

# Chemorheology of Thermosetting Resins. I. The Chemorheology and Curing Kinetics of Unsaturated Polyester Resin

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## Synopsis

The rheological properties and curing kinetics of a general-purpose polyester resin have been determined during isothermal cure. Both steady and oscillatory shearing flow properties were determined using a cone-and-plate rheometer, and the curing kinetics were determined using a differential scanning calorimeter (DSC). It was found that, as cure progresses, the steady shear viscosity increases very rapidly with cure time at all shear rates investigated, and normal forces show *negative* values at low shear rates and *positive* values at high shear rates. The observed *negative* normal forces are believed to result from material shrinkage during cure, and *positive* normal forces from the deformation of large molecules, formed by crosslinking reactions during cure. Note that, in a cone-and-plate rheometer, the shrinkage force acts in the direction *opposite* to that of normal forces. It is, therefore, concluded that extreme caution is needed in the interpretation of normal force measurements with thermosetting resins, subjected to steady shearing flow. Dynamic measurements seem to offer some insight on the onset of gel formation. More specifically, we have found that, when the unsaturated polyester resin was cured at a fast rate, the time at which a maximum in the loss modulus  $G''$  occurs coincides reasonably well with the time  $t_{\eta_{\infty}}$  at which the steady shear viscosity  $\eta$  approaches infinity. However, at a slow rate of cure, the time at which  $\tan \delta$  equals unity agrees fairly well with  $t_{\eta_{\infty}}$ . DSC measurement has permitted us to determine the degree of cure as a function of cure time and the kinetic parameters in an empirical expression for the curing kinetics advanced by Kamal and co-workers. By combining the rheological and DSC measurements, we have constructed plots describing how the viscosity increases with the degree of cure, at various values of isothermal curing temperature.

## INTRODUCTION

In recent years, the processing of thermosetting resins (e.g., unsaturated polyester resin, epoxy resin, phenolics, and urethanes) has received increasing attention from industry, especially from the automotive and aerospace industries. In the processing of thermosetting resins, one always adds other ingredients such as fillers, thermoplastic additive (for shrinkage control), reinforcements, pigments, etc. More importantly, the processing of such compounds is accompanied by chemical reactions. Therefore, unlike the processing of *thermoplastic* resins, the processing of *thermosetting* resins (and their compounds) requires two aspects of fundamental scientific understanding, namely, the rheology and the polymerization reaction kinetics during cure.

The rheology of multicomponent *thermoplastic* compounds in which no chemical reaction takes place is complex enough. The relatively little fundamental literature published on the subject has been summarized in the recent monograph by Han.<sup>1</sup> It is therefore understandable that little basic information has been published on the rheology and processing of multicomponent *ther-*

*mosetting* compounds, which involve chemical reactions and heat transfer, in addition to fluid flow.

In our previous papers,<sup>2-4</sup> we have reported on the rheological behavior of unsaturated polyester resins containing a particulate filler alone, a low-profile additive alone, or a viscosity thickener alone, and combinations of these, *without* a curing reaction taking place. The subjects dealt with are very important to the preparation of polyester molding compounds (e.g., BMC, SMC, TMC). It should be pointed out that if the molding compounds are not prepared correctly, one will encounter many difficulties in processing the materials to achieve the desired properties. In general, the control of the rheological properties of molding compounds plays a significant role in determining the optimum processing conditions, which in turn affect their end-use properties.

In the processing of thermosetting resins, as in the processing of thermoplastic resins, one requires an understanding of the relationship between the processing conditions and the rheological properties of the system under investigation. Difficulty is encountered with the measurement of the rheological properties of thermosetting resins, due to the heat generated by the exothermic chemical reaction during cure. Rheological measurements under isothermal conditions can, however, be carried out by ensuring that the sample has a large surface-to-volume ratio, and/or by reducing the rate of the curing reaction.

