

Kinetic study on epoxy bisphenol-A diacrylate IPN formation

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Abstract: Interpenetrating polymer networks (IPN) based on diglycidyl ether of bisphenol-A (DGEBA) and bisphenol-A diacrylate (BADA) in weight ratios of 100/0, 50/50, and 0/100 were blended and were cured simultaneously by using benzoyl peroxide (BPO) and 4,4'-methylenedianiline (MDA) as curing agents. Kinetic study during IPN formation was carried out at 65, 70, 75 and 80 °C. Absorbance changes at 1623.3 cm⁻¹ and 914 cm⁻¹ relating to concentration changes of C=C and epoxide were monitored with Fourier-transform infrared spectroscopy (FTIR). The epoxide cure kinetic data revealed a combination of non-catalytic bimolecular reaction and a catalyzed termolecular reaction, while the C=C cure kinetic data fitted a first-order reaction. The calculated kinetic parameters indicated decreased rate constants and increased activation energies of the IPN compared with those of the individual components. Presumably, chain entanglements between the two networks provide a sterically hindered environment for the cure reactions and vitrification restrains the chain mobility, accounting for the kinetic parameters.

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Keywords: IPN; kinetics; decreased rate constants; increased activation energy

INTRODUCTION

Epoxy resin is a versatile material which is widely used commercially. The mechanism of epoxy cure by amines has been extensively reported in literature.^{1–8} The different mechanisms and kinetics reported are somewhat ambiguous. Many studies on epoxy-amine cure fit a combination of non-catalytic and catalyzed reactions. However, the detailed reaction mechanisms are still interesting for further study. We are interested in the comparison of kinetic parameters for both IPN and each component based on the established kinetic expression, and try to elucidate the implied factors governing the curing behavior of IPN.

EXPERIMENTAL

DGEBA (Epon 815) with an epoxy equivalent weight of 194.5 was purchased from Shell; BADA was prepared according to the method reported elsewhere.⁹ Weight ratios of BADA/DGEBA = 100/0, 50/50, and 0/100 were blended. BPO (1 phr on BADA) and MDA (in an equivalent amount of DGEBA) were dissolved in small amounts of acetone and were added to the foregoing compositions as curing agents. Liquid films of various compositions were cast on KBr plates and were heated electrically. Kinetic studies were carried out at 65, 70, 75 and 80 °C. Changes of absorbances relating to epoxide and C=C were monitored with a Nicolet model 520 FTIR. The resolution of FTIR was set at 1 cm⁻¹. Difference

spectra were obtained by subtracting the absorbance at time t from that at time zero, using the benzene absorption at 1609 cm⁻¹ as internal standard. Integration of peak areas at 914 and 1623 cm⁻¹ from the difference spectra were related to the concentration changes for the epoxide and C=C. The conversion, α , is defined as

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

where A_0 , A_t and A_∞ are peak areas of the specific functional groups at initial time, time t and after postcure, respectively; C_0 , C_t and C_∞ are the corresponding concentrations.

RESULTS AND DISCUSSIONS

Kinetics of the epoxide cured by MDA

From the kinetic study of our previous paper, a kinetic expression combining the non-catalytic bimolecular reaction between epoxide and amine, and OH-catalyzed termolecular reaction among epoxide, amine and OH was established.^{4,5,8,10,11} The DGEBA/MDA curing kinetics follows the expression:

$$-d[E]/dt = k_1[E][A] + k_2[E][A][OH] \quad (1)$$

where $[E]$ and $[A]$ represent the concentrations of epoxide and amine, $[OH]$ is the concentration of hydroxide group. In this study, the stoichiometric balance was maintained initially such that $[E]_0 = [A]_0$.

