer, in their kinetic study of polyurethane/poly(methyl methacrylate) (PU/PMMA) IPN, reported the validity of the Beer-Lambert law, but did not calculate kinetic parameters.² Xue and coworkers reported on the kinetics of PU/polystyrene (PS) IPNs by infrared (IR) spectroscopy.³ They found that there was no interference between the reaction mechanisms and that increasing the PU/PS proportion enhanced the rate of PU formation, but lessened the rate of PS formation. Until now limited kinetic data on SINs have been disclosed. In this article, we report on a detailed kinetic study and compare the kinetic parameters of model reactions with those of DGEBA, UP, and the SIN of 50/50 DGEBA/UP.

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EXPERIMENTAL

Analytical grades of phenyl glycidyl ether (PGE), benzylamine, and benzyl alcohol were purchased from Merck Co. and were used as received. Model reaction A was carried out at 50, 57, 61, and 67°C by reacting PGE (3.75 g) and benzylamine (2.68 g) in 10 mL of dichloroethane. Model reaction B dealt with the reaction of the same amounts of PGE and benzylamine, at the same temperatures, in the same amounts of dichloroethane, but additionally containing benzyl alcohol (2.70 g). Changes of epoxide concentration were detected with Fourier transform IR (Nicolet 520 FTIR), resolution 1 cm^{-1} .

DGEBA (Epikote 815) was obtained from Shell Co. An epoxy equivalent weight (EEW) of 194.5 was found by titration. General purpose UP was obtained (2660 PT-2; weight average molecular weight, 6,500; Chang-Shing Industrial Co., Taiwan) that contained isophthalic acid, propylene glycol, maleic anhydride, and styrene. UP/DGEBA in weight ratios of 100/0, 50/50, and 0/100 were blended. Cumene hydroperoxide (CHP, 2% based on UP) and *m*-xylene diamine (MXDA, based on stoichiometric EEW of DGEBA) were mixed into the above blends as curing agents. Kinetic data were collected at 43, 53, 58, and 64°C. Samples were cast on KBr plates and were sand-

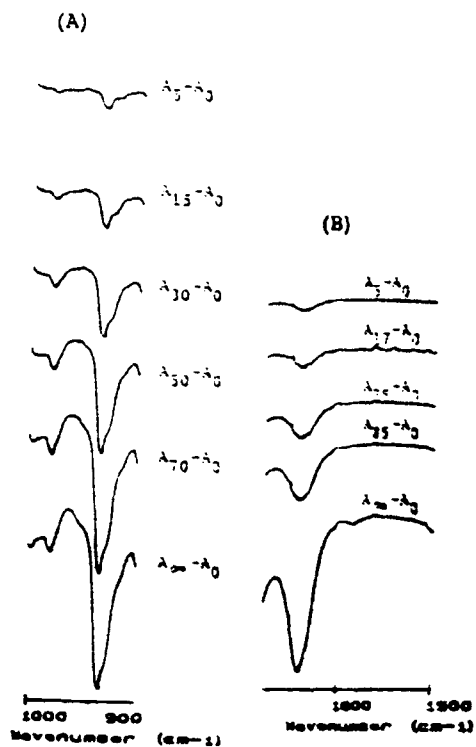


Figure 1 Typical difference spectra for (A) epoxide and (B) C=C bond.

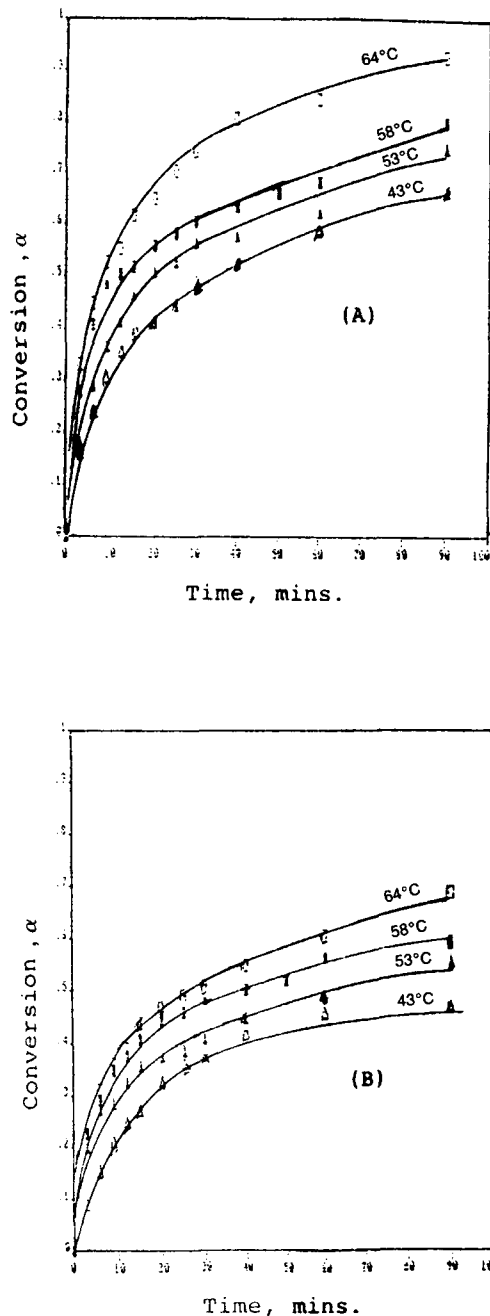


Figure 2 Conversions of C=C bond with time t for (A) pure UP and (B) SIN of 50/50 UP/DGEBA.

