

Synthesis, Characterization, and Kinetic Study of Compatible SIN's Based on Diallyl Phthalate and Epoxy Resin

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SYNOPSIS

Diallyl phthalate (DAP) was blended with diglycidyl ether of bisphenol A (DGEBA) in various weight ratios: 100/0, 75/25, 50/50, 25/75, and 0/100. These blends were then cured simultaneously with dicumyl peroxide (DCP) and hexahydrophthalic anhydride (HHPA) in conjunction with 2-cyanoethyl-4-methyl imidazole (EMI-CN, 0.5% as catalyst) to obtain simultaneous interpenetrating polymer networks (SIN's). H-bonding between DAP and DGEBA was detected with FTIR. The SIN's thus obtained were characterized with rheometric dynamic spectroscopy (RDS) and differential scanning calorimeter (DSC) to check the compatibility of components. Gel fractions were measured with a Soxhlet extractor. Viscosity increases of all SIN's were measured with a Brookfield viscometer at curing temperatures. Conversions of C=C and epoxide versus cure time were monitored with FTIR and kinetic parameters were calculated and discussed. Experimental results revealed that H-bonding in the DAP/DGEBA blends was evidenced from the shift of the IR band ($\nu_{C=O}$) to a lower wave number, as well as the shift of epoxide band (ν_A) to a higher wave number. Complete compatibility between DAP and DGEBA was supported from the single damping peak in DRS and single glass transition in DSC for each of SIN's. Cure dynamic DSC showed shifts of exothermic peaks to higher temperatures for all SIN's. During SIN formation, the slower viscosity increases of SIN's were found, compared with pure DAP and pure DGEBA, indicating retarded cure rates for all SIN's. In addition, lower gel fractions of SIN's were observed, indicating incomplete cure of SIN's. The retarded cure rate was further confirmed by kinetic study. Lower rate constants with higher activation energies for all SIN's were found. An effect of network interlock was proposed to account for these findings. © 1993 John Wiley & Sons, Inc.

Keywords: network interlock • compatible • viscosity increase • SIN's

INTRODUCTION

Although interpenetrating polymer networks (IPN's) are members of the large "polyblends",¹⁻³ there is a significant difference between simple polyblends and IPNs. In general, multicomponent polyblends are more or less incompatible and thus are of microphase-separated structure. Compatible blends are not very common. To improve the compatibility of a given polymer pair, various attempts

have been made. The use of interfacial agents (compatibilizers)⁴ is one of the commonly employed approaches; the incorporation of an attractive group for polymer-polymer interaction is another.⁵ However, IPN's have unique characteristics in this regard. Crosslinking of either component tends to promote phase continuity. IPN materials with both polymers crosslinked tend to develop dual-phase continuity and thus improve the compatibility of the constituent polymers.

In our previous studies on compatible SIN materials,⁶⁻⁷ we found a much lower viscosity increase for SIN samples, compared with those of single constituent network formation. We proposed that network interlock probably played an important role

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in governing the viscosity increase and that this network interlock should affect the kinetics during SIN formation. To understand such a possible effect, we carried out the synthesis, characterization, and kinetic study of this compatible SIN system.

EXPERIMENTAL

Materials

Diallyl phthalate (DAP) and dicumyl peroxide (DCP) were purchased from TCI and Merck Co. DCP was recrystallized from ethanol/water (50/50 by volume) before use. Hexahydrophthalic anhydride (HHPA) and 2-cyanoethyl-4-methyl imidazole (EMI-CN) were obtained from Ta-Fan Co. (Taiwan) and were used (respectively) as curing agent and catalyst for DGEBA. Epoxy resin (DGEBA, Epikote 815) with an epoxy equivalent weight (EEW) of 194.5 was bought from Shell Co.

Instruments

A FTIR spectrometer (Nicolet model 520) with a resolution of 0.5 cm^{-1} was used to detect H-bonding. Samples were cast on KBr plates and were sandwiched. Conversion (α) of $\text{C}=\text{C}$ bond and epoxide were obtained from the FTIR difference spectra ($A_t - A_0$), using 1598 cm^{-1} (benzene absorption) as the internal standard:

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

where A_0 , A_t , and A_∞ are absorbance of $\text{C}=\text{C}$ (1645 cm^{-1}) or epoxide (830 cm^{-1}) before cure, at cure time t , and after postcuring respectively; and C_0 , C_t , and C_∞ are the concentrations of functional group at each corresponding time.

DSC thermograms were recorded with a Seiko model AM 100 instrument, ranging from room temperature to 350°C , at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Dynamic mechanical

behaviors of SINs were obtained with a RDS, Rheometric II, at 1 Hz of frequency, temperature ranged from -100 to 200°C . Gel fractions were measured with a Soxhlet extractor for 48 h continuous extraction with acetone as a common solvent for both DAP and DGEBA. Viscosity changes during SIN formation were measured with a Brookfield viscometer at different curing temperatures: 120, 130, 140, and 150°C . Samples were prepared by casting the SIN's in molds and cured at the aforementioned temperatures.