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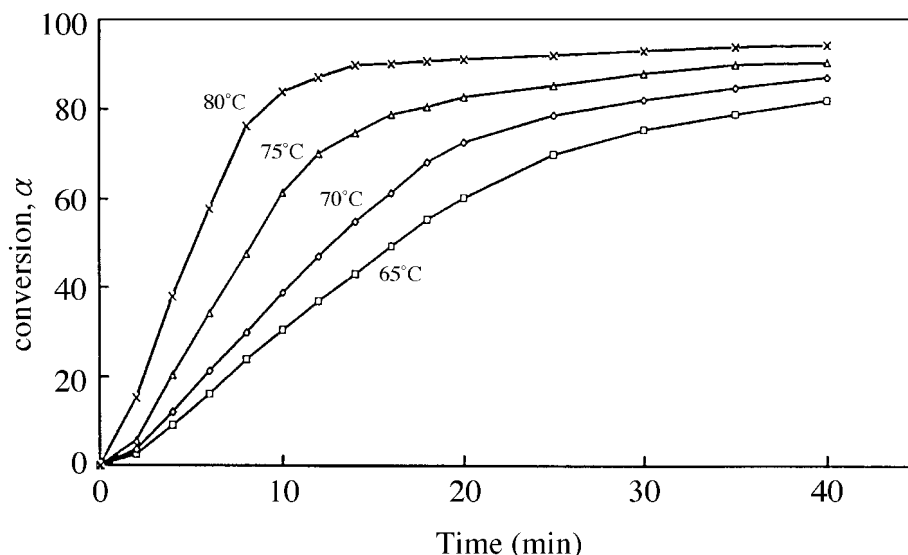


Figure 1. Plots of epoxide conversion, α , for pure DGEBA.

The initial concentrations of epoxide and amine in the pure DGEBA and 50/50 of BADA/DGEBA IPN are $4.76 \text{ mole litre}^{-1}$ and $2.70 \text{ mol litre}^{-1}$, respectively. Since one OH group is newly produced for each epoxide consumed, hence

$$[\text{OH}] = [\text{E}]_0 \alpha \quad (2)$$

and

$$[\text{E}] = [\text{A}] = [\text{E}]_0 (1 - \alpha) \quad (3)$$

where α is the conversion of epoxide. From eqns (1), (2), and (3), eqn (4) is obtained

$$\dot{\alpha} = d\alpha/dt = k_1[\text{E}]_0(1 - \alpha)^2 + k_2[\text{E}]_0^2 \alpha(1 - \alpha)^2 \quad (4)$$

Rearrangement of eqn (4) gives

$$\dot{\alpha}/(1 - \alpha)^2 = k_1[\text{E}]_0 + k_2[\text{E}]_0^2 \alpha \quad (5)$$

Typical plots of conversion α versus time for pure epoxide and epoxide in 50/50 of BADA/DGEBA IPN are given in Figs 1 and 2. The $\dot{\alpha}$ values (ie $d\alpha/dt$) are the slopes of each curve at specific time, and were

measured from Figs 1 and 2. Figure 3 shows the plots of $\dot{\alpha}/(1 - \alpha)^2$ versus α for epoxide in pure DGEBA. Figure 4 shows similar plots for the epoxide in a 50/50 mixture of BADA/DGEBA IPN. The values of $k_1[\text{E}]_0$ and $k_2[\text{E}]_0^2$ can be obtained from the intercept and slope for each of straight line, from which the rate constants k_1 and k_2 at various temperatures can be found. Plots of $\ln k_1$ and $\ln k_2$ versus reciprocal absolute temperature, according to the Arrhenius equation, give the corresponding activation energies (Figs 5 and 6). The calculated activation energies for non-catalyzed activation energy (E_1) and the OH catalyzed activation energies (E_2), together with k_1 and k_2 at various temperatures for the pure DGEBA and IPN are listed in Tables 1 and 2. It is noted that generally, the rate constant of the OH-catalyzed termolecular reaction, k_2 , is higher than that of the non-catalyzed reaction, k_1 , while the corresponding activation energy E_2 is lower than E_1 . In this study, we found that for the pure DGEBA, the activation energy of the OH-catalyzed termolecular reaction is $16.09 \text{ kcal mole}^{-1}$, while that of non-catalytic reaction