Having recognized the importance of the relationships between the rheological behavior and the curing kinetics of thermosetting polyester resins and their compounds, from both the fundamental and technological points of view, we very recently undertook a comprehensive research program to enhance our understanding of the interrelationships among material variables (i.e., the resin chemistry, filler, thermoplastic additive, viscosity thickener), rheological properties (i.e., viscosity, elasticity) of the resin or its compounds, and curing kinetics. We decided to investigate this rather complicated subject with a systematic, stepwise approach, as follows: (1) to investigate the rheological behavior of unsaturated polyester resin during cure, *without* any additives other than peroxide and promoter, and to investigate the curing kinetics using differential scanning calorimetry (DSC); (2) to investigate the effect of particulates on the rheology during cure (i.e., chemorheology) and the curing kinetics of unsaturated polyester resin; (3) to investigate the effect of low-profile additive on the chemorheology and curing kinetics of unsaturated polyester resin.

In this paper, the first of the series, we shall report our findings on the chemorheology and curing kinetics of a general-purpose unsaturated polyester resin. Emphasis will be placed on establishing relationships between the rheological properties and the curing kinetics of the resin.

## PREVIOUS STUDIES

It is fair to say that, compared to thermoplastic resins, relatively little effort has been spent on investigating the rheological behavior of thermosetting resins, and still less on reinforced thermosetting molding compounds. Nevertheless, in the past, some serious attempts were made to take rheological measurements of thermosetting resins in an *controlled* environment (i.e., under *isothermal* conditions), by using a sample having a large surface-to-volume ratio and a catalyst (initiator) having low reactivity. Otherwise, the heat generated by the

exothermic chemical reactions between the resin and the catalyst will increase the temperature of the sample, which in turn will increase the rate of the curing reaction, leading to a highly nonisothermal, chemically reactive system.

One of the effective means of achieving a large sample surface-to-volume ratio is to use a thin gap formed by two parallel plates, or by a cone and plate. For this reason, a cone-and-plate rheometer (e.g., the Weissenberg rheogoniometer; the Rheometrics mechanical spectrometer) has been widely used by various investigators. Using such an instrument, one can conduct steady shear flow experiments, as well as dynamic (oscillatory) shear flow experiments.

Ryan<sup>5</sup> took measurements of the steady shear flow properties of unsaturated polyester resins and epoxy resins during cure. His measurements show that, at a fixed shear rate, the viscosity initially increases slowly and then very rapidly with cure time, approaching very large (almost infinite) values. According to Ryan, at a fixed cure temperature, the time at which the viscosity approaches infinitely large values (often referred to as the gelation time) increases with shear rate, and at a fixed shear rate, the gelation time decreases with temperature. Ryan's measurements show further that the first normal stress difference begins to be measurable just past the gelation time, and it increases thereafter very rapidly with cure time.

Oscillatory shear flow measurements during cure were conducted with unsaturated polyester resins,<sup>5-8</sup> epoxy resins,<sup>5,9-13</sup> urethanes,<sup>14</sup> and diallyl phthalate prepolymer or molding compounds.<sup>15,16</sup> Ryan<sup>5</sup> reports that, at a fixed cure temperature, the dynamic viscosity, storage modulus, and loss modulus of both unsaturated polyester and epoxy resins, initially increase slowly and then very rapidly with cure time.

However, interestingly enough, Imai<sup>6</sup> observed that during the cure of unsaturated polyester resins, the loss modulus ( $E''$ ) initially increases with cure time, goes through a maximum, and then decreases as cure progresses (i.e., as crosslinking reactions continue in the gelled state). He suggested that the maximum value of  $E''$  was caused by the freeze of molecular movement at that particular cure time. Imai also suggested, without presenting any theoretical basis, that  $d \ln E''/dt$  could be used as an index representing the rate of curing reaction. It is worth mentioning that Imai's measurements show that Young's modulus ( $E'$ ) initially increases with cure time and then levels off as the cure progresses.