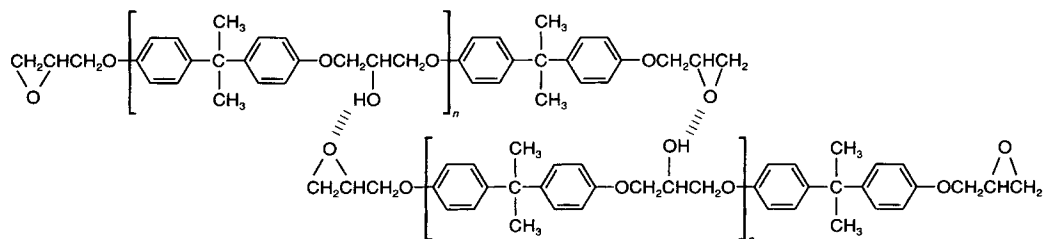
Preparation of SIN's

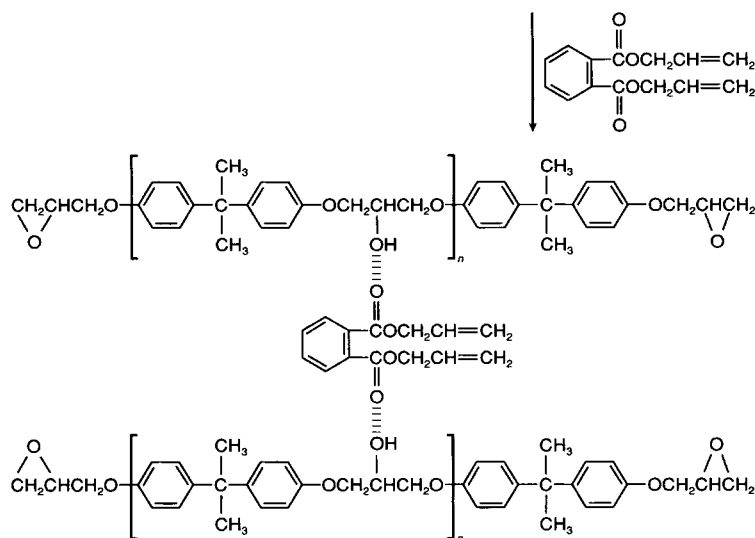
The liquid DAP was blended with liquid DGEBA in different weight ratios: 100/0, 75/25, 50/50, 25/75, and 0/100. DCP (1% based on DAP), HHPA (based on stoichiometric EEW of DGEBA), and EMI-CN (0.5% based on total weight of DGEBA and HHPA) were mixed to each blend. All blends were cast in molds and were cured simultaneously at 120°C for 8 h. The SIN's were further postcured at 180°C for 2 h.

RESULTS AND DISCUSSION

The calculated solubility parameters for DAP, DGEBA, and HHPA by Frisch's method⁹ are 9.39, 9.98, and 9.43, respectively. The close solubility parameters would predict a possible miscibility of the three components. Fischer also reported the effect of solubility parameter and glass transition on the morphology of SINs to predict fully micissible IPNs.¹⁰

FTIR spectra indicated that the original absorption peak of the unbonded $\text{C}=\text{O}$ bond in DAP occurred at 1729.8 cm^{-1} , while the original absorption peak of H-bonded epoxide in DGEBA occurred at 915.6 cm^{-1} . When various ratios of DAP/DGEBA were mixed, a new intermolecular H-bonding between $\text{C}=\text{O}$ of DAP and OH group of DGEBA replaced the original intramolecular H-bonding in DGEBA as shown by the following:





Therefore, the carbonyl peak shifted to a lower wave number (Fig. 1), while the epoxide peak shifted to a higher wave number (Fig. 2). Table I lists the exact wave numbers of carbonyl and epoxide peaks for the various DAP/DGEBA ratios. Since the resolution of the FTIR was set at 0.5 cm^{-1} , and the exact peak location was found by the instrument

searching system, the result is believed to be reliable. This intermolecular H-bonding is believed to further promote the miscibility of DAP and DGEBA in molecular scale.