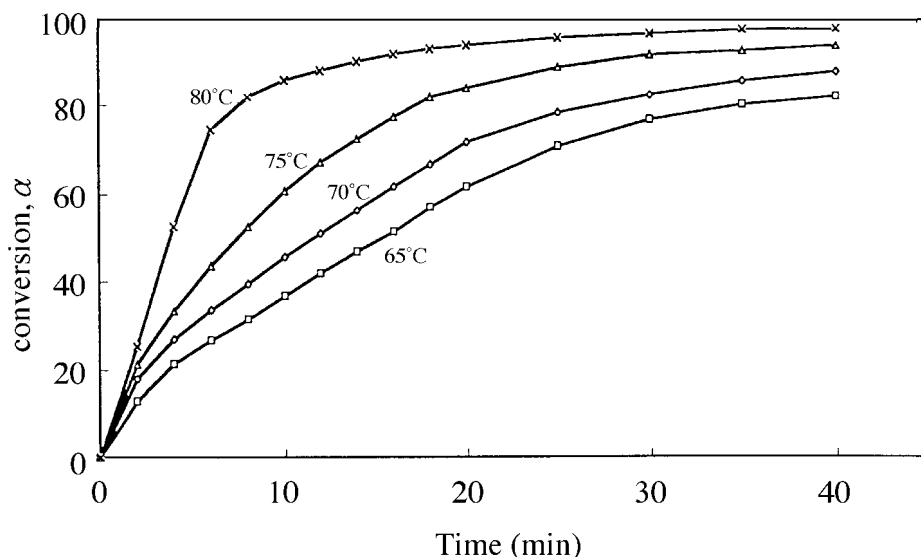


Figure 2. Plots of epoxide conversion, α , for BADA/DGEBA=50/50 IPN.

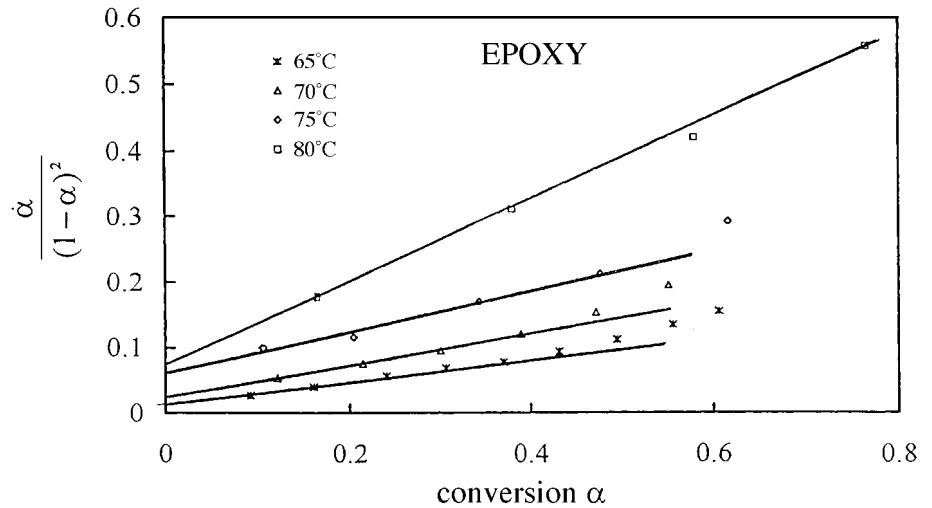


Figure 3. Plots of $\alpha/(1-\alpha)^2$ versus α for pure DGEBA.

