

The Effect of Resin Chemistry on the Curing Behavior and Chemorheology of Unsaturated Polyester Resins

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Synopsis

The effect of the structure of unsaturated polyester resin on its curing and rheological behavior during isothermal cure has been investigated, using three different grades of resin. In the investigation, the structure of the resins was determined, using nuclear magnetic resonance spectrometry (NMR), together with chemical analysis. Both a differential scanning calorimeter (DSC) and an infrared (IR) spectrometer were used to determine the curing kinetics, and a cone-and-plate rheometer was used to determine the variation of rheological properties during isothermal cure. On the basis of the experimental study, we have concluded: (1) at the same styrene-to-fumarate mole ratio, the resin having isophthalates cures slower than the one having none; (2) everything else being equal, the resin having a high styrene-to-fumarate mole ratio cures faster than the resin having a low one; (3) the higher the concentration of initiator, the faster a resin cures. It has been found that a resin that cures faster does not necessarily achieve a higher final degree of cure than one that cures slowly. We have found that a mechanistic kinetic model developed in our previous investigation is very useful for investigating the reactivity of unsaturated polyester resin, by determining the rate constant and activation energy of the propagation reaction. On the basis of rheological investigation, we have concluded that both $t_{\eta_{\infty}}$ determined from steady shearing flow measurement and $t_{\tan \delta = 1}$ determined from oscillatory shearing flow measurement may be used as a measure of gel time.

INTRODUCTION

Unsaturated polyester resin is very versatile in its applications. It is used in the fabrication of a broad range of products, including structural parts of automobiles, boat hulls, building materials, coating materials, electrical parts, and appliances. Consequently, there are a variety of resin formulations, depending on specific applications, as well as on fabrication processes. For instance, unsaturated polyester resin and its composites may be processed using spray-up, decorative coating, compression molding, transfer molding, injection molding, pultrusion, and reaction injection molding. More recently, industry has developed ultraviolet(UV)-curable resin, interpenetrating network-type resins, and also reaction injection-moldable resins. Formulations are very tightly guarded by the industries concerned.

In general, unsaturated polyester resin is polymerized by condensation reactions of mixtures of saturated and unsaturated decarboxylic acids with glycols. It is then diluted with unsaturated monomer (e.g., styrene). Variations

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in the type and amounts of individual components allow an enormous flexibility in the design of resin formulations. For example, it is generally known that a resin having isophthalates gives improved water and chemical resistances and high heat distortion temperatures.

The amount of fumarates and the type of saturated acids and glycols used in the preparation of unsaturated polyester resin have a profound influence on its curing behavior as well as on the physical properties of the final products. It has been reported, for instance, that the amount of fumarates in unsaturated polyester resin affects its rate of cure and the physical properties of the cured specimens.^{1,2} The amount of unsaturated monomer in a resin formulation also affects the curing behavior of unsaturated polyester resin.^{3,4}

The purpose of this paper is to report our recent investigation on the effect of resin structure on curing behavior and the variation of rheological properties during isothermal cure.

EXPERIMENTAL

Three different grades of proprietary unsaturated polyester resins were used in this study. The following analytical techniques were used to characterize the structure of the resin: (1) the acid number was determined by titrating the chain ends of the resin with potassium hydroxide (KOH), and the number-average molecular weight (\bar{M}_n) was determined by following the procedure described in a paper by Han and Lem;⁵ (2) nuclear magnetic resonance (NMR) spectroscopy was employed to determine the various constituents in the resins. As initiator, *tert*-butyl perbenzoate (Pennwalt Corporation) was used to cure the resins. In all cases, the resin/initiator ratio was 100/1 on a weight basis.

Differential scanning calorimetry (DSC) was used to investigate the curing behavior of resin, using a DuPont 1090 Thermal Analyzer equipped with a 910 DSC module. The experimental procedures used were the same as those described in a paper by Han and Lem.⁵ For each sample investigated, isothermal DSC runs were made at 110, 120, and 130°C. Following an isothermal run, the sample was further heated to 200°C at a heating rate of 10°C/min.

In order to accurately determine the degree of cure, infrared (IR) spectroscopy was used to determine the number of double bonds in a resin system before cure began and the amount of residual double bonds after the sample was postcured (i.e., after the completion of isothermal cure followed by the heating of the sample to 200°C). This information, together with the information on the heat generated in the isothermal runs, was used to determine the rate of cure, as well as the degree of cure, during the entire period of the isothermal cure.

The glass transition temperature of the resins was also determined, using a DuPont 1090 Thermal Analyzer equipped with a DuPont 982 Dynamic Mechanical Analyzer (DMA) module. For this, resins were first cured in a silicone mold at 120°C in an air-heated oven for 1 hour, then heated up to 150°C and kept there for 12 hours.

For rheological measurements, both steady and oscillatory shearing flow properties were determined, using a Model 16 Weissenberg rheogoniometer

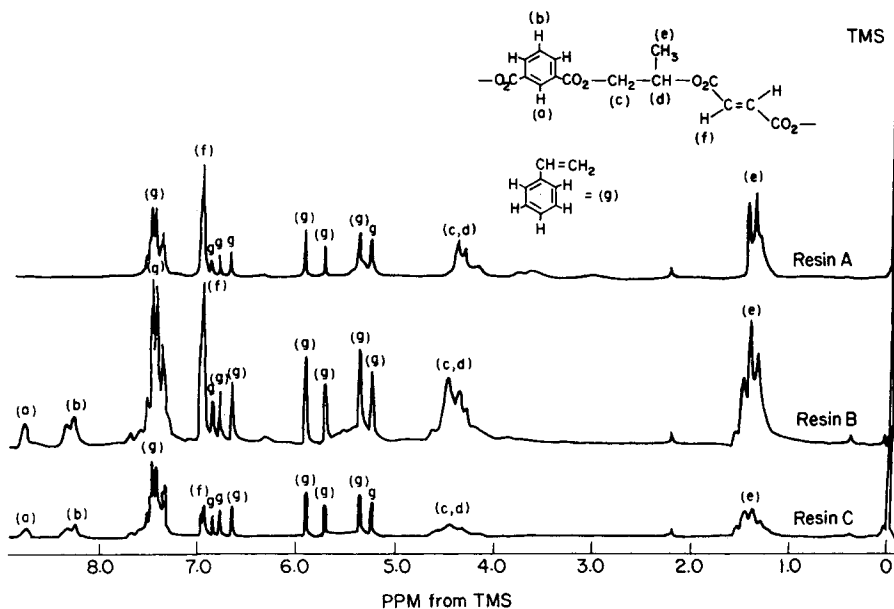


Fig. 1. NMR spectra of the resins investigated.

(Sangamo Controls). The experimental procedures used were the same as those described in the paper by Han and Lem.⁵

RESULTS AND DISCUSSION

The Resin Structure

The NMR spectra of the three resins investigated are given in Figure 1 in which, for identification purposes, the structure of the constituent components in each resin system is described. It is seen in Figure 1 that there is isophthalate in Resins B and C, but none in Resin A. Moreover, Resin B has more isophthalate than Resin C. Following the procedure suggested by Percival and Stevens,⁶ a semiquantitative determination of various constituents in the respective resin was performed and the results are summarized in Table I.