Figure 3 shows the dynamic DSC thermograms of the SIN curing behaviors. DAP (curve A) shows a maximum exothermic peak at 183.7°C , while the maximum exothermic peak of DGEBA occurs at a lower temperature of 171.3°C (curve E). Surprisingly, when DGEBA and DAP were mixed and

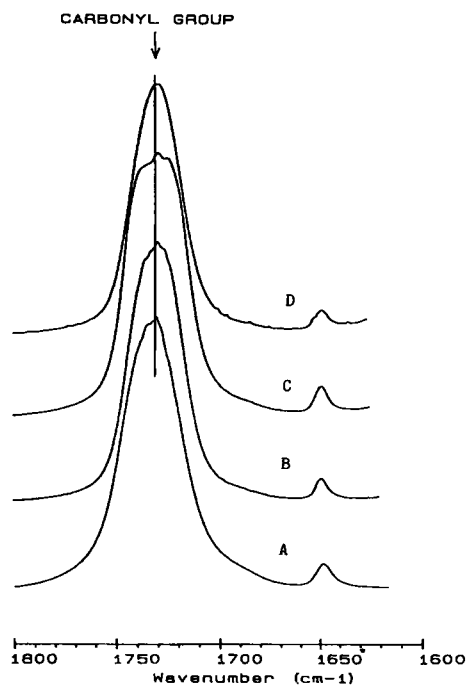


Figure 1. Shift of absorption peak for $\text{C}=\text{O}$ bond in FTIR. DAP/DGEBA = (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75.

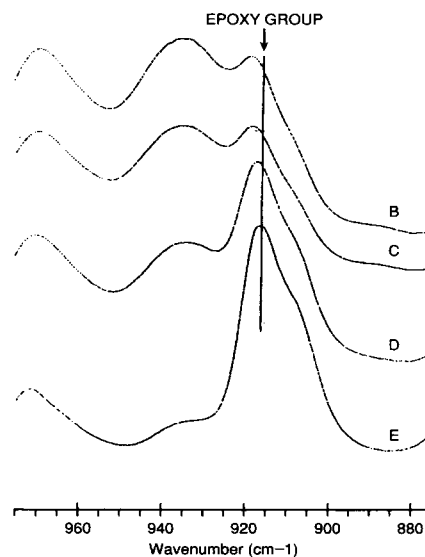


Figure 2. Shift of absorption peak for epoxide group in FTIR. DAP/DGEBA = (A) 75/25, (B) 50/50, (C) 25/75, (D) 0/100.

Table I. Shifts of C=O and Epoxide Groups in FTIR Spectra

Sample No.	Ratio of DAP/DGEBA	Peak of C=O (cm ⁻¹)	Peak of Epoxide (cm ⁻¹)
A	100/0	1729.8	—
B	75/25	1729.5	919.0
C	50/50	1729.2	918.3
D	25/75	1728.9	917.0
E	0/100	—	915.6

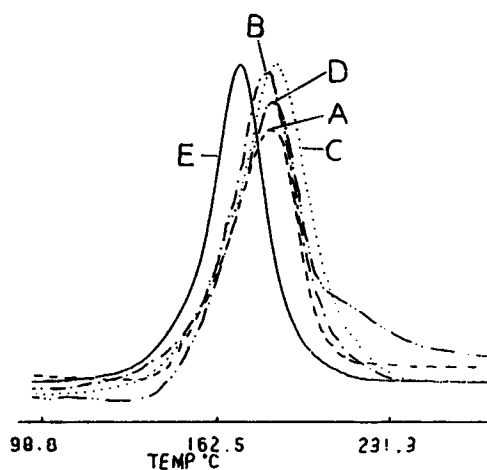
cured, the maximum exothermic peak shifted to a higher temperature. The SIN's of DAP/DGEBA = 75/25, 50/50, and 25/75 shifted maximum peaks to 184, 187.2, and 185.5°C, respectively. As mentioned earlier, the intermolecular H-bonding probably restricted chain mobilities of both DAP and DGEBA. Furthermore, an additional barrier due to possible network interlock (mutual entanglement) would provide a sterically-hindered environment for cure reactions. Network interlock and decreased chain mobility would retard cure rates and could be possibly compensated by raising the cure temperature; therefore, higher maximum curing peaks were observed for all SIN's. Other similar phenomena were found in our laboratory.⁶ The observed exothermic peaks are all single shapes; presumably all samples are of homogeneous single-phase materials.

Figure 4 shows the RDS of the SIN samples. A maximum damping peak at 182°C for DAP (curve A) and a maximum damping peak at 103°C for DGEBA (curve E) are found. Each of other SIN's indicates a single damping peak at 100°C (curve B, DAP/DGEBA = 75/25), 70°C (curve C, DAP/DGEBA = 50/50), and 98°C (curve D, DAP/DGEBA = 25/75). Table II lists the gel fractions for the SIN system. Each SIN apparently shows a lower gel fraction than its components, especially for the SIN of equal parts of components (sample C), presumably because large steric hindrance due to network interlock make it difficult to complete cure. Sample C is believed to have the largest extent of network interlock during cure reaction because it contained the largest extent of chain entanglement between DAP and DGEBA. Therefore, sample C is expected to be the most difficult for complete cure, thus showing the lowest gel fraction.