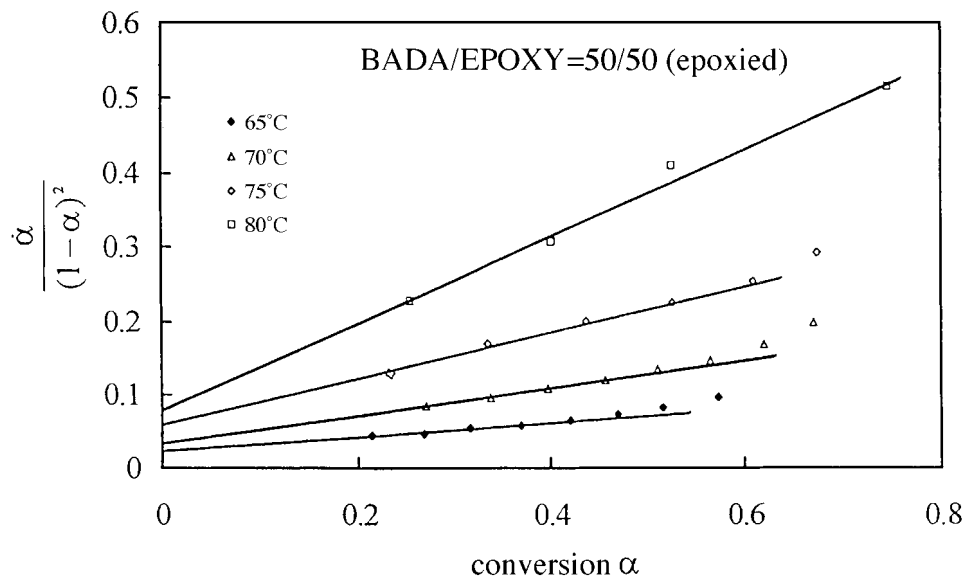


Figure 4. Plots of $\alpha/(1-\alpha)^2$ versus α for BADA/DGEBA=50/50 IPN.

is 22.21 kcal mole⁻¹. Riccardi, *et al.*,⁷ in their study of DGEBA cured with ethylenediamine (EDA) found an autocatalytic activation energy of 14 kcal mole⁻¹ and a non-catalytic activation energy of 24.5 kcal mole⁻¹,

while Moroni, *et al.* in their cure kinetics of epoxy resins and aromatic diamine, revealed a catalyzed activation energy of 13.5 kcal mole⁻¹ and a non-catalytic activation energy of 22.3 (± 0.2) kcal mole⁻¹.⁸ In addition, it

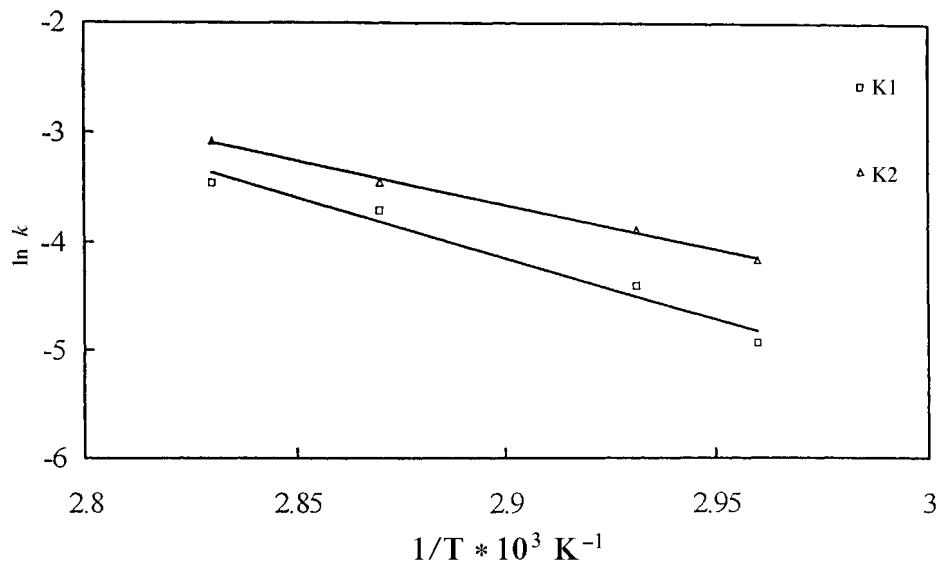


Figure 5. Plots of $\ln k_1$ and $\ln k_2$ versus $1/T$ for pure DGEBA.