As may be seen in Table I, we have found that the mole fraction of propylene glycol was not the same as the sum of the mole fractions of

TABLE I
The Structure of Unsaturated Polyester Resins Determined by NMR

	Identification used	Mole fractions of constituents		
		Resin A	Resin B	Resin C
Isophthalates	(a, b)	—	0.063	0.118
Propylene glycol	(c, d)	0.372	0.391	0.294
Fumarates	(f)	0.350	0.266	0.190
Styrene	(g)	0.278	0.281	0.398

TABLE II
 Characteristics of the Unsaturated Polymer Resins Used

	Resin A	Resin B	Resin C
Acid number	34	18	10
Mole ratio of glycol/fumarate/ isophthalate	50/50/00	50/40/10	50/31/19
Mole ratio of styrene/fumarate	0.79/1.0	1.06/1.0	2.09/1.0
Molecular weight (\bar{M}_n)	3,300	6,200	11,200

isophthalates and fumarates in the resin. We speculate that this is attributable to the addition of other types of glycols and saturated acids, in order to impart certain properties desired in the cured resin. Since these resins contain proprietary ingredients, we have no way of confirming our speculation at this time. Therefore, we have assumed that the ratio of glycols to dicarboxylic acids is 1.0 in determining the mole ratio of glycol to fumarate to isophthalate, and the results are summarized in Table II. It is seen in Table II that, among the three resins, Resin C has the largest amount of isophthalates and the highest styrene-to-fumarate mole ratio. This information is very useful for interpreting the cure behavior of the resins investigated. Also given in Table

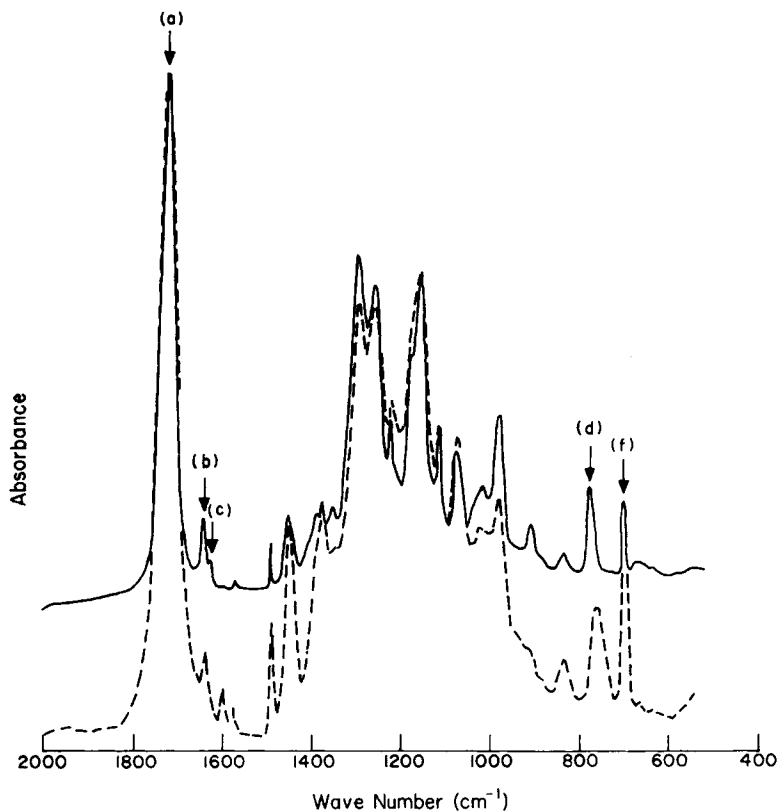


Fig. 2. IR spectra of resin A: (—) before cure; (---) after cure.

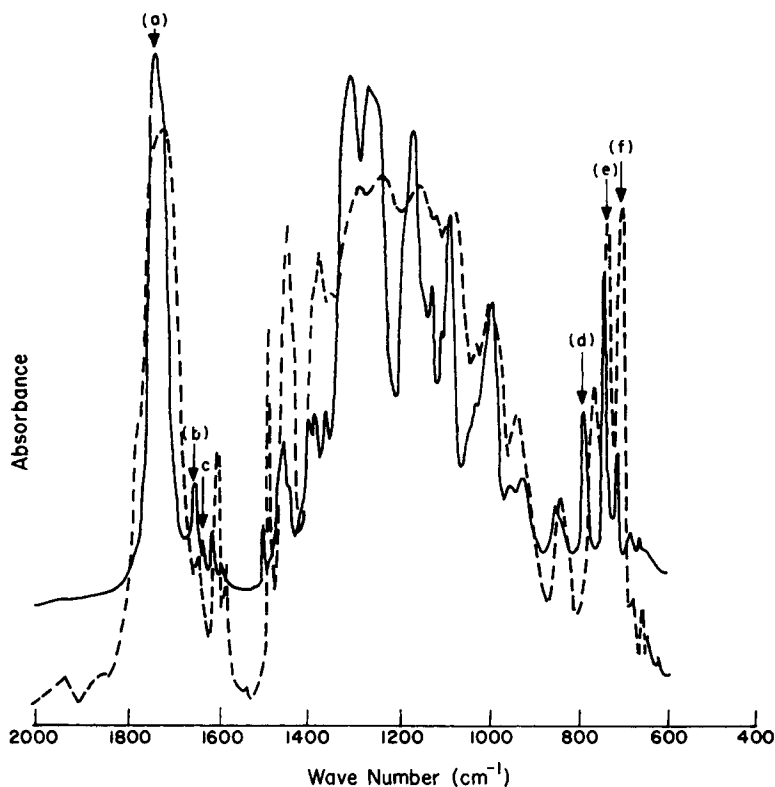


Fig. 3. IR spectra of resin B: (—) before cure; (---) after cure.

II are the acid number and number-average molecular weight of the three resins investigated.

Curing Behavior Determined from Analysis of DSC Runs and IR Spectra

In order to determine the degree of cure after a resin is cured, we have used IR spectra of the resin before and after cure. IR spectra of the three resins are given in Figures 2 to 4. The procedure used for analyzing the IR spectra is the same as that described in our previous paper.⁷ Basically, we determined the total quantity of double bonds available (D_a) in both the fumarate and styrene in a resin before cure, and the residual amount of double bonds (D_b) in the cured resin which underwent an isothermal cure followed by a postcure at a heating rate of 10°C/min. In other words, the total degree of cure, α_{TOT} , determined from IR spectral is defined by

$$\alpha_{TOT} = (D_a - D_b)/D_a \quad (1)$$

Table III gives a summary of the values of α_{TOT} determined from IR spectra for the three resins investigated.

Using DSC, we have determined the total heat generated Q_{TOT} , being the sum of the measured heat Q_T generated during an isothermal DSC run and

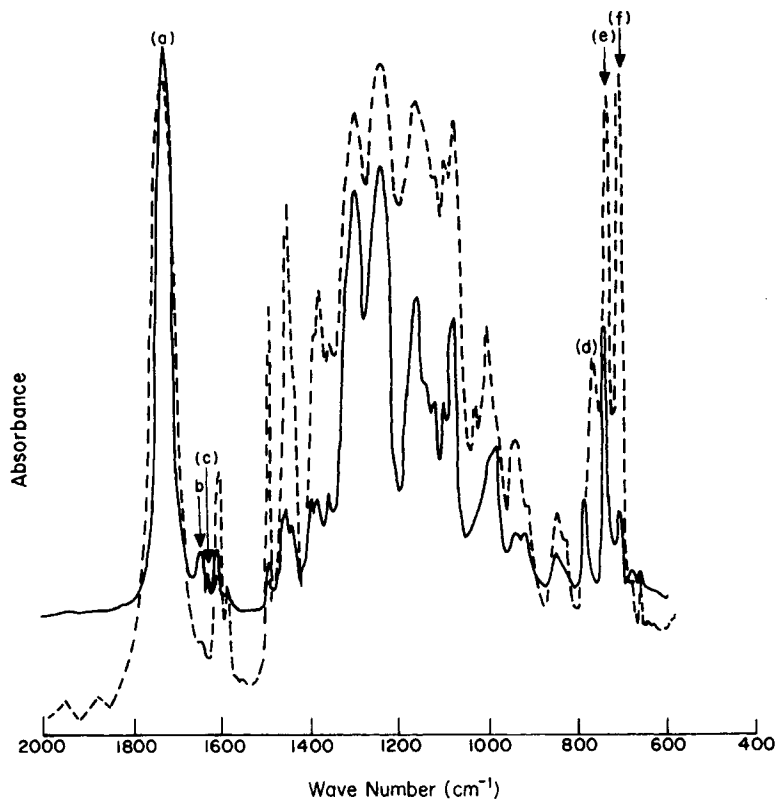


Fig. 4. IR spectra of resin C: (—) before cure; (---) after cure.