wiched and mounted on the FTIR sample holder. Changes of concentrations in epoxide and C=C bond were monitored with FTIR (Nicolet 520 FTIR, 1 cm^{-1} of resolution). Difference spectra were obtained by subtracting the absorbance at time zero from those at time t 's, using the benzene absorbance at 1608 cm^{-1} as internal standard. Integration of peak areas at 916 and 1646 cm^{-1} from the difference

spectra were related to the changes of concentrations for epoxide and double bond. The conversion, α , is defined as

$$\alpha = (A_t - A_0)/(A_\infty - A_0) = (C_t - C_0)/(C_\infty - C_0)$$

where A_0 , A_t , and A_∞ are peak areas of the specific functional group at initial time, time t , and after postcure, respectively. C_0 , C_t , and C_∞ are the corresponding concentrations. Typical difference spectra for epoxide and C=C bond are shown in Figure 1.

RESULTS AND DISCUSSION

It is well known that the curing of epoxy with diamine proceeds via a stepwise mechanism⁴; the cross-linking of UP with peroxide goes via a radical chain mechanism.⁵ The two mechanisms are expected to proceed independently and not interfere with each other, as concluded by Xue and coworkers,³ thus an SIN formed in the recipe of UP/DGEBA = 50/50. The chemorheology of this IPN system has been discussed in the literature.¹

Table I Kinetic Parameters for C=C Bond in Pure UP and SIN of 50/50 UP/DGEBA

Temp. (°C)	<i>k</i> Values for	
	Pure UP ($\times 10^2$)	SIN ($\times 10^2$)
43	3.944	2.321
53	4.938	3.868
58	8.059	4.915
64	9.952	6.240

Kinetics of UP

Figure 2(A,B) show the conversions of C=C with time for pure UP and for SIN of 50/50 UP/DGEBA. Obviously, SIN has a lower cure rate, compared with pure DGEBA. Free radical polymerization of vinyl compounds normally follows the first order of reaction⁵:

$$-d[M]/dt = k_p(k_d f[I]/k_t)^{1/2}[M] \quad (1)$$

where k_d is the dissociation rate constant of the initiator, k_p and k_t are rate constants of chain propa-

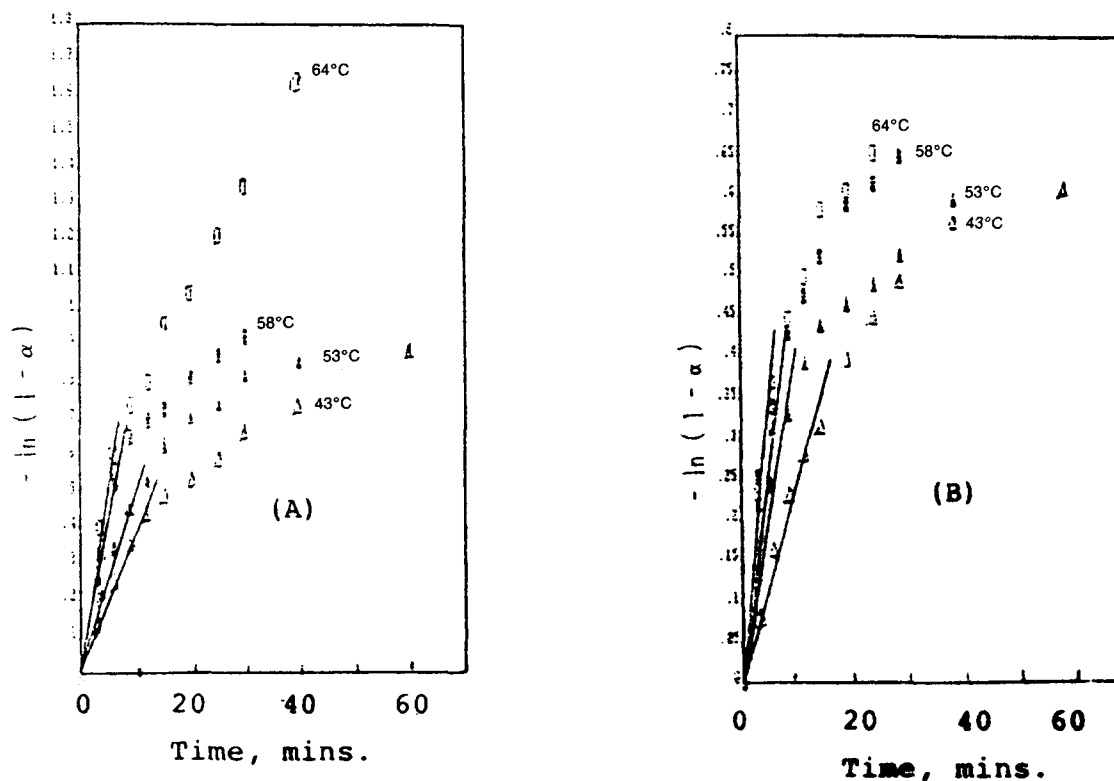


Figure 3 Plots of $-\ln(1 - \alpha)$ vs. time for C=C bond in (A) pure UP and (B) SIN of 50/50 UP/DGEBA.