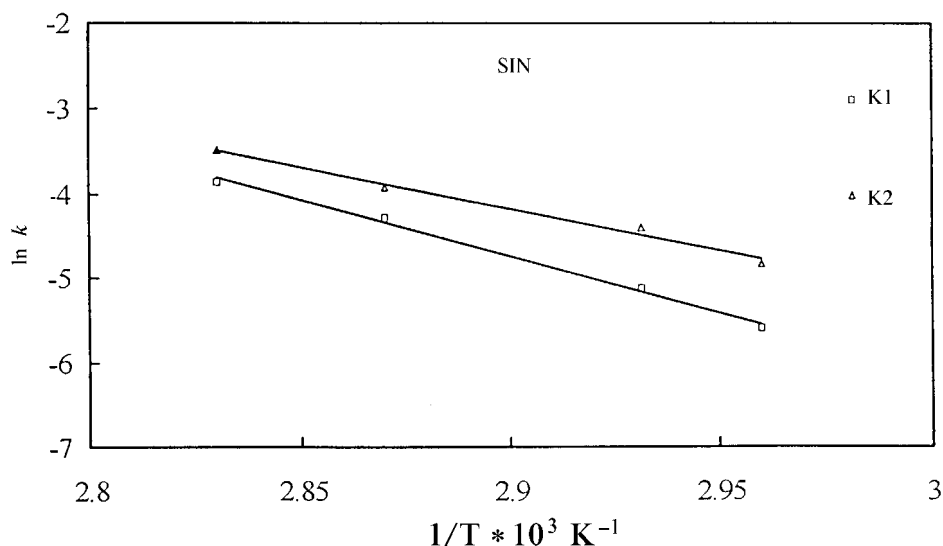


Figure 6. Plots of $\ln k_1$ and $\ln k_2$ versus $1/T$ for BADA/DGEBA=50/50 IPN.

is also noted that both k_1 and k_2 of the IPN are generally lower than those of pure DGEBA. On the other hand, both E_1 and E_2 of the IPN are generally higher than those of pure DGEBA. A possible interpretation of this unusual result could be due to the effect of entanglements between the two closely interlocked BADA and DGEBA networks. When one network is growing in the presence of the other growing network, the increased viscosity of the system and/or vitrification restrains the chain mobility in the highly sterically hindered environment, leading to an increase of activation energies and a decrease of rate constants.

Kinetics of the BADA cured by BPO

BADA cured by BPO follows the first-order free radical polymerization,^{12,13} assuming the homolysis of BPO is the rate-determining step for the initiation, and a steady-state reaches:

$$-d[M]/dt = k_p(k_d f[I]/k_t)^{1/2}[M] \quad (6)$$

Integration of eqn (3) gives

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

Where $[M]_0$ and $[M]$ are the concentration of C=C in BADA initially and at time t , respectively, and f is the initiator efficiency, $[I]$ is the initiator concentration, k_d is the dissociation rate constant of the initiator, and k_p and k_t are rate constants of chain propagation and termination. Assume that f and $[I]$ do not change too much at early stages of cure such that $k_p(k_d f[I]/k_t)$ is nearly constant as an approximation, and is equal to k , the result of eqn (4) can be expressed as

$$-\ln(1 - \alpha) = kt \quad (7)$$

Where, again, α is the conversion of C=C, with $[M] = [M]_0(1 - \alpha)$ by neglecting the C=C concentration after postcure. Figures 7 and 8 show the conversions of C=C for the pure BADA and for the BADA/DGEBA=50/50 IPN. Figures 9 and 10 show

Table 1. Kinetic parameters of epoxide in pure DGEBA

Temp (°C)	$k_1 * 10^3$ (L mol ⁻¹ min ⁻¹)	$k_2 * 10^3$ (L ² mol ⁻² min ⁻¹)	E_1 (k cal mol ⁻¹)	E_2 (k cal mol ⁻¹)
65	7.23	15.61		
70	12.28	20.44	22.21	16.09
75	24.48	31.74		
80	31.43	45.96		

$[E]_0 = [A]_0 = 4.76$ mol litre⁻¹.