TABLE III
Summary of the Heat Generated during Isothermal DSC Runs
and Ultimate Degree of Cure

	Resin A	Resin B	Resin C
Final degree of cure (α_{TOT}) ^a	0.634	0.528	0.806
Total heat of reaction (Q_{TOT}) (J/g)	335	328	327
Ultimate heat of reaction (Q_{UT}) (J/g)	528	621	405

^aAt 130°C.

the residual heat Q_R that was released when the sample was then heated to 200°C at the rate of 10°C/min, i.e.,

$$Q_{TOT} = Q_T + Q_R \quad (2)$$

In order to determine the rate of cure da/dt and the degree of cure α during the isothermal curing reaction with the aid of thermograms (i.e., the rate of heat generated $(dQ/dt)_T$ obtained from isothermal DSC runs at temperature

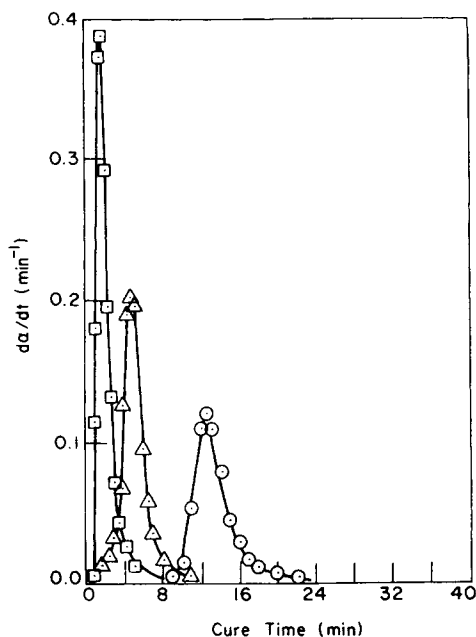


Fig. 5. $d\alpha/dt$ vs. cure time for Resin A at various isothermal DSC runs: (○) 110°C; (△) 120°C; (□) 130°C.

T), we had to estimate the ultimate heat Q_{UT} that would have been generated if complete conversion were achieved. This is because there are residual double bonds remaining in the cured resin, as demonstrated above in Table III (see also Ref. 7). Therefore we have used the following expressions

$$\frac{d\alpha}{dt} = \frac{1}{Q_{UT}} \left(\frac{dQ}{dt} \right)_T \quad (3)$$

and

$$\alpha = \frac{1}{Q_{UT}} \int_{t_i}^t \left(\frac{dQ}{dt} \right)_T dt \quad (4)$$

where Q_{UT} is defined by

$$Q_{UT} = Q_{TOT}/\alpha_{TOT} \quad (5)$$

Table III gives a summary of the values of Q_{TOT} and Q_{UT} determined for the three resins investigated.

Using the information given in Table III and Eqs. (3) and (4), we have analyzed the isothermal DSC runs, and the results are displayed in Figures 5 through 10. It is seen in Figures 5 to 7 that the peak value of $d\alpha/dt$ is larger in Resin A than in Resin B, and it is larger in Resin C than in Resin B. Note further that a peak in the $d\alpha/dt$ versus cure time plots appears at much a

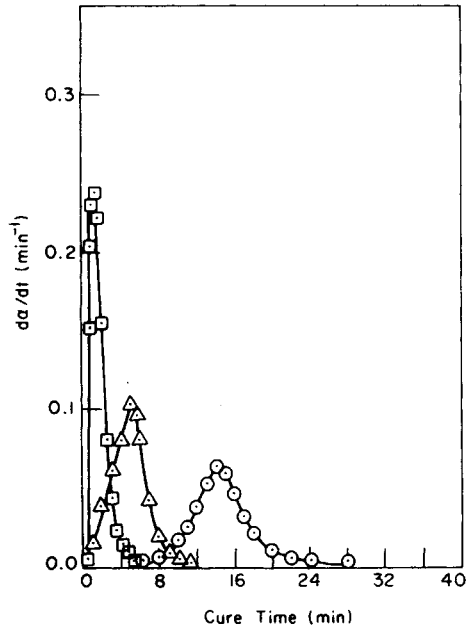


Fig. 6. da/dt vs. cure time for Resin B at various isothermal DSC runs. Symbols are the same as in Figure 5.

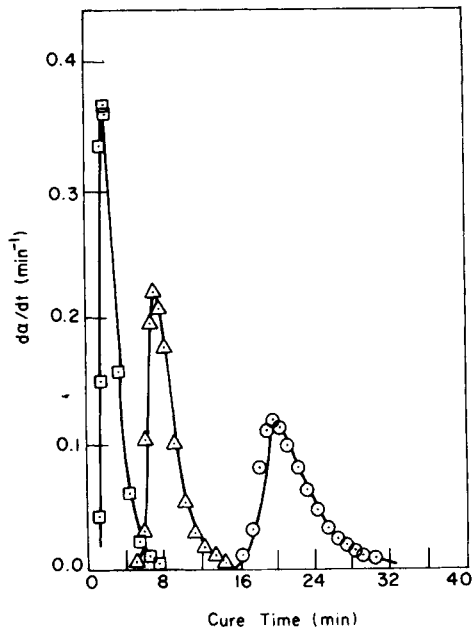


Fig. 7. da/dt vs. cure time for Resin C at various isothermal DSC runs. Symbols are the same as in Figure 5.

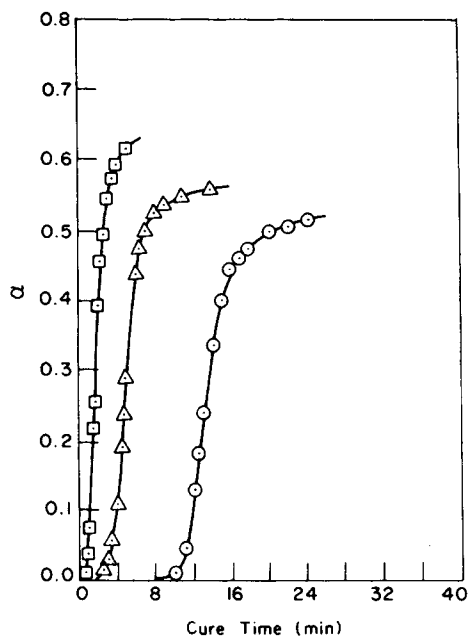


Fig. 8. α vs. cure time for Resin A at various isothermal DSC runs. Symbols are the same as in Figure 5.

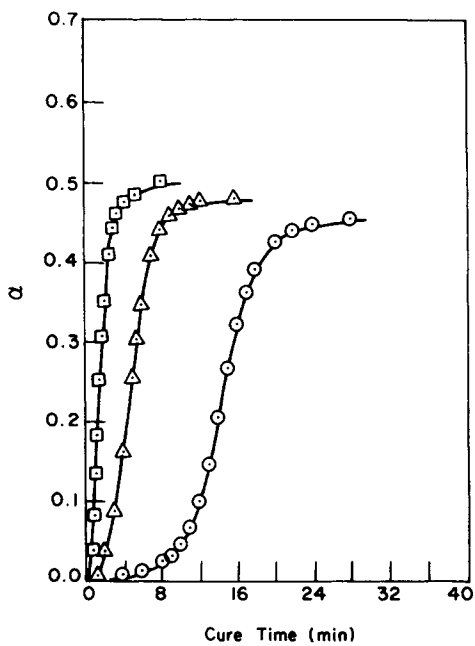


Fig. 9. α vs. cure time for Resin B at various isothermal DSC runs. Symbols are the same as in Figure 5.

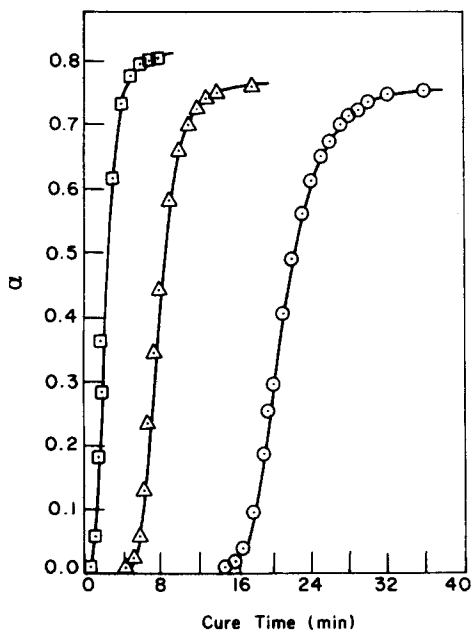


Fig. 10. α vs. cure time for Resin C at various isothermal DSC runs. Symbols are the same as in Figure 5.

later stage of cure in Resin C than in Resin A and Resin B. Figures 8 to 10 show that the ultimate value of α is larger in Resin A than in Resin B, and it is larger in Resin C than in Resin A.