Acetone is a common solvent for both uncured DAP and DGEBA. After SIN samples were continuously extracted with acetone for 2 days, the extracted samples indicated higher T_g 's than the cor-

responding nonextracted ones. Figure 5 shows DSC thermograms of SIN's for both extracted and non-extracted samples. It is noted that all samples have single T_g 's, indicating good compatibility between DAP and DGEBA. Nonextracted DAP has a T_g 's of 127.5°C, compared with 130.6°C for the extracted sample; while nonextracted DGEBA has a T_g of 95.8°C, compared with 98.3°C for the extracted DGEBA. Nonextracted compositions B (DAP/DGEBA = 75/25), C (DAP/DGEBA = 50/50), and D (DAP/DGEBA = 25/75) have T_g 's of 97.2, 91.8, and 95.3°C, respectively; while the corresponding extracted samples have T_g 's of 103.5, 97.9, and 98.5°C, respectively. Clearly, nontracted samples have lower T_g 's, presumably, partly because the uncured DAP and/or DGEBA act as plasticizers to the SIN's. Furthermore, since SIN's have lower gel fractions, they may contain lower crosslinking densities, thus significantly lowering the transition temperatures as observed in RDS and DSC. Again, composition C shows the lowest T_g and lowest damping peak, because it contains the lowest gel fraction, due to the possible highest extent of network interlock between DAP and DGEBA. Both RDS and DSC evidence are in good agreement and strongly support the compatibility of the SIN system. One single transition for each SIN suggested that each SIN is of single-phase material. This argument agrees well with Fischer's report dealing with the effect of solubility parameter and glass transition to predict fully miscible IPNs.¹⁰

Figure 6 shows the viscosity increases of the SIN's cured at 150°C. DGEBA (curve E) shows the fastest

**Figure 3.** Exothermic curing peaks for SINs. DAP/DGEBA = (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

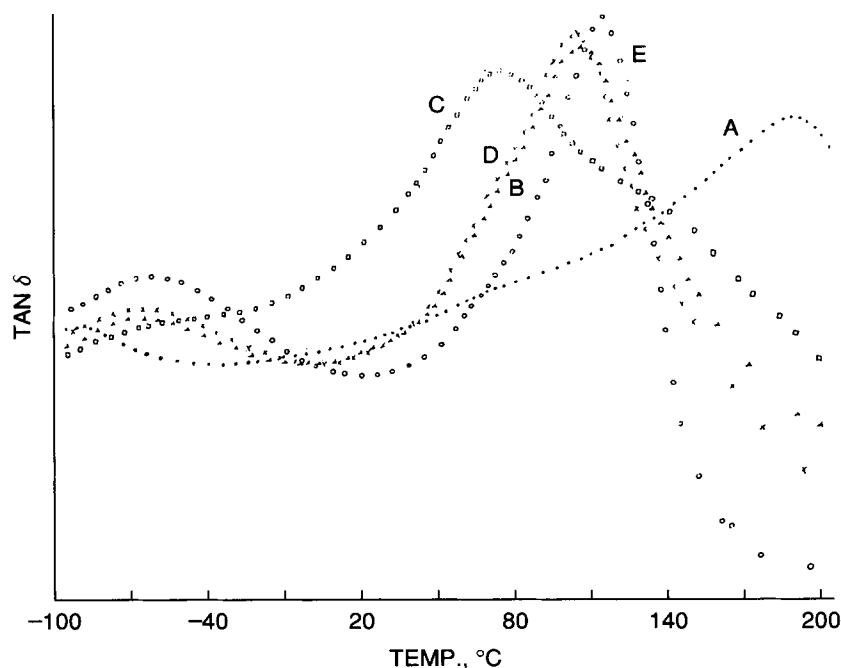


Figure 4. Damping peaks in RDS for SINs. DAP/DGEBA = (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

viscosity increase with a pot-life of 8 min. DAP (curve A) also indicates a fast cure behavior with a pot-life of 10 min. For the other SIN's, the viscosity increases are much slower. Compositions B, C, and D have a pot-life of 15, 17, and 13 min, respectively. It is noted that composition C indicates the slowest viscosity increase with the longest pot-life presumably because it has the largest extent of network interlock as discussed earlier. Again, the network interlock has a measurable effect on viscosity increase during cure reactions. Figure 7 shows the viscosity increases of the SIN's cured at 120°C. By comparison with 150°C, the initiator DCP decomposed at a much slower rate at 120°C, and the relatively low concentration of peroxide caused DAP

cure at a lower rate, subsequently reflecting in a slower viscosity increase with a longer pot-life. Apparently, the cure rate of DAP largely dominated the viscosity increases of the SINs. Thus, the more DAP the SIN contains, the longer the pot-life it has. Nevertheless, the effect of network interlock on the slower viscosity increase is obvious for compositions B and C.