Table 2. Kinetic parameters of epoxide in BADA/DGEBA=50/50 IPN

Temp (°C)	$k_1 * 10^3$ L mol ⁻¹ min ⁻¹	$k_2 * 10^2$ L ² mol ⁻² min ⁻¹	E_1 (kcal mol ⁻¹)	E_2 (kcal mol ⁻¹)
65	3.69	7.99		
70	5.98	12.28	26.71	19.64
75	13.84	19.84		
80	21.28	30.80		

$[E]_0 = [A]_0 = 2.70$ mol litre⁻¹.

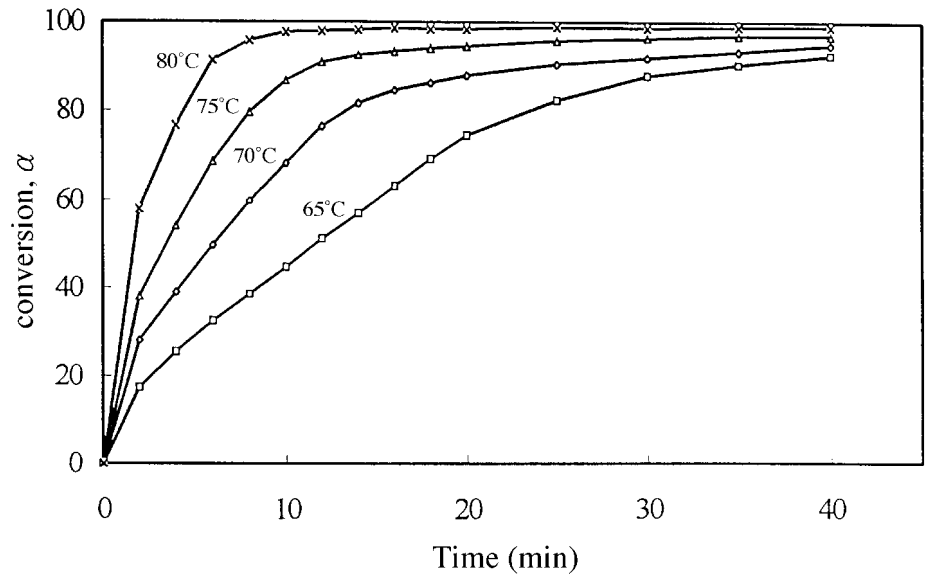


Figure 7. Plots of C=C conversion, α , for pure BADA.

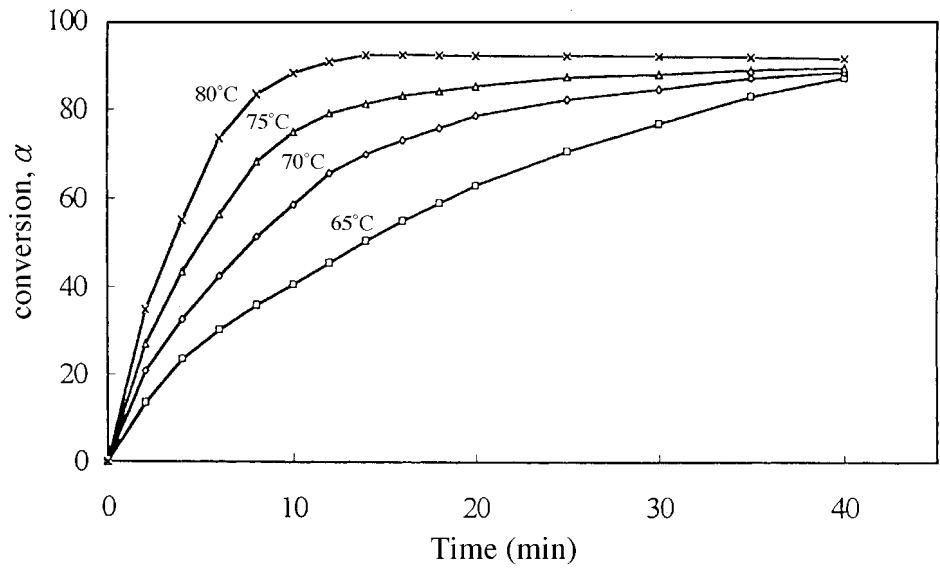


Figure 8. Plots of C=C conversion, α , for BADA/DGEBA=50/50 IPN.