Earlier, Horie et al.¹ studied the effect of the structure of unsaturated polyester resin on its curing behavior, and reported that the final degree of

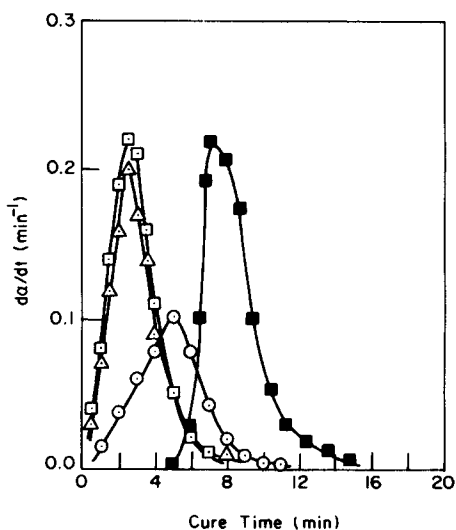


Fig. 11. $d\alpha/dt$ vs. cure time at 120°C for: (■) Resin C, and Resin B with various styrene-to-fumarate mole ratios: (○) 1.0; (△) 1.5; (□) 2.0.

cure under isothermal cure conditions decreases markedly with an increase in the amount of fumarates in the resin. In their study, succinic acids were used in order to control the amount of fumarates in unsaturated polyester resin, and the styrene-to-fumarate mole ratio was varied from 1.0 to 3.3 for a fixed amount of styrene. According to Kubota,⁸ the mole ratio of reactive diluent (i.e., styrene in this case) to fumarate affected the final degree of cure and a mole ratio of 1.6 to 2.0 yielded a maximum in the final degree of cure. More recently, Chern and Sundberg³ studied the curing behavior of unsaturated polyester resin using DSC, and reported that the final degree of cure increased when the styrene-to-fumarate mole ratio was increased. A similar observation was also reported by Huang et al.⁴

In the context of the previous investigations referred to above, the following interpretation may be given of the curing behavior of the three resins investigated, based on the results presented in Table III and Figures 5 to 10. First, in spite of the fact that Resin B has a higher styrene-to-fumarate mole ratio than Resin A, a comparison of Figure 5 with Figure 6, and Figure 8 with Figure 9, indicates that Resin B has both a peak value of $d\alpha/dt$ and a final value of α smaller than does Resin A. This may be attributable to the fact that Resin B has sterically bulky isophthalates, while Resin A has none. It is a well-known fact today that steric hindrance in a polymer reduces its reactivity by shielding the reactive double bonds. Second, in spite of the fact that Resin C has a greater amount of isophthalates than Resin B, a comparison of Figure 6 with 7, and Figure 9 with Figure 10, indicates that Resin C has both a peak value of $d\alpha/dt$ and a final value of α larger than does Resin B. In

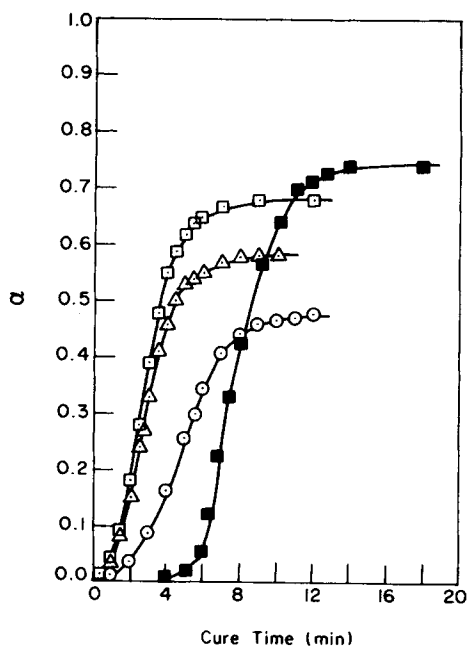


Fig. 12. α vs. cure time at 120°C for Resin B and Resin C. Symbols are the same as in Figure 11.

the beginning, we speculated that this might be due to the fact that the styrene-to-fumarate mole ratio is much higher in Resin C than in Resin B.

However, in order to prove or disprove this speculation, we performed additional cure experiments by adding styrene to Resin B in order to increase its styrene-to-fumarate mole ratio to the same level as Resin C. Figure 11 gives plots of $d\alpha/dt$ versus cure time, and Figure 12 plots of α versus cure time, at 120°C, for Resin B having three different styrene-to-fumarate mole ratios, 1.0, 1.5, and 2.0, and for Resin C with a styrene-to-fumarate mole ratio, 2.09. It is seen in Figure 11 that a peak in the $d\alpha/dt$ versus cure time plots occurs at much a later stage of cure in Resin C than in Resin B. This may be attributable to the presence of a rather large amount of isophthalates in Resin C. Note further in Figure 11 that at approximately the same styrene-to-fumarate mole ratio, the peak value of $d\alpha/dt$ in Resin B is essentially the same as that in Resin C. On the other hand, it is seen in Figure 12 that the final value of α for Resin B is still smaller than for Resin C, at approximately the same styrene-to-fumarate mole ratio. We believe that this observed difference in the final value of α between Resin B and Resin C is due to an inherent difference in reactivity of the two resins. In order to obtain quantitative information on the reactivity of the three resins investigated, we analyzed the experimentally observed curing behavior, using a mechanistic kinetic model developed in our previous investigation.⁷

Theoretical Prediction of the Curing Behavior

On the basis of the kinetic model developed in our previous investigation,⁷ we have the following system equations:

$$d[Z]/dt = -k_z[Z][R.] \quad (6)$$

$$d[I]/dt = -k_d[I] \quad (7)$$

$$d[R.]/dt = 2fk_d[I] - k_z[Z][R.] \quad (8)$$

$$d\alpha/dt = k_p(1 - \alpha)[R.] \quad (9)$$

in which $[Z]$ is the inhibitor concentration, $[I]$ is the concentration of initiator, $[R.]$ refers to the radical concentration (assumed to be the sum of the concentrations of polyester radical $[E.]$, styrene radical $[S.]$, and initiator radical $[I.]$), α is the degree of cure, k_z is the rate constant of the inhibition reaction, f is the efficiency of the initiator, k_d is the decomposition rate constant of the initiator, and k_p is the rate constant of the propagation reaction. In the derivation of Eqs. (6)–(9), based on our previous investigation,⁷ we have assumed that the termination reaction is negligibly small compared to the propagation reaction.

Equations (6)–(9) must be solved for $[Z]$, $[I]$, $[R.]$, and α with the given initial conditions, i.e., $[Z(0)] = [Z]_0$, $[I(0)] = [I]_0$, $[R.(0)] = 0$, and $\alpha(0) = 0$. However, before Eqs. (6)–(9) are solved, one must specify values of the rate constants, k_z and k_p , and the initiator efficiency f .

In order to incorporate a diffusion-controlled propagation reaction into k_p , we have used the following expression:⁷

$$k_p = k_{p0} [1 - (\alpha/\alpha_f)]^m \quad (10)$$

in which α_f is the final degree of conversion, m is a constant and the rate constant k_{p0} has been found to follow the Arrhenius relationship

$$k_{p0} = A_0 \exp(-E_p/RT) \quad (11)$$

where A_0 is a pre-exponential factor, E_p is the activation energy of the propagation reaction, R is the universal gas constant, and T is the absolute temperature.

In solving Eqs. (6)–(9), one must also specify the value of the initiator efficiency f . For this, we have used the following expression:⁷

$$f = \frac{f_0^2 [1 - (\alpha/\alpha_f)]^2}{2(1 - f_0)([I]/[I]_0)} \left\{ \left[1 + \frac{4(1 - f_0)([I]/[I]_0)}{f_0^2 [1 - (\alpha/\alpha_f)]^2} \right]^{1/2} - 1 \right\} \quad (12)$$

where f_0 is the initial value of the initiator efficiency and $[I]_0$ is the initial concentration of initiator. Note that Eq. (12) indicates that f decreases with increasing α .