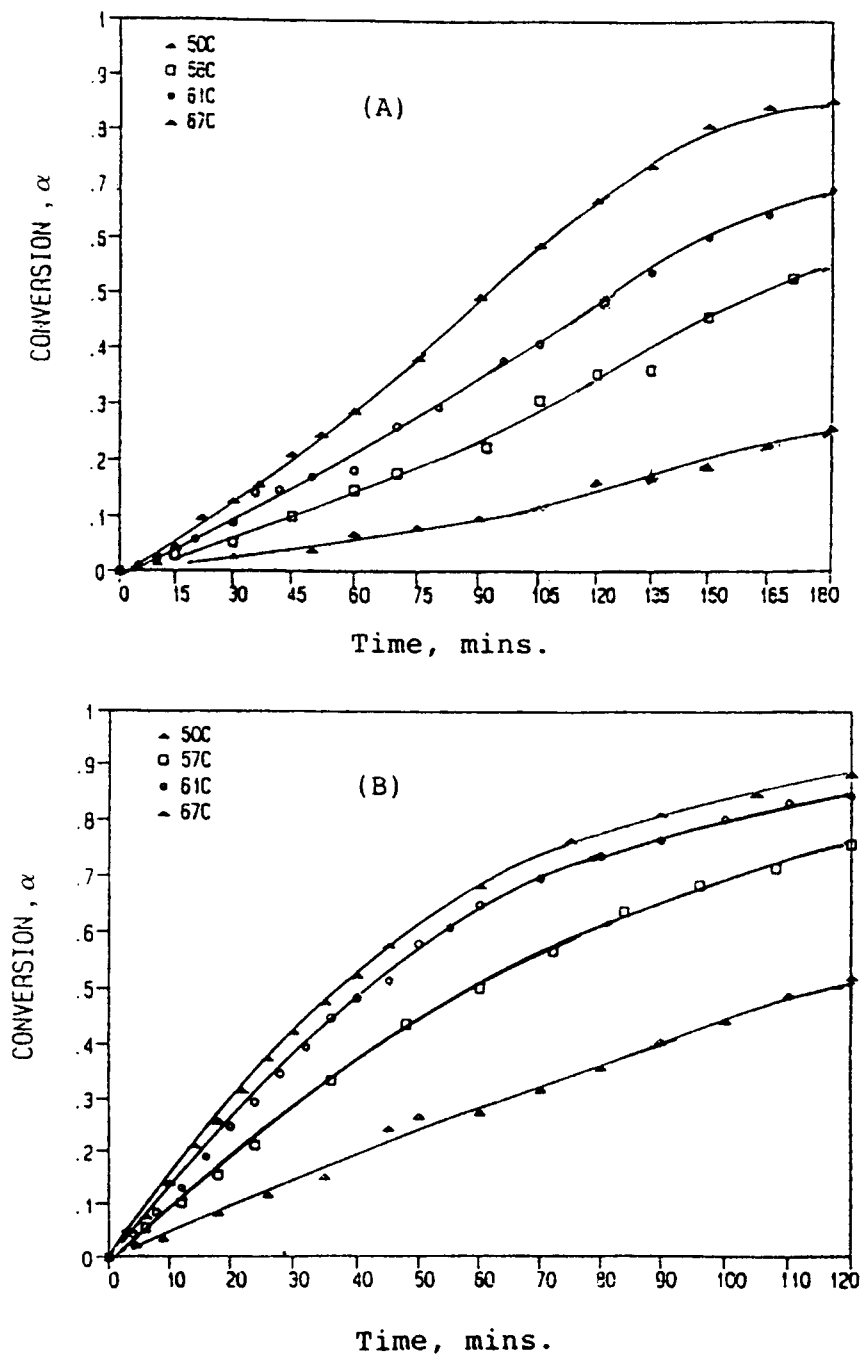


Figure 4 Conversions versus reaction time for (A) model reaction A and (B) model reaction B.

gation and chain termination, f is the initiator efficiency, and $[I]$ is the concentration of the initiator. Integration of Eq. (1) may be expressed as:

$$-\int_{[M]_0}^{[M]} \frac{d[M]}{[M]} = \int_0^t k_p(k_{df}[I]/k_t)^{1/2} dt \quad (2)$$

with $[M] = [M]_0(1 - \alpha)$, where α is the conversion of the C=C bond at time t . At the early stage of cure, assuming that $[I]$ was close to the initial concentration $[I]_0$, and f was nearly constant, integration of Eq. (2) gives:

$$-\ln(1 - \alpha) = kt \quad (3)$$

with $k = k_p(k_d f [I]/k_t)^{1/2}$. Figure 3(A) shows plots of $-\ln(1 - \alpha)$ vs. t for UP cured by 2% of CHP at various temperatures. Figure 3(B) shows similar plots for the SIN of 50/50 DGEBA/UP. The values of k at various temperatures can be found from the slopes of lines at low conversion and are listed in Table I. At later stages of cure reactions (higher conversions), the plots of $-\ln(1 - \alpha)$ versus t are no

longer straight lines. Presumably f and $[I]$ keep changing with time. Furthermore, gel effect⁵ may also play an important role affecting the observed kinetics. It is clear from Table I that the SIN of 50/50 DGEBA/UP has lower k values than pure UP. This finding can be interpreted by the network interlock effect.^{1,6} During SIN formation, the interlock between the DGEBA and UP networks not only