Figures 8(a) and 8(b) show typical difference spectra of epoxide and C=C bond. Figures 9(a) and 9(b) show plots of epoxide conversions versus cure time for DGEBA and for SIN's. It is noted that, in general, DGEBA has higher cure rate than SIN's. Many studies on kinetics of DGEBA cured by anhydride can be found in the literature.¹¹⁻¹⁶ Tanaka

Table II. Summary of Gel Fractions, Maximum Curing Peaks, Damping Peaks, and Glass Transitions

Sample (DAP/DGEBA)	Maximum Curing Peak (°C)	Gel Fraction (%)	RDS Peak (°C)	T_g (°C)	
				Nonextracted	Extracted
A (100/0)	183.7	95.57	182	127.5	130.6
B (75/25)	184.0	92.48	100	97.2	103.5
C (50/50)	187.2	91.65	70	91.8	97.9
D (25/75)	185.5	93.15	98	95.3	98.5
E (0/100)	171.3	97.40	103	95.8	98.3

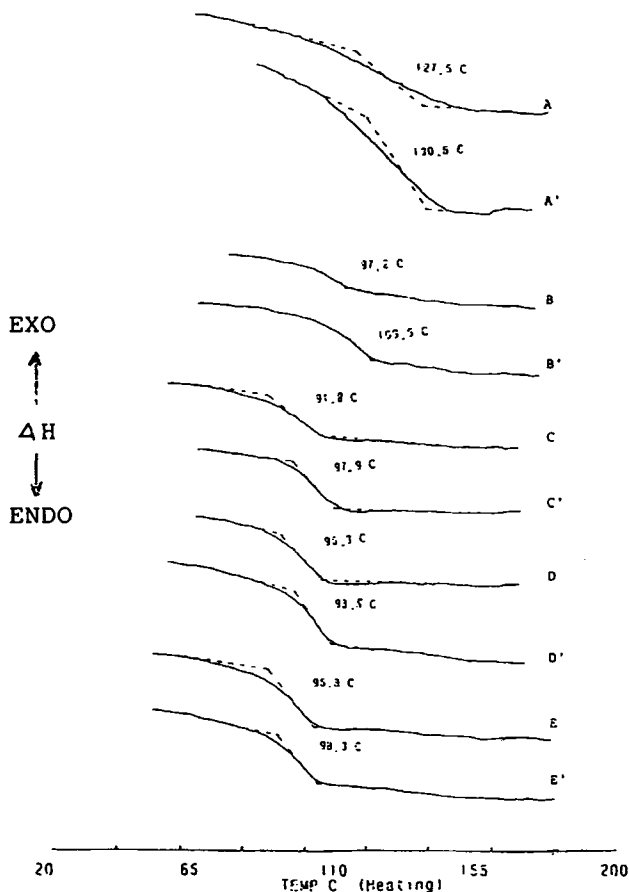


Figure 5. DSC thermograms showing T_g 's for nonextracted (A, B, C, D, E) and extracted (A', B', C', D', E') SIN's. Same compositions as in Figure 4.

and Kakiuchi reported a first order on epoxide when DGEBA was cured by HHPA with tri-2,4,6-dimethylaminomethyl phenol;¹⁵ while they reported a third order on epoxide when DGEBA was cured by HHPA with triethylamine (catalyst) and alcohol (cocatalyst).^{11a} In a case where epoxide was cured by HHPA in conjunction with tertiary amine as catalyst, Fischer¹⁰ and Antoon and Koenig¹² found a zeroth order on epoxide with the reaction rate depending only on the catalyst (a tertiary amine). We found that when DGEBA was cured with an equimolar mixture of HHPA alone, the cure rate was too sluggish to be detected. Therefore, 0.5% of EMI-CN (a tertiary amine), was added as a catalyst in our experiment. Kinetic data were tested and applied to different orders of epoxide. However, the best-fitted rate expression was a zeroth order on epoxide up to about 70% of conversion; beyond 70%, deviations were found. Our result is in good agreement with

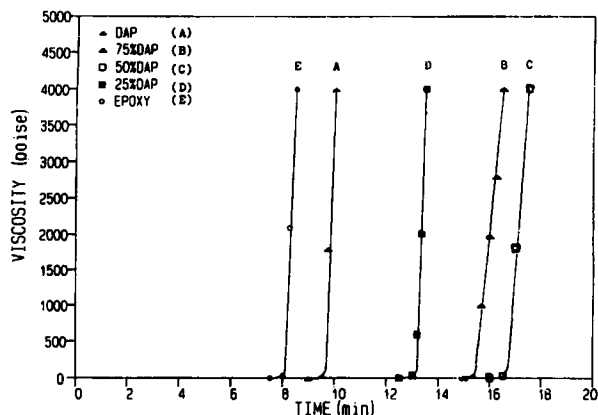


Figure 6. Viscosity increases for SIN's cured at 150°C. DAP/DGEBA = (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

the reports of Fischer¹⁰ and Antoon and Koenig.¹² The kinetic data fitted a zeroth order on epoxide:

$$-d[E]/dt = k \quad (1)$$

Integration of this expression gives

$$\alpha = kt/([E]_0 - [E]_\infty) \approx kt/[E]_0 \quad (2)$$

by neglecting epoxide concentration after postcure, $[E]_\infty$. Here $[E]_0$, $[E]$, and k are the concentration of epoxide at initial, time t , and rate constant, respectively. The value of $k/[E]_0$ can be obtained from slopes of straight lines at various temperatures [Fig. 9(a) and 9(b)]. Activation energies for DGEBA and for each SIN can be calculated from an Arrhenius