Willard<sup>15</sup> observed that, during the cure of diallyl phthalate molding compounds at 120°C and at a fixed angular frequency, the storage modulus ( $G'$ ) initially increases slowly with cure time and goes through a slight maximum as the curing reaction progresses. On the other hand, the dynamic viscosity ( $\eta'$ ) initially decreases very rapidly with time (due to the heating of the molding compound), next it increases, going through a maximum, and then it decreases with cure time, leveling off finally as the cure progresses. Similar findings have also been reported by Senich et al.,<sup>17</sup> who employed dynamic spring analysis (DSA) to study the dynamic mechanical behavior of epoxy resins during isothermal cure. They observed a maximum in loss modulus, which is in agreement with the observation made earlier by Imai.<sup>6</sup> More recently, Yap and Williams<sup>8</sup> have reported similar observations, using the same experimental technique, in a curing study of unsaturated polyester resins.

It is worth pointing out that the curing reaction increases the glass transition

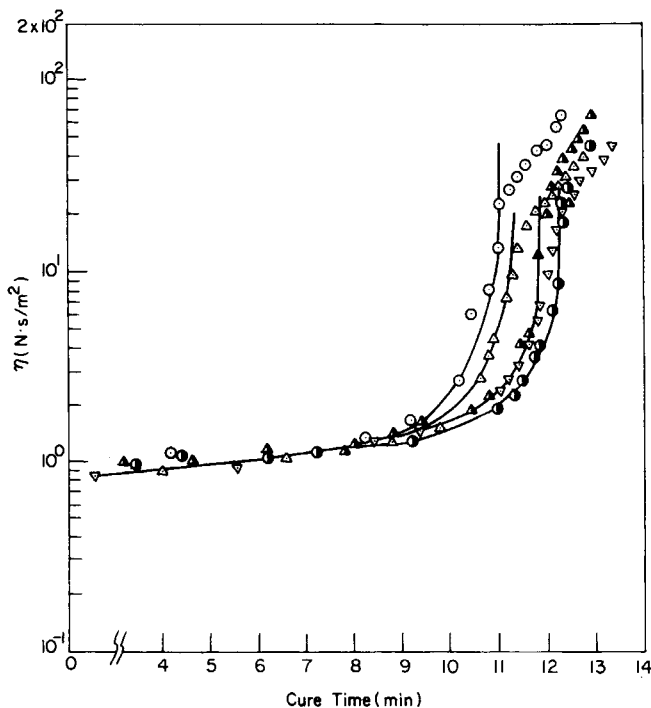


Fig. 1. Viscosity vs. cure time ( $T = 30^{\circ}\text{C}$ ) at various shear rates ( $\text{s}^{-1}$ ): ( $\odot$ ) 1.07; ( $\triangle$ ) 1.70; ( $\nabla$ ) 4.27; ( $\bullet$ ) 6.77; ( $\blacktriangle$ ) 10.7.

( $T_g$ ) of a thermosetting polymer by introducing restrictions on the motions of polymer chains, and that, consequently, the modulus at temperatures above the  $T_g$  of a crosslinked polymer increases significantly.<sup>18-23</sup> Note further that the degree of cure (hence the mechanical properties) of a thermosetting polymer may be influenced greatly by the curing temperature.

In recent years, Gillham and co-workers<sup>24,25</sup> have advanced a theory of gelation and vitrification for thermosetting resins. According to them, the cure temperature governs the extent of gelation and vitrification of a thermosetting resin during cure, and gelation may occur without vitrification when a thermosetting resin is cured at a temperature above the maximum softening point of the system,  $T_{g\infty}$  (i.e.,  $T_g$  for the fully cured polymer). According to Gillham and co-workers,<sup>24,25</sup> vitrification can occur before gelation, when cure is carried out at a temperature below  $T_{gg}$ , which is defined as the temperature at which gelation and vitrification may occur simultaneously. Using torsional braid analysis (TBA),<sup>26</sup> they<sup>24,25</sup> have observed two peaks in the mechanical damping during the isothermal cure of epoxy resins, and have attributed the first peak to gelation and the second to vitrification. On the other hand, other investigators,<sup>8,17</sup> who employed other types of dynamic mechanical experiments, have observed only one peak in the loss modulus. This difference observed by two different groups of researchers must be reconciled in future research.