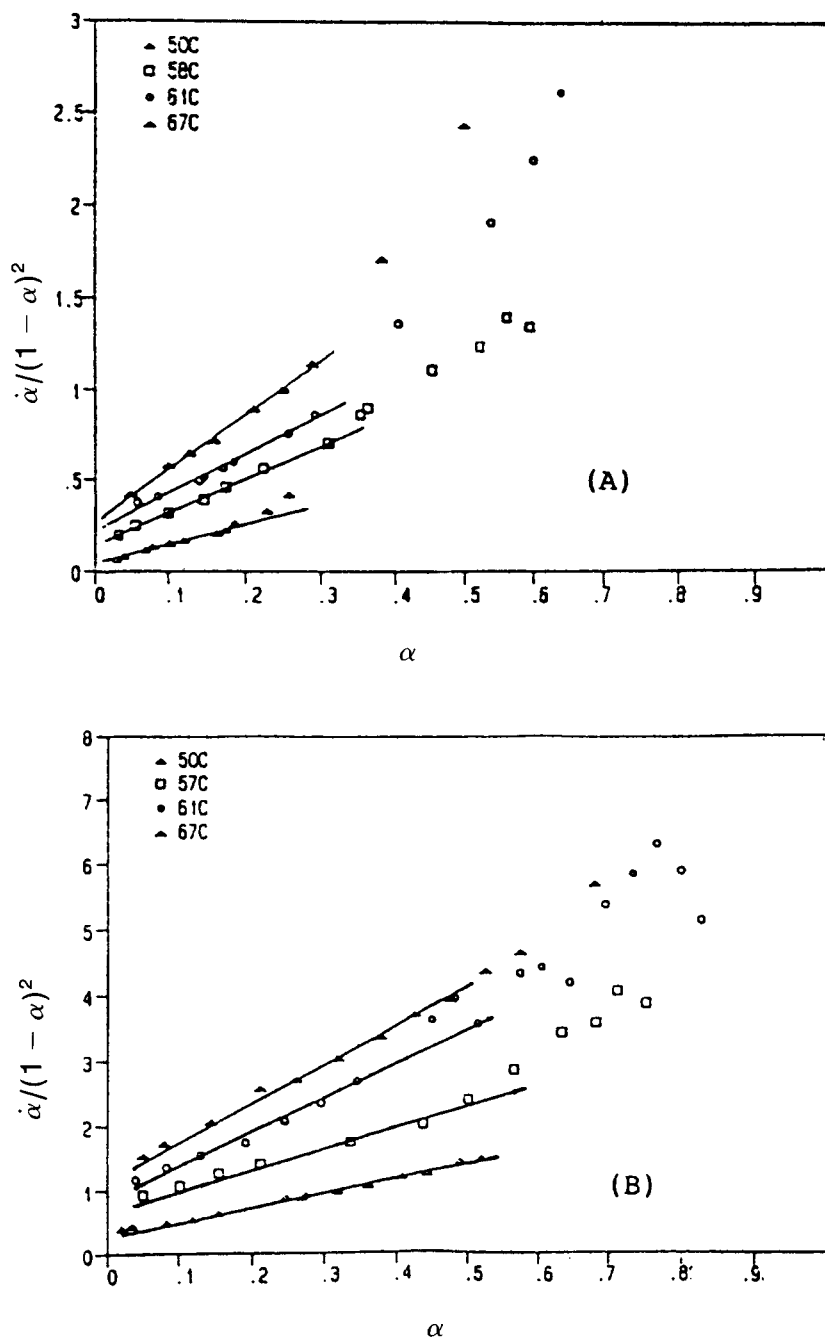


Figure 5 Plots of $\dot{\alpha}/(1 - \alpha)^2$ vs. α for (A) model reaction A and (B) model reaction B.

provided a sterically hindered environment for cure reactions, but also restrained chain mobilities, thus retarding cure rates.

Kinetics of Epoxide

Many studies on kinetics of DGEBA cured by diamines have been reported in the literature⁶⁻¹³ and

different rate expressions have been proposed. In order to clarify the preferred rate expression in the literature,⁶⁻¹³ we carried out model reactions A and B, which deal with the reaction of PGE and benzylamine in dichloroethene (model A), and, additionally (model B) containing benzyl alcohol. In model B, benzyl alcohol was used to simulate the presence of the hydroxyl end group of UP in a si-