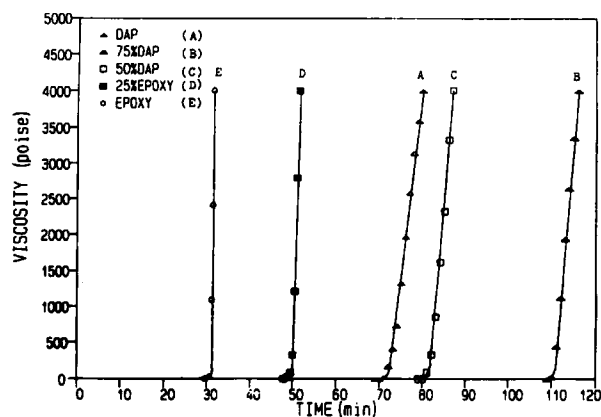


Figure 7. Viscosity increases for SIN's cured at 120°C. DAP/DGEBA = (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

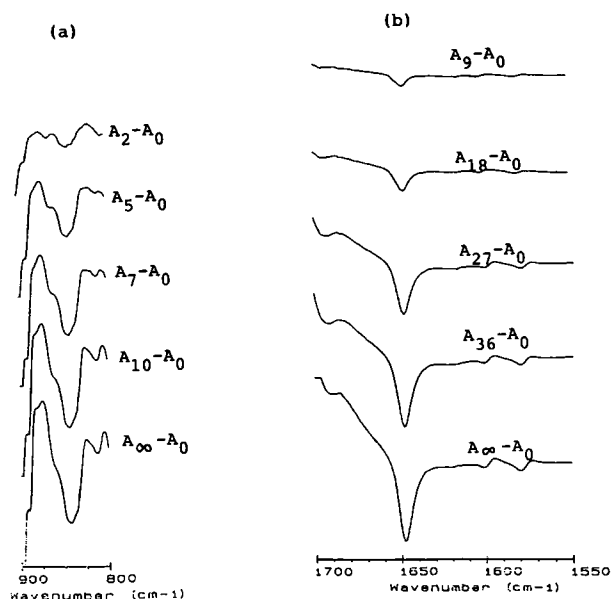


Figure 8. (a) Typical difference spectra of epoxide at 830 cm⁻¹, ($A_t - A_0$), and (b) difference spectra of C=C bond at 1645 cm⁻¹, using the absorbance of benzene at 1598 cm⁻¹ as internal standard (t , in minutes).

plot (Fig. 10). The calculated kinetic parameters for epoxide are given in Table III. By comparison with DGEBA, lower rate constants with higher activation energies were found for all SIN's. It is also noted that the more DAP the SIN contains, the lower rate constant and the higher activation energy the SIN has. This is probably due to an increase in steric hindrance when another DAP network is present during curing of DGEBA, i.e., the network interlock effect. Network interlock not only provides a sterically-hindered environment for cure reactions, but also may restrain DGEBA chain mobility and, consequently slow down the cure rate of DGEBA. This lower rate constant with higher activation energy for SIN accounts for the slow viscosity increase for SINs (Fig. 6 and 7). This difficulty of SIN cure may also interpret the lower gel fractions (Table II) for SIN's.

Figure 11(a) shows plots of conversion of C=C bond for DAP versus time at various temperatures. Figure 11(b) shows similar plots for a typical SIN composition of 50/50 in DAP/DGEBA ratio. Again, by comparing Figures 11(a) and 11(b), pure DAP showed a higher cure rate than other SIN's. Our data indicated a first order in C=C bond when DAP was cured with DCP, which is in accordance with a normal polymerization of vinyl monomer:¹⁷