We have pointed out above that, as the cure of a thermosetting resin progresses, the viscosity increases, because the molecules get bigger due to crosslinking reactions. Therefore, it is quite natural for one to relate the viscosity measure-

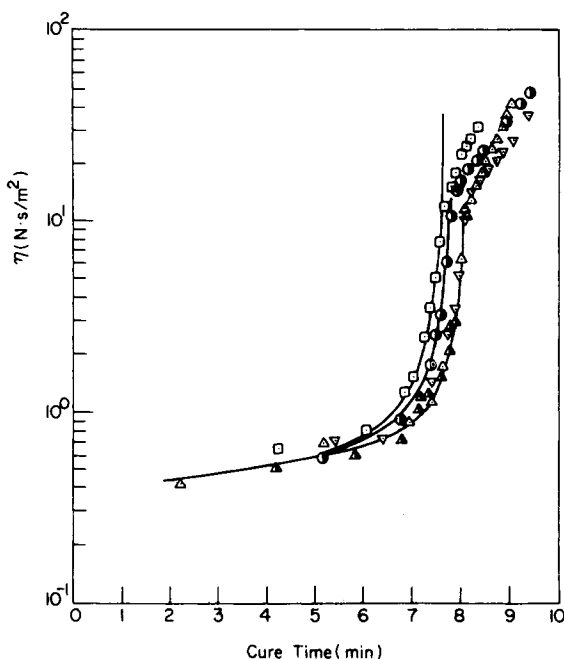


Fig. 2. Viscosity vs. cure time ( $T = 40^{\circ}\text{C}$ ) at various shear rates ( $\text{s}^{-1}$ ): ( $\Delta$ ) 2.69; ( $\square$ ) 4.27; ( $\nabla$ ) 10.7; ( $\bullet$ ) 17.0; ( $\blacktriangle$ ) 26.9.

ments, taken during the various stages of cure, to the molecular weight of the cured material. In turn, an increase in molecular weight during cure is related to the degree of cure (i.e., the extent of polymerization). As a matter of fact, some attempts<sup>14,16,27</sup> were made at relating the viscosity, measured during cure, to molecular parameters (or the extent of reaction) prior to the incipient gel point.

Lipshitz and Macosko<sup>27</sup> studied the rheology of a urethane curing system by measuring the steady shear viscosity and the first normal stress difference, using a cone-and-plate rheometer. They related the viscosity, measured during cure, to the weight-average molecular weight ( $\bar{M}_w$ ). In their study, Lipshitz and Macosko determined the extent of reaction by using a titration method, and then calculated the values of  $\bar{M}_w$  from a general condensation polymerization equation. Hartley and Williams<sup>14</sup> also studied the rheology of a urethane curing system with oscillatory shear flow measurements, and related the zero-shear viscosity to  $\bar{M}_w$ . In their study, Hartley and Williams determined  $\bar{M}_w$ , using gel permeation chromatography (GPC). A similar approach was also taken by Sundstrom and Burkert,<sup>16</sup> who studied the rheology of partially cured diallyl phthalate polymers, using a cone-and-plate rheometer, and determined the viscosity-average molecular weight of the sample with the aid of intrinsic viscosity measurements. They presented an empirical viscosity-molecular weight-temperature relationship capable of superposing the viscoelastic properties of several partially cured diallyl phthalate polymers.