that the plots of $-\ln(1-\alpha)$ versus time for the C=C in BADA and in IPN are straight lines at the early stages of cure reaction, while at the later stages,

deviations were observed in which, presumably, diffusion and other complicated effects, such as vitrification, were involved. It was found that full cure

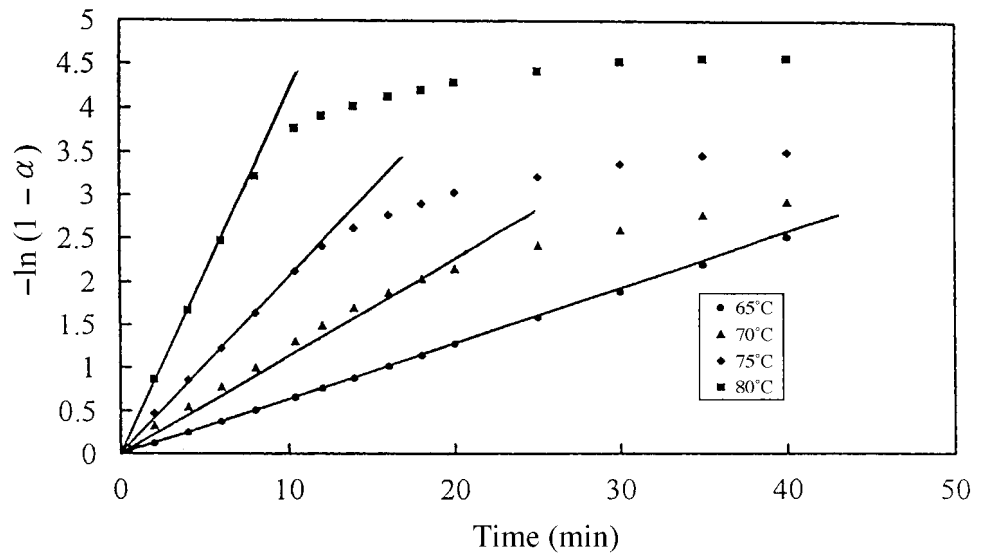


Figure 9. Plots of $-\ln(1-\alpha)$ versus time for pure BADA.

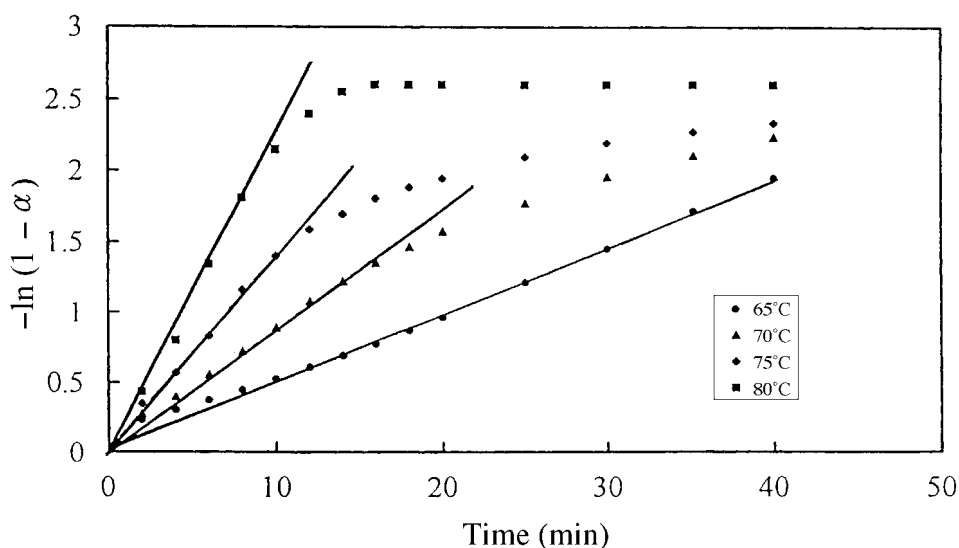


Figure 10. Plots of $-\ln(1-\alpha)$ versus time for BADA/DGEBA=50/50 IPN.