TABLE IV
Summary of the Kinetic Parameters Determined
for the Resins Investigated at 120°C

Temp. (°C)	k_z (L/mol.min)	k_{p0} (L/mol.min)	m	f_0	A_0^a	E_p^b (Kcal/mol)
Resin A						
110	5.106×10^5	2.154×10^3	0.65	0.17	2.78×10^{11}	14.26
120	1.547×10^5	2.818×10^3	0.71	0.17		
130	1.047×10^4	5.480×10^3	1.45	0.20		
Resin B						
110	5.309×10^4	1.320×10^3	0.84	0.16	4.16×10^4	2.63
120	2.185×10^4	1.428×10^3	0.85	0.19		
130	1.365×10^4	1.567×10^3	0.98	0.53		
Resin C						
110	3.891×10^5	1.604×10^3	0.65	0.13	3.45×10^{14}	19.86
120	7.809×10^5	3.116×10^3	0.65	0.12		
130	1.514×10^5	5.856×10^3	0.65	0.15		
Resin B with different styrene content						
120 ^c	2.427×10^4	1.274×10^3	0.95	0.42		
120 ^d	3.072×10^4	1.706×10^3	1.02	0.41		

^aPre-exponential factor in Eq. (11).

^bThe activation energy of the propagation reaction (see Eq. (11)).

^cMole ratio of styrene/fumarate, 1.5 : 1.0.

^dMole ratio of styrene/fumarate, 2.0 : 1.0.

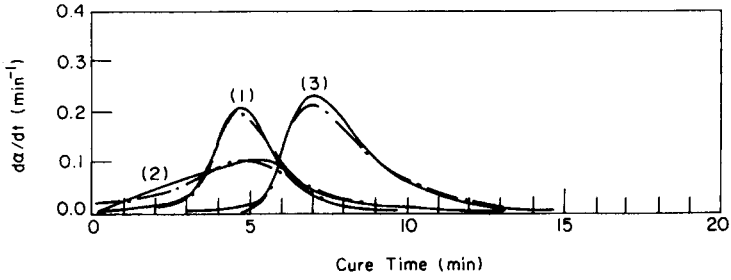


Fig. 13. Comparison of the experimental results (solid curves) with the theoretically predicted profiles (broken curves) of da/dt at 120°C for: (1) Resin A; (2) Resin B; (3) Resin C.

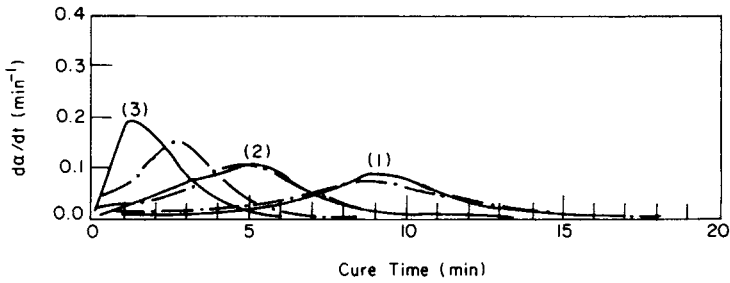


Fig. 14. Comparison of the experimental results (solid curves) with the theoretically predicted profiles (broken curves) of da/dt at 120°C for Resin B for various resin/initiator ratios (by wt): (1) 100/0.5; (2) 100/1.0; (3) 100/2.0.

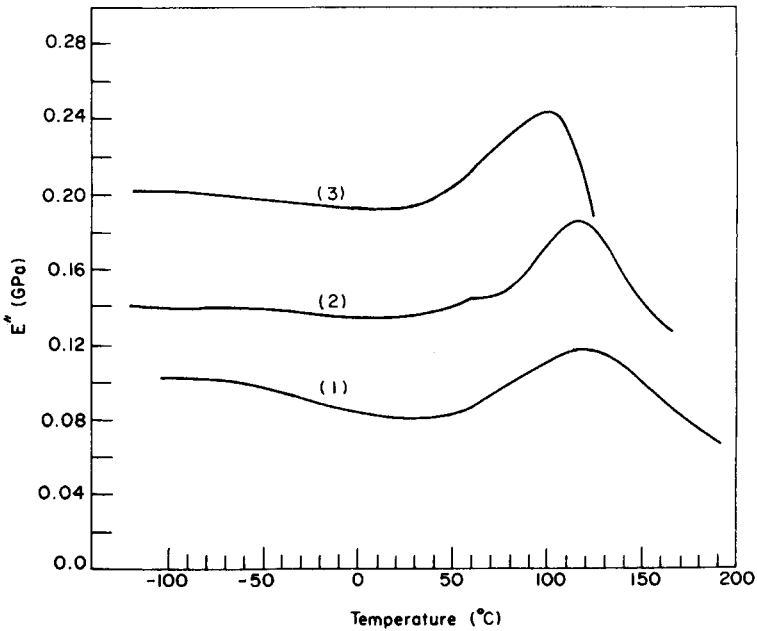


Fig. 15. Loss modulus vs. temperature for fully cured samples: (1) Resin A; (2) Resin B; (3) Resin C.

In carrying out the computation, we have used the following numerical values: (a) the initial concentration of inhibitor $[Z]_0 = 5.09 \times 10^{-4}$ M/L; (b) the initial concentration of initiator $[I]_0 = 5.716 \times 10^{-2}$ M/L, corresponding to 1 part of initiator for 100 parts of resin; (c) the rate constant of the initiator decomposition reaction k_d was estimated from the following expression:

$$k_d = k_{d0} \exp(-E_d/T) \quad (13)$$

in which $k_{d0} = 8.524 \times 10^{15}$ and $E_d = 1.632 \times 10^4$ for the *tert*-butyl perbenzoate used in our experiment.

Table IV gives a summary of the kinetic parameters determined from computation for the unsaturated polyester resins investigated. Note that these parameters were determined as part of the solution of the system equations, while numerically solving Eqs. (6)–(9) together with Eqs. (10) and (12) until the predicted values of both $d\alpha/dt$ and α agreed with the experimentally determined ones, within a prescribed tolerance.

It is of interest to note in Table IV that the rate constant k_{p0} and the activation energy E_p for Resin B are smaller than those for Resin A and Resin C, whereas the value of the parameter m for Resin B is larger than that for Resin A and Resin C. It is now clear from Table IV that, among the three

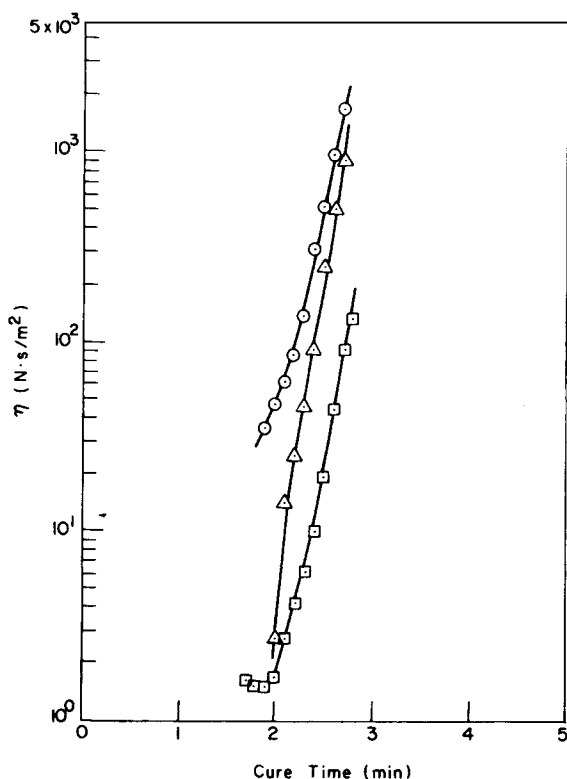


Fig. 16. Viscosity vs. cure time for Resin A at 110°C, at various shear rates (s^{-1}): (○) 1.07; (▲) 2.69; (◻) 17.0.

resins investigated, the reactivity of Resin C is greater than that of Resin A and Resin B, and the reactivity of Resin A is greater than that of Resin B.