Kamal and co-workers<sup>28,29</sup> appear to be the first who tried to combine the rheological data measured with a cone-and-plate rheometer with the curing kinetics data obtained with DSC. DSC has proven to be a very useful experimental

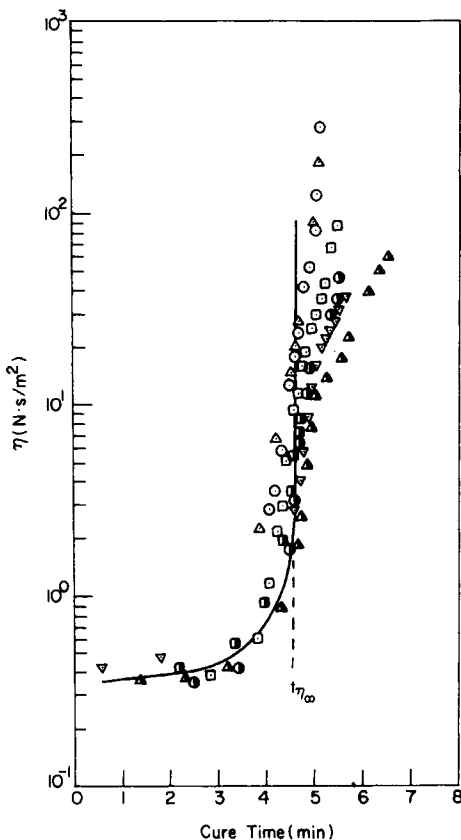


Fig. 3. Viscosity vs. cure time ( $T = 50^{\circ}\text{C}$ ) at various shear rates ( $\text{s}^{-1}$ ): (○) 0.269; (△) 1.07; (▽) 4.27; (●) 6.77; (●) 10.7; (▲) 17.0; (■) 26.9.

technique for studying the thermokinetics of some polymerization initiators,<sup>30</sup> and the curing kinetics of thermosetting resins, such as unsaturated polyester resin<sup>5,28,31-35</sup> and epoxy resin.<sup>5,28,36-46</sup> Basically, with DSC, one obtains a thermogram of the rate of heat generation (or absorption) as a function of temperature and, then, calculates the amount of heat generated (or absorbed) during the curing reaction. In the use of DSC for studying the isothermal curing kinetics of thermosetting resins, one assumes that the amount of heat generated due to the curing reaction is directly proportional to the degree of cure (or the extent of reaction) of the sample at that time, and then one relates the rate of cure,  $d\alpha/dt$ , to the rate of heat generated,  $dQ/dt$ , by

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

in which  $Q_T$  represents the total heat generated. Integrating eq. (1) with respect to time, one obtains the relative degree of cure,  $\alpha$ ,

$$\alpha = \frac{1}{Q_T} \int_{t_i}^t \left( \frac{dQ}{dt} \right) dt \quad (2)$$

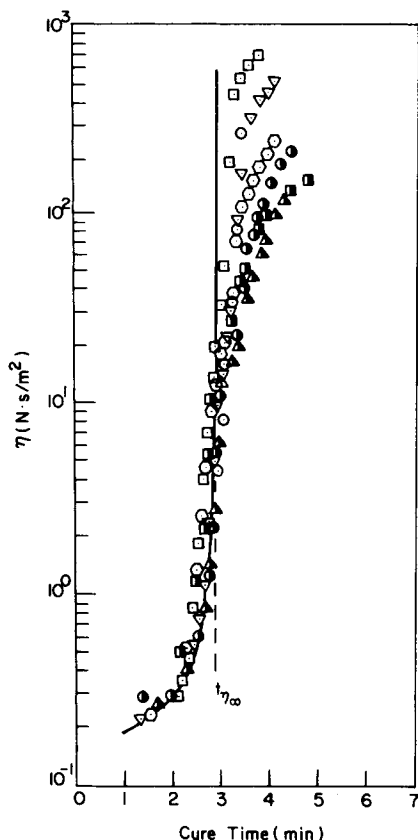


Fig. 4. Viscosity vs. cure time ( $T = 60^{\circ}\text{C}$ ) at various shear rates ( $\text{s}^{-1}$ ): ( $\odot$ ) 0.269; ( $\Delta$ ) 1.07; ( $\square$ ) 2.69; ( $\nabla$ ) 4.27; ( $\odot$ ) 6.77; ( $\bullet$ ) 10.7; ( $\blacktriangle$ ) 17.0; ( $\blacksquare$ ) 26.9.