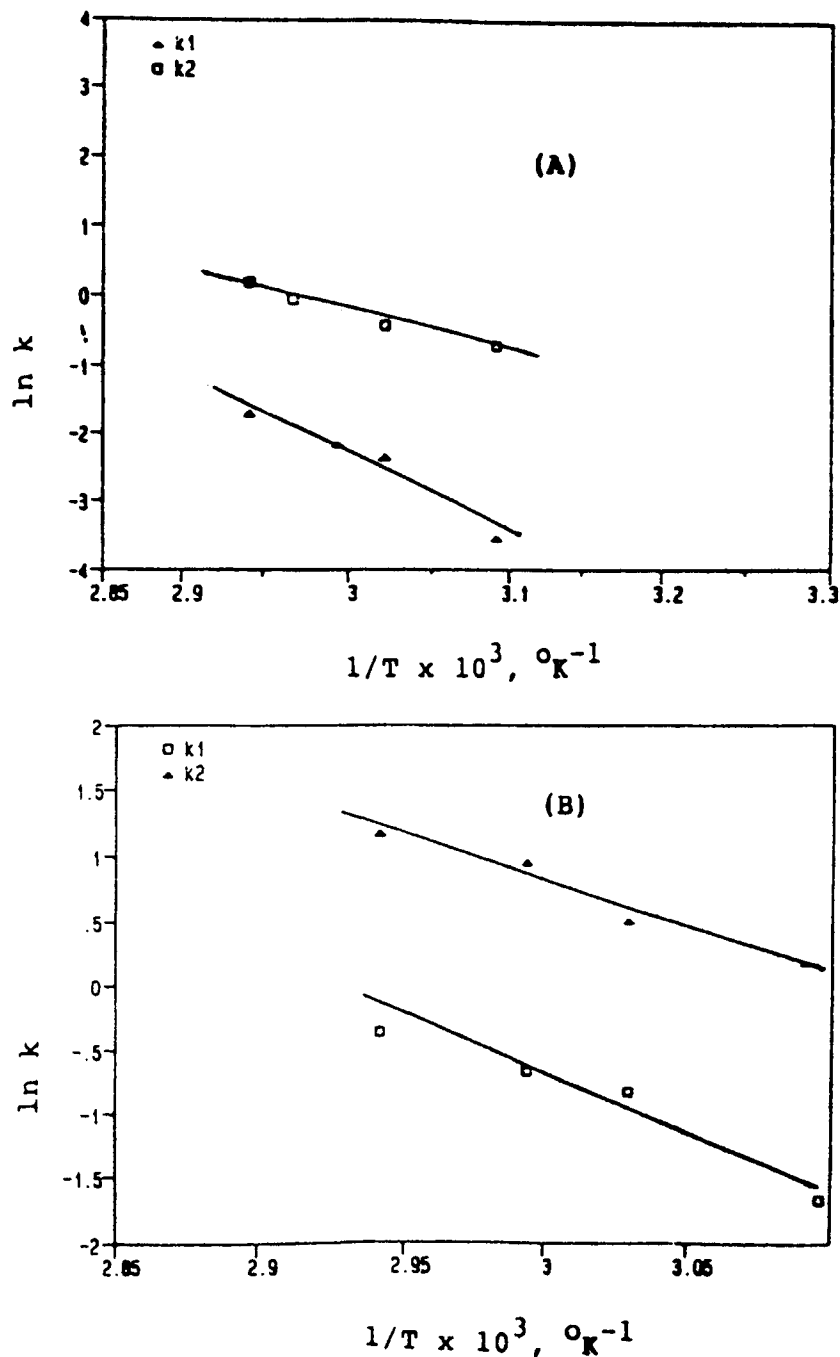


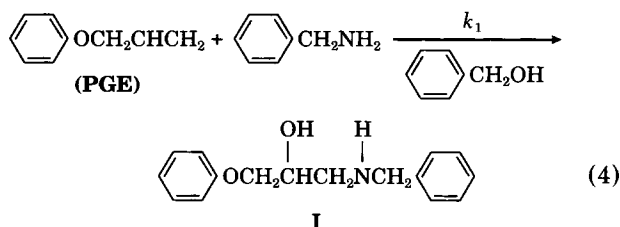
Figure 6 Plots of $\ln k$ vs. reciprocal absolute temperature $1/T$ for (A) model reaction A and (B) model reaction B.

Table II Kinetic Parameters of PGE in Model Reaction A

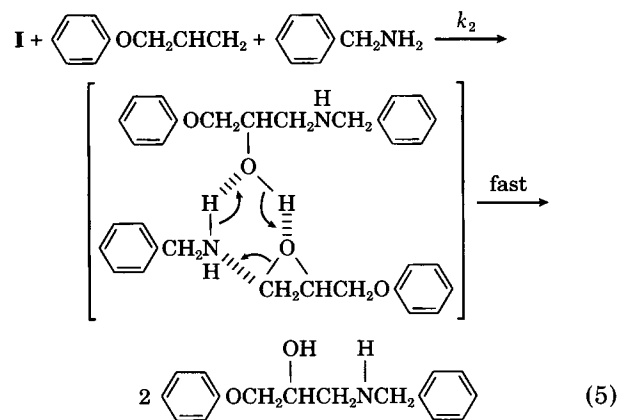
Temp. (°C)	$k_1 \times 10^3$ (L/mol-min)	$k_2 \times 10^2$ (L ² /mol ² -min)	E_1 (kcal/mol)	E_2 (kcal/mol)
50	0.293	0.491	24.13	19.16
58	0.950	0.666	24.13	19.16
61	1.128	0.967	24.13	19.16
67	1.821	1.223	24.13	19.16

$$[E]_0 = [A]_0 = 1.55 \text{ mol/L.}$$

multaneous DGEBA/UP SIN environment. The uncatalyzed reaction between PGE and benzylamine is given as:



However, the newly produced hydroxyl group in I further catalyzes the reaction, according to Eq. (5):



Let $[E]$ and $[A]$ be concentrations of epoxide and amine at time t . It is clear that $[E]$ and $[A]$ are related to their initial concentrations $[E]_0$ and $[A]_0$ by

$$[E] = [E]_0(1 - \alpha) \quad (6)$$

$$[A] = [A]_0(1 - \alpha). \quad (7)$$

Here α is the conversion of the epoxide. Because a new OH is produced for every epoxide consumed, according to Eq. (4), so

$$[\text{OH}] = [E]_0\alpha. \quad (8)$$

Amine with a stoichiometric EEW of epoxide was maintained in our experiment, therefore

$$[E] = [A] = [E]_0(1 - \alpha). \quad (9)$$

Typical changes of conversion with time are given in Figure 4. From Eqs. (4) and (5),

$$-\frac{d[E]}{dt} = k_1[E][A] + k_2[E][A][\text{OH}] \quad (10)$$

where k_1 and k_2 are rate constants for uncatalyzed and catalyzed reactions, respectively. By combining Eqs. (6)–(10), Eq. (11) is obtained:

$$\dot{\alpha} = \frac{d\alpha}{dt} = k_1[E]_0(1 - \alpha)^2 + k_2[E]_0^2(1 - \alpha)^2\alpha \quad (11)$$

that is,

$$\dot{\alpha}/(1 - \alpha)^2 = k_1[E]_0 + k_2[E]_0^2\alpha \quad (12)$$

Table III Kinetic Parameters of PGE in Model Reaction B

Temp. (°C)	$k_1 \times 10^3$ (L/mol-min)	$k_2 \times 10^2$ (L ² /mol ² -min)	E_1 (kcal/mol)	E_2 (kcal/mol)
50	1.90	1.19	16.58	13.71
57	4.34	1.69	16.58	13.71
61	5.12	2.63	16.58	13.71
67	7.04	3.21	16.58	13.71

$$[E]_0 = [A]_0 = 1.34 \text{ mol/L.}$$

where $\dot{\alpha}$ can be found as the slope of the conversion curve versus t [Fig. 4(A,B)]. In fact, Eq. (12) is similar to the generally accepted rate expression for epoxy cure⁸⁻¹⁰:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (13)$$

with $m = n = 1$ in our consideration of mechanisms

[Eqs. (4)–(12)]. The plot of $\dot{\alpha}/(1 - \alpha)^2$ vs. α , according to Eq. (12), gives a straight line, with an intercept of $k_1[E]_0$ and a slope of $k_2[E]_0^2$ as shown in Figure 5(A,B) for models A and B. Plots of $\ln k_1$ and $\ln k_2$ vs. reciprocal absolute temperatures $1/T$ give the corresponding activation energies, E_1 and E_2 [Fig. 6(A,B)]. The resultant rate constants and corresponding activation energies for PGE in models

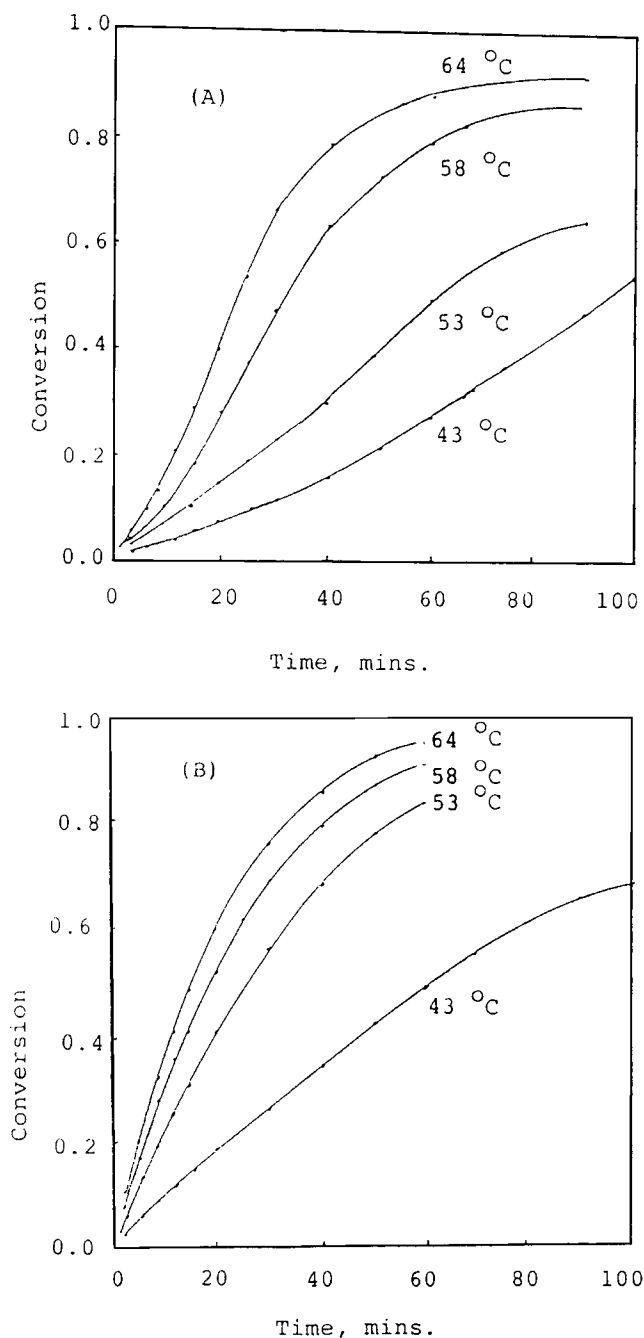


Figure 7 Conversions vs. cure time for epoxide in (A) pure DGEBA and (B) SIN of 50/50 UP/DGEBA.