Figure 13 gives comparisons of the experimental results with the theoretically predicted profiles of $d\alpha/dt$ during the entire period of the cure reaction for the three resins investigated. It can be concluded that the theoretical predictions of the curing behavior are very good indeed.

Also investigated in the present study is the effect of the concentration of initiator on the curing behavior of unsaturated polyester resin. For this, we conducted cure experiments by having two additional resin formulations, namely (1) resin/initiator = 100/0.5 (parts by weight), and (2) resin/initiator = 100/2 (parts by weight). Note that the results presented above are based on the formulation, resin/initiator = 100/1 (parts by weight). It is generally expected that the concentration of initiator in a resin formulation will affect the curing behavior of the resin. Our primary purpose here was to examine how well the kinetic model can predict the effect of the concentration of initiator on the curing behavior of unsaturated polyester resin. Figure 14 gives comparisons of the experimental results with the theoretical predicted profiles of $d\alpha/dt$ during the entire period of the curing reaction, for Resin B with three different concentrations of initiator. It is seen in Figure 14 that the rate of cure increases with increasing concentration of initiator, and that the

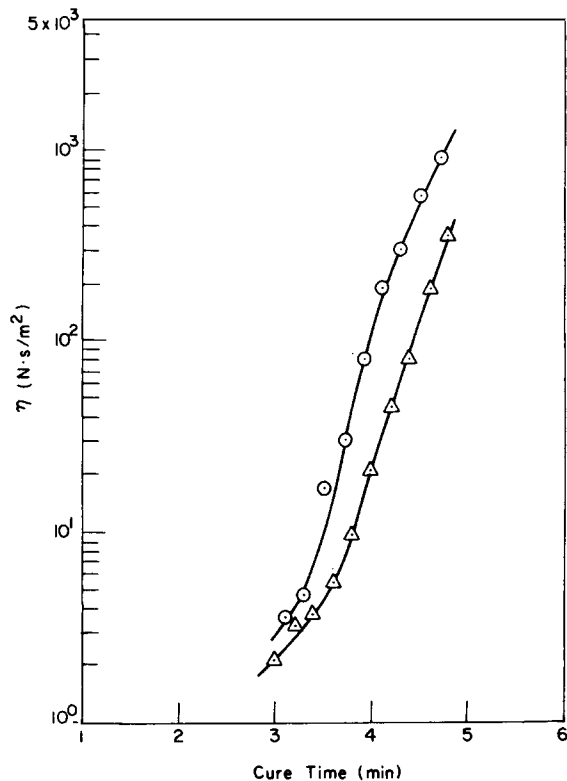


Fig. 17. Viscosity vs. cure time for Resin B at 110°C, at various shear rates (s^{-1}): (○) 0.43; (Δ) 2.69.

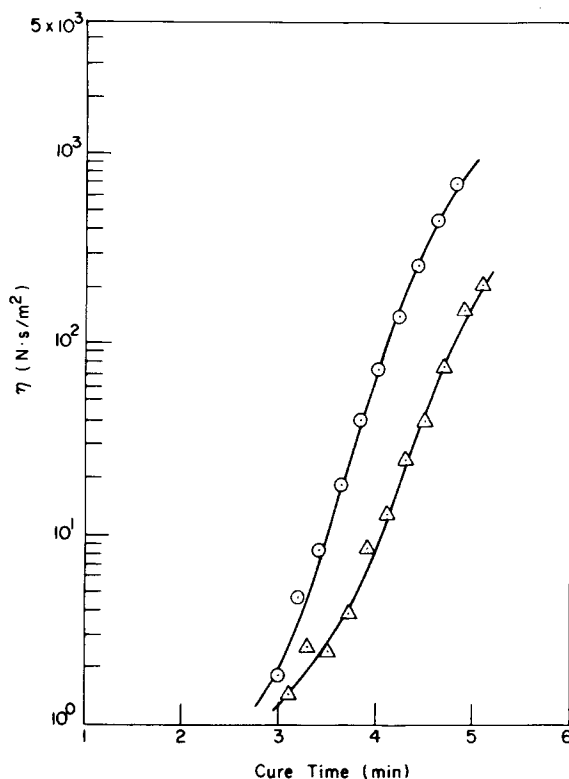


Fig. 18. Viscosity vs. cure time for Resin C at 110°C, at various shear rates (s^{-1}): (○) 0.43; (▲) 1.07.

kinetic model predicts the curing behavior reasonably well, except for the resin formulation that has highest initiator concentration of the three. It should be pointed out that, in the prediction of curing behavior presented in Figure 14, we have used the same value for the initial efficiency of initiator f_0 in all three cases. It is entirely possible that the value of f_0 may vary with resin formulation.

Glass Transition Behavior of Cured Resins

Figure 15 gives plots of loss modulus (E'') versus temperature for cured resins, determined from DMA. It is seen that the glass transition temperature (i.e., the peak value of E'') of cured resin is 120°C for Resin A, 116°C for Resin B, and 100°C for Resin C.

Shibayama and Suzuki² have reported that glass transition temperature (T_g) increases with increasing crosslink density of polymers, which depends on the amount of fumarates present in an unsaturated polyester resin. Our measurements of glass transition temperature, together with information on the structure of the resins investigated (see Tables I and II), show a trend that is consistent with the observations made by Shibayama and Suzuki (i.e., Resin A, which has the largest amount of fumarates of the three resins, has the highest T_g , and Resin C, which has the least amount of fumarates of the three resins, has the lowest T_g).

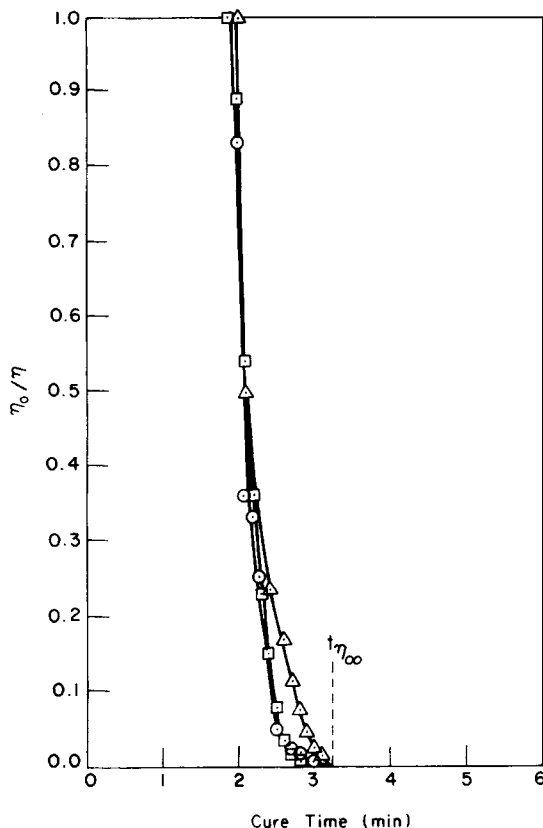


Fig. 19. η_0/η vs. cure time for Resin A. Symbols are the same as in Figure 16.

Rheological Behavior During Cure

Figures 16, 17, and 18 describe the variation of viscosity (η) with cure time at various shear rates ($\dot{\gamma}$) for Resin A, Resin B, and Resin C, respectively. The following observations are worth noting in these figures: (1) in all three resins, the viscosity increases with cure time, but the rate of increase in viscosity is greater for Resin A than for Resin B and Resin C; (2) shear-dependent viscosity is observed in all three resins.

As may be seen in Figures 16 to 18, the η does not approach infinity (η_∞) and therefore we cannot determine the time t_{η_∞} , often referred to as gel time, at which the η approaches infinity. However, plotting the ratio of the initial viscosity (η_0) to the viscosity during cure (η), η_0/η , against cure time, we obtain the results given in Figures 19 to 21 for Resin A, Resin B, and Resin C, respectively. Note in these figures that η_0 values were read off from Figures 16 to 18 at each shear rate. Since η increases with cure time, the η_0/η ratio decreases with cure time.