Recently, Kamal and co-workers<sup>28,29</sup> have proposed the following empirical expression:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (3)$$

for describing the isothermal curing kinetics of some thermosetting resins (namely, unsaturated polyester and epoxy resins), in which  $k_1$  and  $k_2$  are rate constants, which depend on temperature, and  $m$  and  $n$  are constants (the sum of  $m$  and  $n$  is the reaction order). More recently, Pusatcioglu et al.<sup>34</sup> have reported that eq. (3) was in good agreement with their experimental results for unsaturated polyester resins. Ryan and Dutta<sup>47</sup> suggested a method that may be used to rapidly estimate the parameters in eq. (3) from information on the initial reaction rate and the peak of the curing rate curve.

One can determine the degree of cure ( $\alpha$ ) as a function of cure time ( $t$ ) by integrating eq. (3). In principle, it is possible to express the change of rheological properties in terms of the degree of cure, instead of cure time, when both the rheological and DSC measurements are performed under identical experimental conditions. Indeed, such an attempt was made by Ryan.<sup>5</sup>

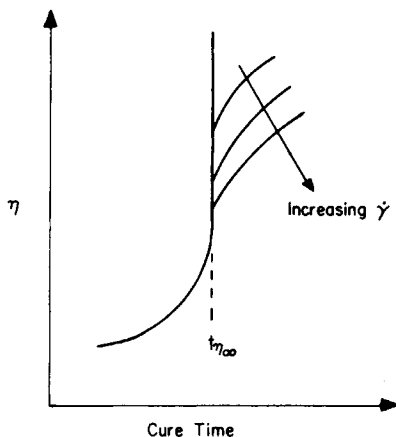


Fig. 5. Schematic describing the viscosity–cure time curve at various shear rates.

## EXPERIMENTAL

### Materials and Sample Preparation

A general-purpose unsaturated polyester resin (Aropol 7030, Ashland Chemical Co.) was used for the study. Although the chemistry of the resin was not disclosed by the resin producer, we believe that it was prepared by the reaction of propylene glycol with a mixture of maleic anhydride and isophthalic anhydride. We used benzoyl peroxide in granular form (Cadox BFF-60 WET, Noury Chemical Corp.) as initiator, and a solution of 5 wt % *N,N*-dimethylaniline (Aldrich Chemical Co.) diluted in styrene as promoter.

In preparing the sample for curing, the formulation used was: resin/initiator/promoter = 60/2.0/1.2 (by weight). We prepared Solution A by mixing the resin and initiator, and Solution B by mixing the resin and promoter. The individual solutions were kept separately in glass jars equipped with glass stoppers, sealed with silicone grease in order to prevent the evaporation of the styrene. The solutions were kept in a refrigerator maintained at 10°C in order to avoid any premature polymerization when they were not in use. They were discarded after 3 weeks storage and fresh samples were then prepared. When needed, we mixed equal amounts of Solution A and Solution B, stirred the mixture vigorously with a wooden tongue blade for about 30 s at room temperature, and then placed the sample immediately either into the rheometer for rheological measurement or into the DSC aluminum pan for thermokinetic measurement.

### Rheological Measurement

For rheological measurements, we employed a Model R-16 Weissenberg rheogoniometer (Sangamo-Weston Controls, Bognor Regis, Sussex, England), fitted with a flat plate and a cone (4°, 2.5 cm in diameter). We conducted both steady and oscillatory shearing flow measurements under isothermal conditions, at various temperatures. Since the gap opening between the cone and plate was very small (160  $\mu\text{m}$ ), we assumed, in the analysis of the experimental data, that