of the vinyl groups was not attained, presumably due to vitrification. The apparent rate constant at various temperatures, k , can be calculated from the slope of each line. Similarly, the activation energy can be measured from the Arrhenius plot (Fig 11). The kinetic parameters are listed in Table 3. Again, the IPN has lower apparent rate constant and higher activation energy than the pure BADA. It appears that the entanglements between the two respective networks provide a sterically hindered environment for the cure reaction and the increased viscosity and/ or vitrification of the IPN system restrains the chain mobilities and prevents diffusion of the reactive species, thus accounting for such a result.

CONCLUSIONS

In kinetic studies of BADA/DGEBA=50/50 IPN and the two individual components, the IPN displayed decreased rate constants with increased activation

Table 3. Comparison of C=C kinetic parameters for pure BADA and BADA/DGEBA=50/50 IPN

Temp ($^{\circ}\text{C}$)	k values	
	BADA (C=C)	SIN (C=C)
65	0.0750	0.0456
70	0.1160	0.0797
75	0.1957	0.1347
80	0.2516	0.2220
E_a (kcal mol $^{-1}$)	18.801	23.753

energies compared with the corresponding components. Chain entanglements between networks apparently provide a sterically hindered environment for the curing reactions and the increased viscosity and/ or vitrification restrains the chain mobility and prevents the diffusion of the reactive species account for the experimental results.

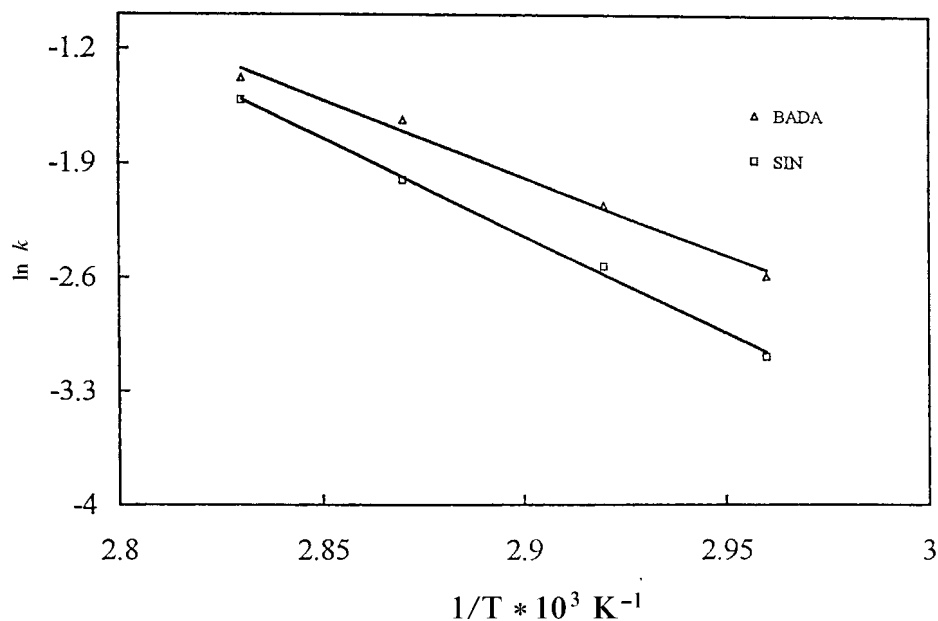


Figure 11. Plot of $\ln k$ versus $1/T$ for (A) pure BADA, and (B) BADA/DGEBA=50/50 IPN.

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