It is of great interest to note in Figures 19 to 21 that the η_0/η ratio approaches zero, independent of shear rate, as cure time approaches t_{η_∞} . The values of t_{η_∞} determined from Figures 19 to 22 are given in Table V. It is of

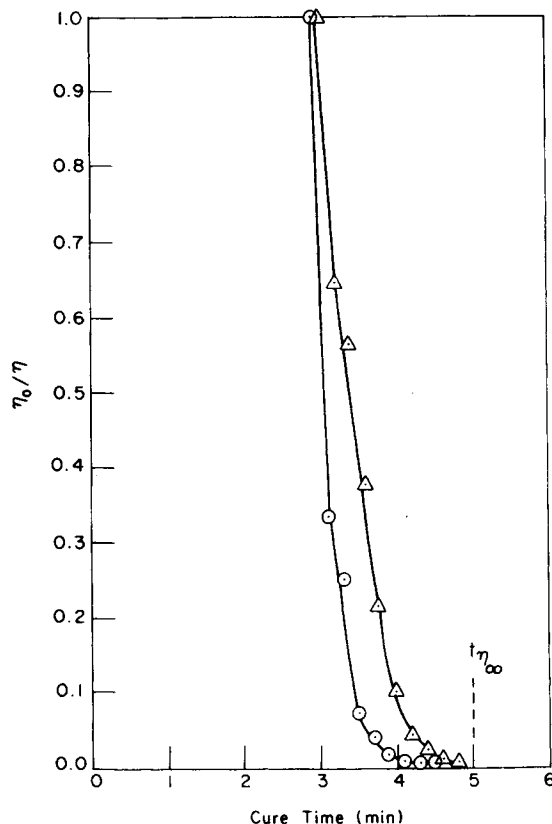


Fig. 20. η_0/η vs. cure time for Fluid B. Symbols are the same as in Figure 17.

great interest to observe in Table V that $t_{\eta_{\infty}}$ is 3.25 min for Resin A and 5.0 min for both Resin B and Resin C. This observation seems to point to the fact that Resin A cures at a much faster rate than do Resin B or Resin C. Such an indication is in agreement with the independent cure measurements conducted using DSC (see Figures 1 to 3, and Figure 13).

Figure 22 gives plots of storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$) versus cure time for Resin A at the low frequency ω of 1.89 rad/s, and Figure 23 gives similar results at the higher frequency of 29.95 rad/s. It is seen that, at the low frequency ($\omega = 1.89$ rad/s), G' monotonically increases with cure time while G'' goes through a maximum. But at the high frequency ($\omega = 29.95$ rad/s), G'' tends to approach a constant value as cure continues. The frequency-dependent oscillatory shearing flow properties are very similar to those reported earlier by Han and Lem.⁹ Figures 24 and 25 give oscillatory shearing flow properties for Resin B and Resin C, respectively, at $\omega = 29.95$ rad/s.

Whereas steady shearing flow properties only characterize the rheological behavior of a material in the liquid state, oscillatory shearing flow properties are also useful for characterizing the rheological behavior of material in both

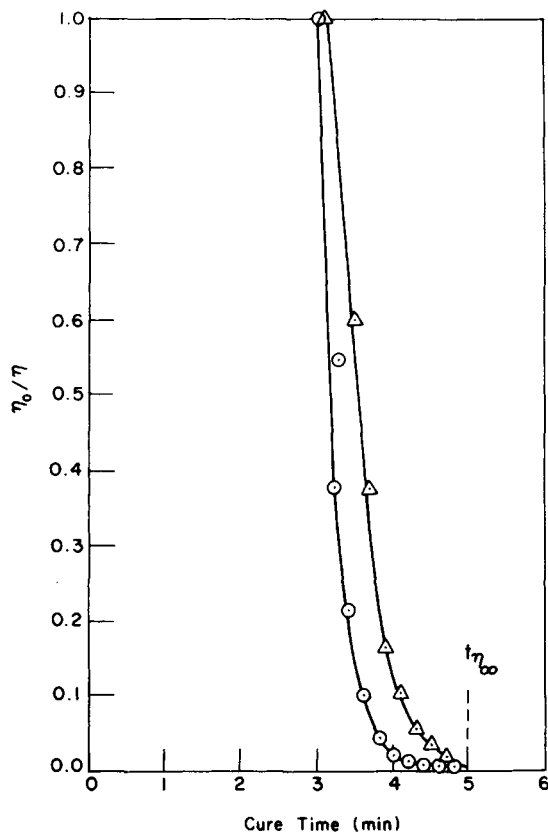


Fig. 21. η_0/η vs. cure time for Fluid C. Symbols are the same as in Figure 18.

TABLE V
Summary of the Characteristic Cure Time

	$t_{\eta_{\infty}}$ (min)	$t_{\tan \delta = 1}$ (min) ^a
Resin A	3.25	2.25
Resin B	5.00	4.70
Resin C	5.00	4.30

^aAt $\omega = 29.95$ rad/s.

the rubbery and glassy states. This implies that oscillatory measurements can be used after the material enters the gelation stage. Very recently, Tung and Dynes¹⁰ reported that the time at which the crossover of G' and G'' occurred (i.e., $t_{\tan \delta = 1}$) during the isothermal cure of epoxy resins coincided with the gel time independently measured by the standard gel time test (ASTM D2471-72). We have determined values of $t_{\tan \delta = 1}$ for the three resins under consideration from Figures 23 to 25, and they are given in Table V. It is seen, in Table V, that $t_{\tan \delta = 1}$ is 2.25 min for Resin A, 4.7 min for Resin B, and 4.3 min for

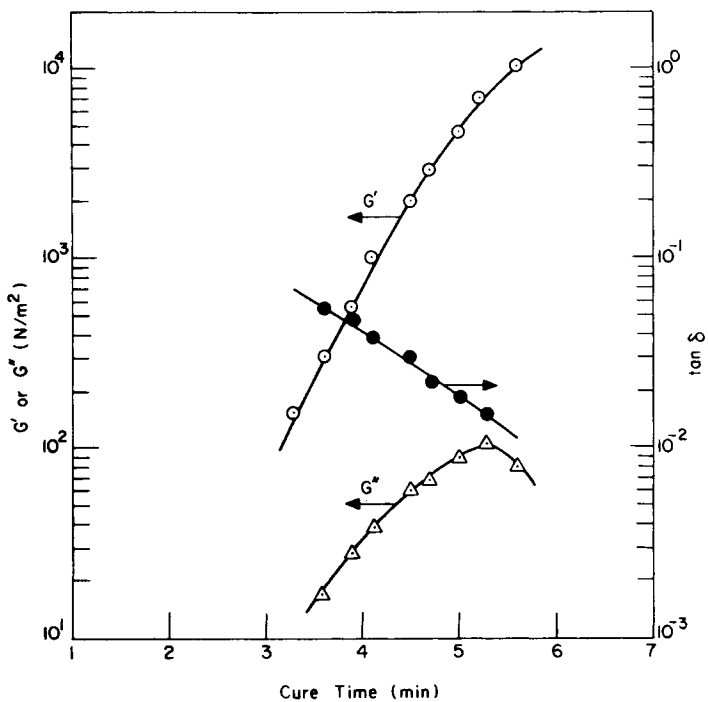


Fig. 22. G' , G'' , and $\tan \delta$ vs. cure time for Resin A at $\omega = 1.89 \text{ s}^{-1}$ (110°C).