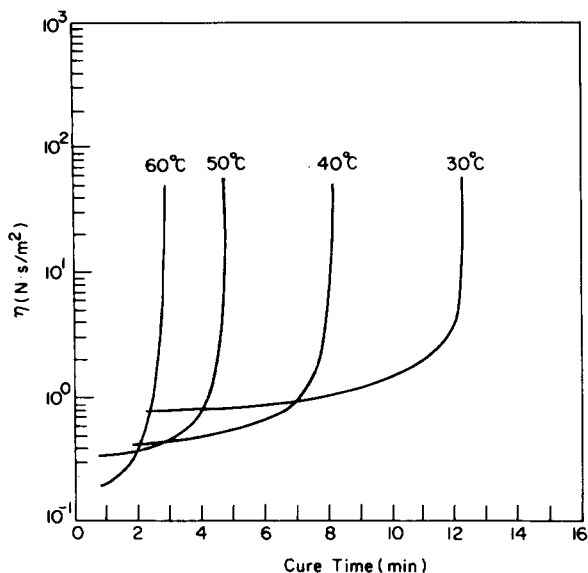


Fig. 6. Viscosity vs. cure time at various temperatures ( $\dot{\gamma} = 10.7 \text{ s}^{-1}$ ).

any temperature variation during cure, due to the exothermic reaction, had only a negligible effect on the accuracy of measurements.

### Thermokinetic Measurement

DSC was used in investigating the curing kinetics of the unsaturated polyester resin. For the study, we used a DuPont 1090 Thermal Analyzer equipped with a 910 DSC Module. Indium was used for temperature and calorimetric cali-

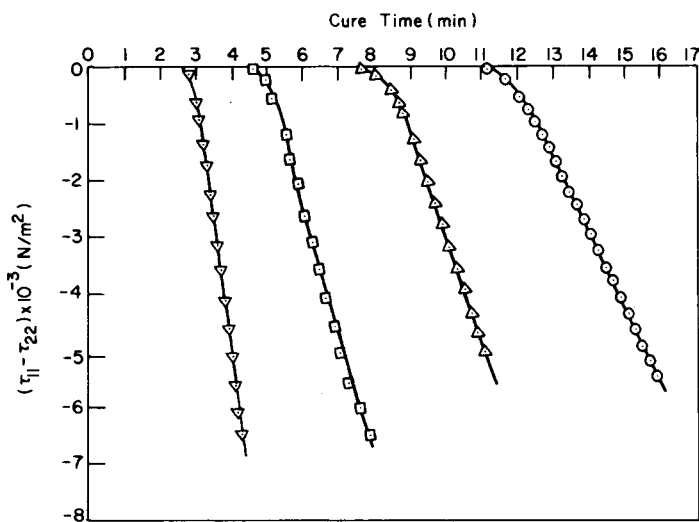


Fig. 7.  $-(\tau_{11} - \tau_{22})$  vs. cure time for the fluid at rest ( $\dot{\gamma} = 0.0 \text{ s}^{-1}$ ) at various temperatures ( $^{\circ}\text{C}$ ): (○) 30; (△) 40; (□) 50; (▽) 60.

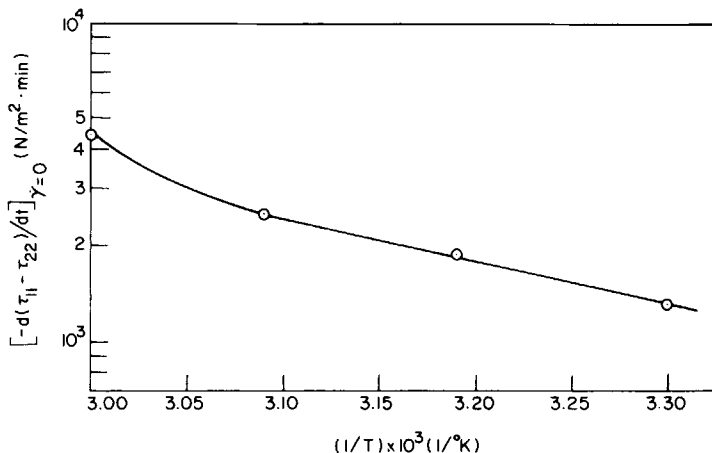


Fig. 8.  $[-d(\tau_{11} - \tau_{22})/dt]_{\gamma=0}$  vs.  $1/T$ .

brations, following the procedure described in the operating manual of the instrument.