$$-d[M]/dt = k_p(k_d f[I]/k_t)^{1/2}[M] \quad (3)$$

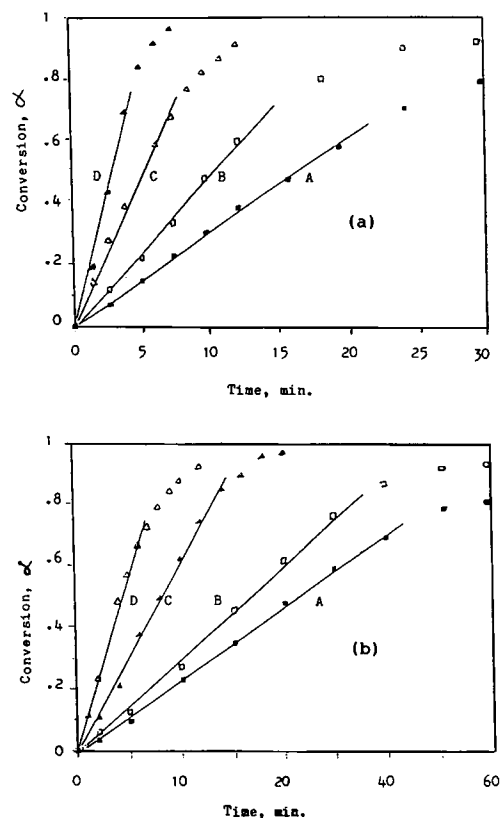


Figure 9. Plots of epoxide conversions versus cure time at different temperatures for (a) DGEBA and (b) SIN's: (A) 120°C, (B) 130°C, (C) 140°C, (D) 150°C.

where $[I]$ is initiator concentration, f is initiator efficiency, k_d is the dissociation constant of initiator, and k_p and k_t are rate constants of chain propagation and chain termination, respectively.

Integration of eq. (3), gives:

$$-\int_{[M]_0}^{[M]} d[M]/[M] = \int_0^t k_p(k_d f[I]/k_t)^{1/2} dt \quad (4)$$

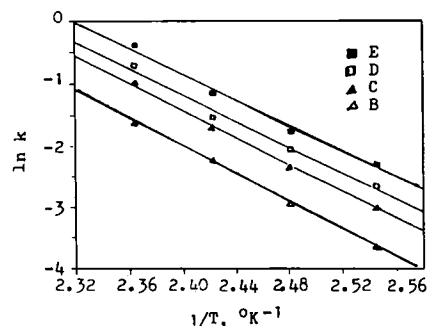


Figure 10. Plots of $\ln k$ vs. $1/T$ for epoxide and SIN's of various compositions. DAP/DGEBA = (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

Table III. Kinetic Parameters for Epoxide in DGEBA and SIN's

Sample (DAP/DGEBA)	$k \times 10^4$ (mol L ⁻¹ s ⁻¹)				E (kcal/mol)
	120°C	130°C	140°C	150°C	
B (75/25)	1.38	2.58	5.28	9.56	22.51
C (50/50)	4.88	9.33	17.5	35.5	21.66
D (25/75)	10.2	18.7	31.8	71.7	20.94
E (0/100)	20.1	33.2	62.7	130.0	20.49

Assume that at early stages of cure reaction, the initiator efficiency f and initiator concentration $[I]$ did not change too much, then $k' = k_p(k_d f [I]/k_t)^{1/2}$ is nearly constant, and eq. (4) becomes:

$$-\ln(1 - \alpha) = k't \quad (5)$$

Figures 12(a) and 12(b) show the plots of $-\ln(1 - \alpha)$

$-\alpha$) vs. t for DAP and for the SIN of DAP/DGEBA = 50/50. It was found that the experimental data fitted a first order up to about 30% of conversion for DAP. Beyond 30%, a deviation was observed, presumably because of the variety in f and $[I]$ and the gel effect.¹⁷ Willard, in his kinetic study of DAP with DSC, also reported a first order on DAP.¹⁸ The kinetic data for SIN of DAP/DGEBA = 50/50 fit the first order of C=C bond only up to 20% of

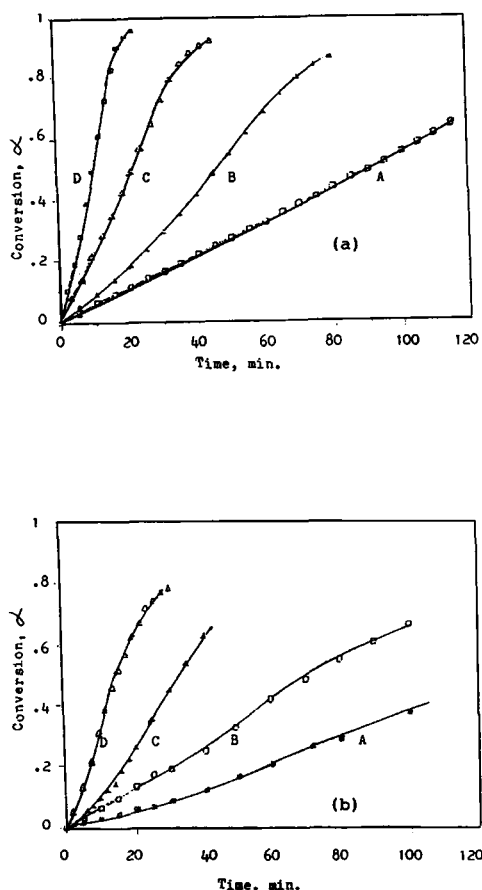


Figure 11. (a) Plots of conversions of C=C bond versus cure time for DAP and (b) the same plots for SIN of DAP/DGEBA = 50/50: (A) 120°C, (B) 130°C, (C) 140°C, (D) 150°C.