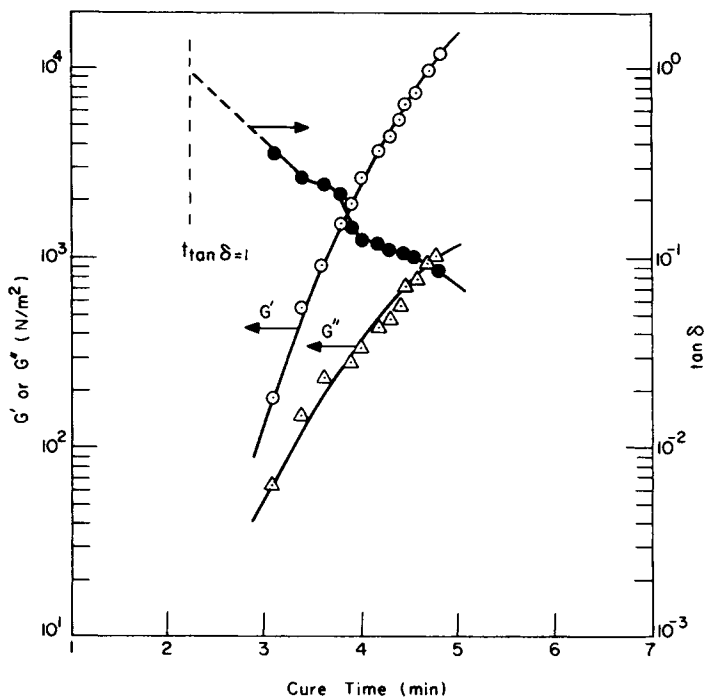


Fig. 23. G' , G'' , and $\tan \delta$ vs. cure time for Resin A at $\omega = 29.95 \text{ s}^{-1}$ (110°C).

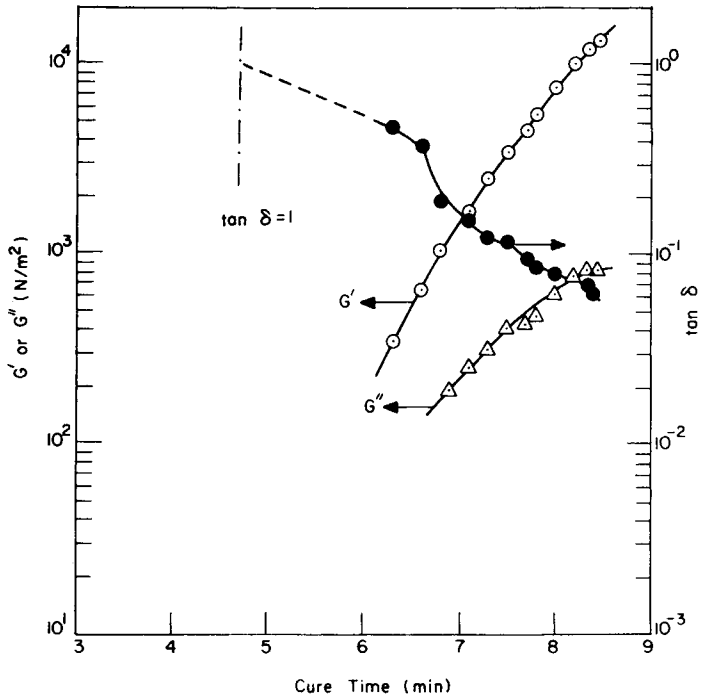


Fig. 24. G' , G'' , and $\tan \sigma$ vs. cure time for Resin B at $\omega = 29.95 \text{ s}^{-1}$ (110°C).

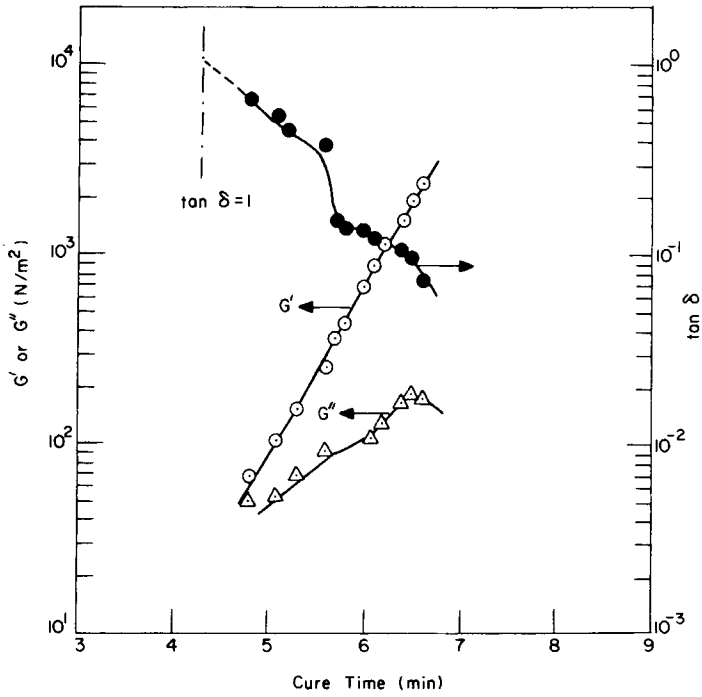


Fig. 25. G' , G'' , and $\tan \delta$ vs. cure time for Resin C at $\omega = 29.95 \text{ s}^{-1}$ (110°C).

Resin C. Within the uncertainties of rheological measurement, it is difficult to claim genuine differences in the value of $t_{\tan \delta=1}$ between Resin B and Resin C. However, there is no question that the value of $t_{\tan \delta=1}$ for Resin A is definitely smaller than the corresponding values for Resin B and Resin C. Following the argument given by Tung and Dynes,¹⁰ it can be concluded that Resin A cures much faster than Resin B or Resin C. This conclusion is consistent with the independent cure measurements conducted using DSC (see Figure 1 to 3, and Figure 13). It is of great interest to observe in Table V that both steady shearing flow measurement and oscillatory shearing flow measurement give consistent results on the gel time during the cure of unsaturated polyester resin.

CONCLUDING REMARKS

The effect of the structure of unsaturated polyester resin on its curing behavior and rheological behavior during isothermal cure has been investigated, using three different grades of resin. The following conclusions have been reached, based on our experimental investigation of the cure of unsaturated polyester resin: (1) at the same styrene-to-fumarate mole ratio, a resin having isophthalates cures slower than one having none; (2) everything else being equal, a resin having a high styrene-to-fumarate mole ratio cures faster than a resin having a low one; (3) the higher the concentration of initiator, the faster a resin cures.

It has been found that a resin that cures faster does not necessarily achieve a higher final degree of cure than one that cures slowly. In order to investigate the reactivity of different resins, we have employed a mechanistic kinetic model, developed in our previous investigation, to simulate their curing behavior, and have determined the rate constant and activation energy of the propagation reaction. This effort has revealed information otherwise not available. We have concluded that the kinetic model employed is very useful for determining the reactivity of unsaturated polyester resin.

For the resin that does not show an infinite viscosity during isothermal cure, it was not possible to obtain the gel time from steady shearing flow measurement. However, plots of the viscosity ratio, η_0/η , versus cure time allowed us to determine a characteristic time t_{η_∞} , that may be used as a measure of gel time. (η_0 is the initial viscosity and η is the viscosity during cure.) Further, using oscillatory shearing flow measurement, we have determined the time $t_{\tan \delta=1}$ at which the shear modulus and the loss modulus cross each other when they are plotted against cure time. We have concluded that both t_{η_∞} and $t_{\tan \delta=1}$ may be used as a measure of gel time. We have found that the smaller the value of either t_{η_∞} or $t_{\tan \delta=1}$, the faster the resin cures, which is consistent with the conclusions reached from independent DSC measurement.

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References

1. K. Horie, I. Mita, and H. Kambe, *J. Polym. Sci.*, A-1, **8**, 2839 (1970).
2. K. Shibayama and Y. Suzuki, *J. Polym. Sci.*, Part A, **3**, 2637 (1965).
3. C. S. Chern and D. C. Sundberg, Paper presented at the Winter AIChE Meeting, Atlanta, Georgia, March 1984.
4. Y. J. Huang, T. J. Hsu, and L. J. Lee, Tech. Paper, 42nd SPE Annu. Tech. Conf., p. 1022 (1984).
5. C. D. Han and K. W. Lem, *J. Appl. Polym. Sci.*, **28**, 763 (1983).
6. D. F. Percival and M. P. Stevens, *Anal. Chem.*, **36**, 1574 (1964).
7. C. D. Han and D. S. Lee, *J. Appl. Polym. Sci.*, **33**, 2859 (1987).
8. H. Kubota, *J. Appl. Polym. Sci.*, **19**, 2279 (1975).
9. C. D. Han and K. W. Lem, *J. Appl. Polym. Sci.*, **28**, 3155 (1983).
10. C. M. Tung and P. J. Dynes, *J. Appl. Polym. Sci.*, **27**, 569 (1982).

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