A and B are listed in Tables II and III, respectively. It is noted that the rate constant for the catalyzed reaction (k_2) is about an order of magnitude higher than that for the uncatalyzed reaction (k_1) and, the

activation energy for the catalytic reaction is generally less than that for the uncatalyzed reaction (Tables II and III). Furthermore, the rate constants in model B are generally higher than the corresponding ones in model A; the activation energies in model B are generally lower than those in model

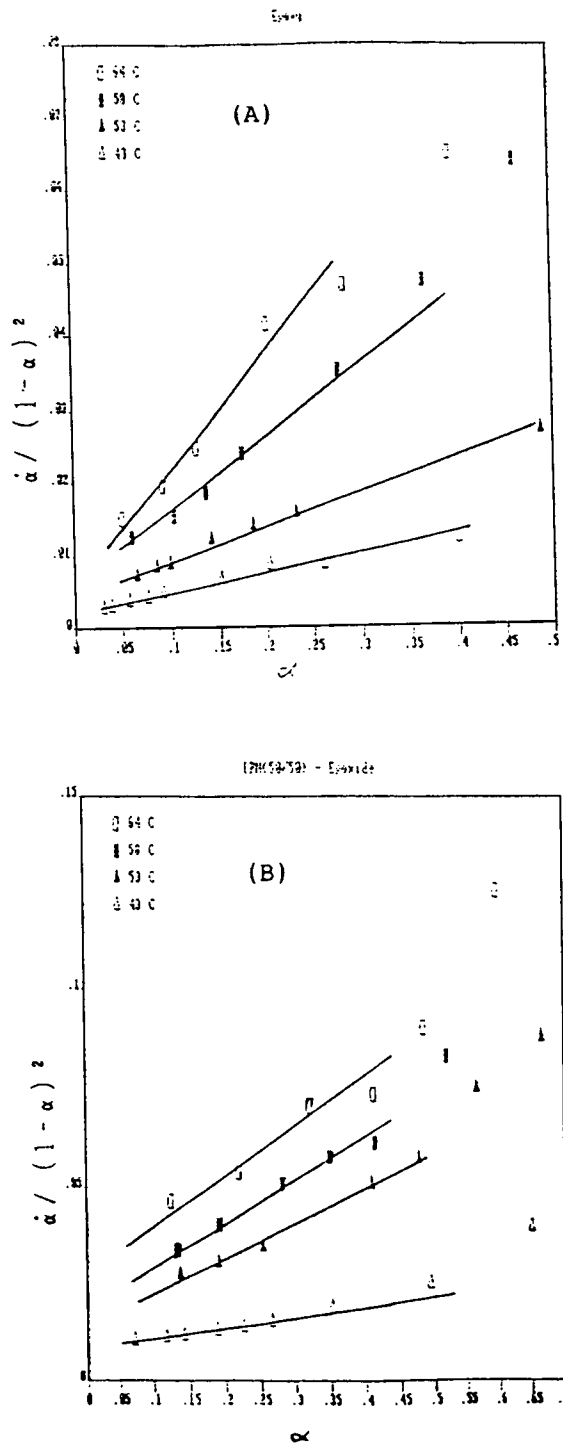


Figure 8 Plots of $\alpha / (1 - \alpha)^2$ vs. α for (A) pure DGEBA and (B) SIN of 50/50 UP/DGEBA.