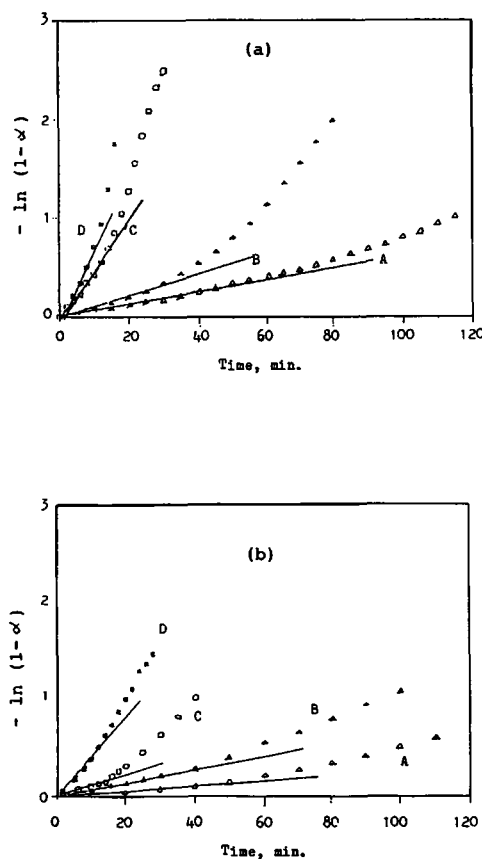


Figure 12. (a) Plots of $-\ln(1 - \alpha)$ versus time for DAP and (b) the same plots for SIN of DAP/DGEBA = 50/50: (A) 120°C, (B) 130°C, (C) 140°C, (D) 150°C.

Table IV. Kinetic Parameters for C=C Bond in DAP and SIN's

Sample (DAP/DGEBA)	$k' \times 10^5 \text{ (s}^{-1}\text{)}$				E' (kcal/mol)
	120°C	130°C	140°C	150°C	
A (100/0)	9.20	19.2	63.2	109	27.27
B (75/25)	5.74	12.9	25.9	70.9	27.71
C (50/50)	3.59	9.03	20.1	46.9	28.37
D (25/75)	2.87	8.10	18.7	42.1	29.69

conversion; the gel effect probably shifted to an earlier stage during SIN formation because network interlock restrained chain mobility and diffusion control occurred earlier. The apparent rate constant k' at various curing temperatures can be found from the slope of each line (Fig. 12). A plot of $\ln k'$ versus reciprocal absolute temperature $1/T$ gives the apparent activation energy E' (Fig. 13), with $E' = E_p + \frac{1}{2}(E_d - E_t)$. Here E_d is the activation energy of initiator dissociation, and E_p and E_t are activation energies of chain propagation and chain termination, respectively.^{17a} The results of kinetic parameters for DAP and SINs are listed in Table IV.

Again, it is noted that SINs indicates lower apparent rate constants with higher activation energies than pure DAP. The more DGEBA the SIN contains, the lower the apparent rate constant and the higher the apparent activation energy the SIN has. The effect of network interlock was again observed and this effect accounts for the slow viscosity increase (Figs. 6 and 7) and lower cure rates for SIN's compared with pure DAP [Figs. 11(a) and 11(b)].

CONCLUSIONS

Close solubility parameters and H-bonding between DAP and DGEBA predicted this SIN system in

complete compatibility. The observed single damping peak in RDS and single T_g in DSC for each SIN strongly supported complete compatibility of the SIN's. During SIN formation, the restriction of chain mobilities and network interlock between DAP and DGEBA were compensated by the higher temperature cure as it was observed from the shift of exothermic curing peaks to higher temperature. The network interlock also provided a sterically-hindered environment for the curing reactions. Therefore, a lower viscosity increase due to retarded cure reaction and incomplete cure were observed during SIN formation, which subsequently led to a lower gel fraction for all SIN's. Because of incomplete cure, SIN's contained lower gel fractions, and, the uncured DAP and/or DGEBA acted as plasticizers in SIN's. Thus, SIN's have lower damping peaks in RDS and lower T_g 's in DSC.

The network interlock is also reflected in the lower rate constant with higher activation energy for SIN as found from the kinetic study of epoxide and C=C bond.

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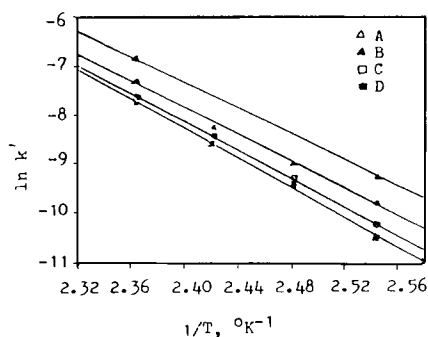


Figure 13. Plot of $\ln k'$ versus reciprocal absolute temperatures $1/T$ for DAP and SIN's of various compositions.

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