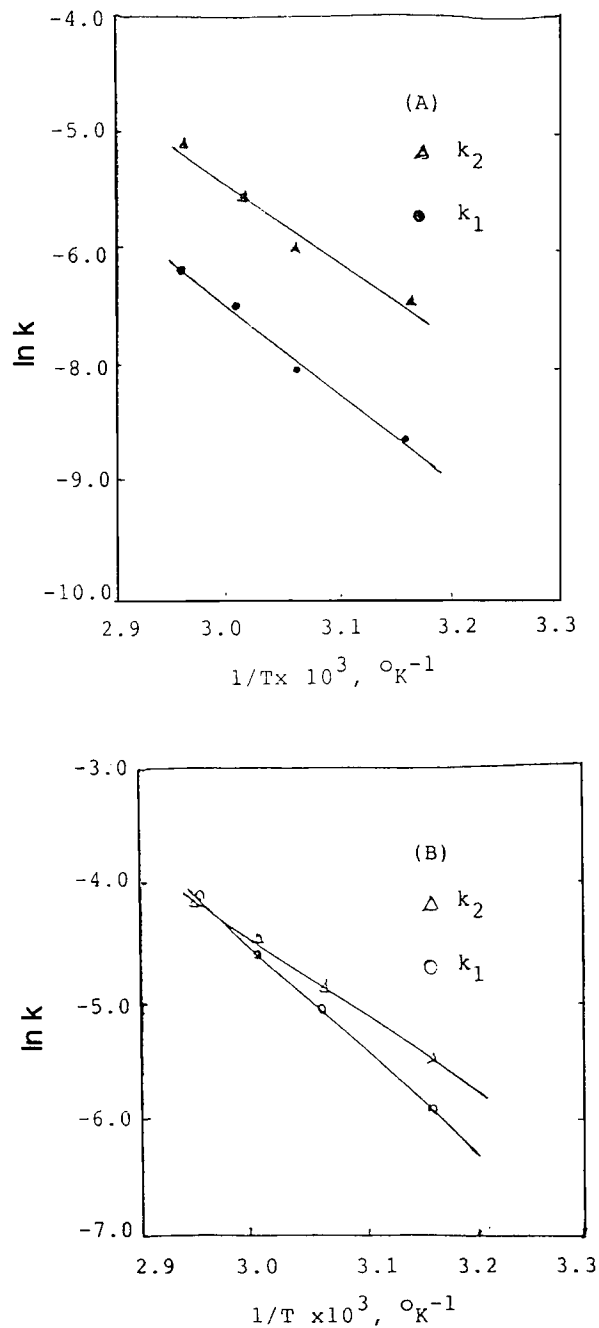


Figure 9 Plots of $\ln k_1$ and $\ln k_2$ vs. reciprocal temperature $1/T$ for (A) pure DGEBA and (B) SIN of 50/50 UP/DGEBA.

Table IV Kinetic Parameters of Epoxide for Pure DGEBA

Temp. (°C)	$k_1 \times 10^3$ (L/mol-min)	$k_2 \times 10^3$ (L ² /mol ² -min)	E_1 (kcal/mol)	E_2 (kcal/mol)
43	0.272	1.65	19.88	12.14
53	0.815	2.31	19.88	12.14
58	1.615	3.48	19.88	12.14
64	1.755	5.62	19.88	12.14

$$[E]_0 = [A]_0 = 4.76 \text{ mol/L.}$$

A. Therefore, the OH group in benzyl alcohol provided a favorably catalytic environment for the reaction of PGE and this catalytic effect is very clear.

Equation (12) was adopted for the rate expression of DGEBA cure in our kinetic study. The first term in the right side of Eq. (12) relates to the uncatalyzed reaction [Eq. (4)]; the second term relates to the catalyzed reaction [Eq. (5)]. Typical changes of conversion α versus time are shown in Figure 7(A,B) for pure DGEBA and SIN. Figure 8(A,B) show the plots of $\dot{\alpha}/(1-\alpha)^2$ vs. α for pure DGEBA and SIN, from which the intercept and slope give $k_1[E]_0$ and $k_2[E]_0^2$ as known from Eq. (12). Kinetic parameters are listed in Table IV. The activation energies for uncatalyzed and catalyzed reactions, E_1 and E_2 , were calculated from Arrhenius plots (Fig. 9). As expected, the rate constant for the catalyzed reaction was much faster than that of the uncatalyzed reaction; the activation energy of the catalyzed reaction was less than that of the uncatalyzed reaction (Tables IV and V).

The experimental results clearly indicate that the corresponding rate constants k_1 and k_2 for SINs are generally higher than those of the pure DGEBA, presumably because the hydroxyl end group in UP provides a favorably catalytic environment for DGEBA cure, a similar effect as in model reactions A and B (Tables II, III). Ohashi and coworkers reported a similar effect by curing epoxy resin having hydroxy methyl groups.¹⁴ This finding is in good agreement with the unusual viscosity increase and

much shorter gelation time for a 50/50 UP/DGEBA SIN cure behavior in our previous report.¹ On the other hand, the corresponding activation energies for SIN are lower than those of pure DGEBA. From the faster curing behavior of SIN, it appears that the catalytic effect of hydroxyl groups on epoxide overcame and predominated in effect on network interlock.

CONCLUSIONS

In a kinetic study of simultaneous DGEBA/UP SIN formation, it was found that the C=C bond in a SIN of 50/50 UP/DGEBA showed a lower curing rate than the pure UP. This phenomenon can be interpreted as an effect of network interlock. Network interlock apparently not only gave an additional sterically hindered environment to the curing reaction, but also restrained the chain mobility of UP, thus accounting for the observed phenomenon. On the other hand, the DGEBA in a 50/50 of UP/DGEBA SIN indicated higher rate constants and lower activation energies than the pure DGEBA, presumably because the hydroxyl end group of UP in the SIN provided a favorably catalytic environment for DGEBA cure. This catalytic effect overcame and predominated in the network interlock effect. The observed phenomena were in good agreement with our previous findings in the chemoreology investigation for this SIN system.

Table V Kinetic Parameters for Epoxide in SIN of 50/50 DGEBA/UP

Temp. (°C)	$k_1 \times 10^3$ (L/mol-min)	$k_2 \times 10^3$ (L ² /mol ² -min)	E_1 (kcal/mol)	E_2 (kcal/mol)
43	0.277	0.408	15.56	11.89
53	0.769	0.816	15.56	11.89
58	1.043	1.119	15.56	11.89
64	1.253	1.278	15.56	11.89

$$[E]_0 = [A]_0 = 2.70 \text{ mol/L.}$$

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