The experimental procedure employed is very similar to that described in the literature.<sup>29,46</sup> Briefly stated, the procedure employed is as follows. A drop of sample containing the catalyst (i.e., the mixture of Solutions A and B described above) was introduced to a preweighed DSC aluminum pan. Hermetic DSC pans were used to minimize losses of volatile materials during the heating of the sample in the DSC cell. The pans were sealed using a hermetic die press. The weight of the sample was determined accurately by differential weighing using a mi-

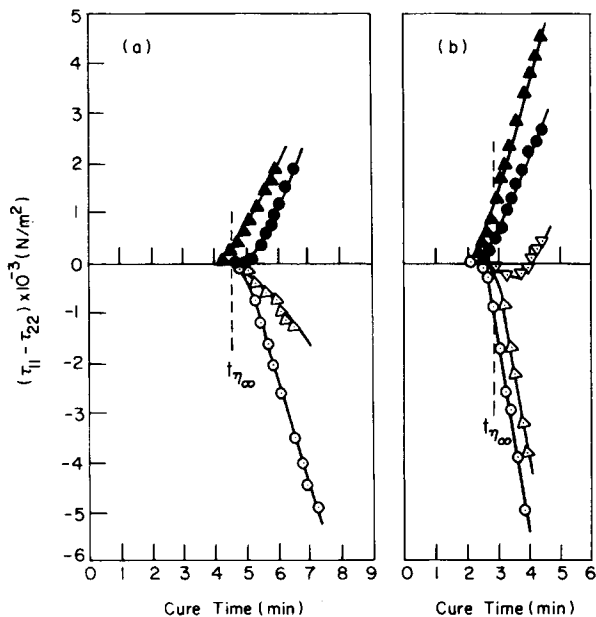


Fig. 9.  $\tau_{11} - \tau_{22}$  vs. cure time at various shear rates ( $s^{-1}$ ): (a)  $T = 50^\circ C$ : ( $\odot$ ) 0.0; ( $\Delta$ ) 4.27; ( $\bullet$ ) 6.77; ( $\blacktriangle$ ) 26.9; (b)  $T = 60^\circ C$ : ( $\odot$ ) 0.0; ( $\Delta$ ) 2.69; ( $\nabla$ ) 6.77; ( $\bullet$ ) 17.0; ( $\blacktriangle$ ) 26.9.

TABLE I  
Summary of  $t_{\eta_{\infty}}$  at Various Isothermal Cure Temperatures

Temperature ( $^{\circ}\text{C}$ )	$t_{\eta_{\infty}}$ (min)
30	11.0-12.3
40	7.7-8.1
50	4.7
60	2.9

crobalance. The weight loss during the experiment was negligible over the range of temperature employed. The size of sample ranged from 5 to 10 mg. A small sample was required in order to achieve isothermal operation during cure, particularly for samples cured at high temperatures.

The amount of heat evolved by the curing reaction was measured by completing the reaction isothermally, at various temperatures. In the experiment, the initial base line was determined by equilibrating the instrument at a predetermined curing temperature with an empty sample pan, and a run was initiated by inserting a pan containing the sample. Equilibrium in temperature of the sample and reference holders was achieved in less than 1 min after the sample was placed in the DSC cell. The time required for the completion of the curing reaction was determined by the thermogram (i.e., the plot of the rate of heat generated vs. time) when it leveled off at the base line very close to the initial base line. The area under the thermogram was determined by integrating the output signal using an interactive DSC program that was built into the DuPont 1090 Thermal Analyzer. After completion of an isothermal curing reaction at a predetermined temperature, the sample was heated to  $200^{\circ}\text{C}$  at the rate of

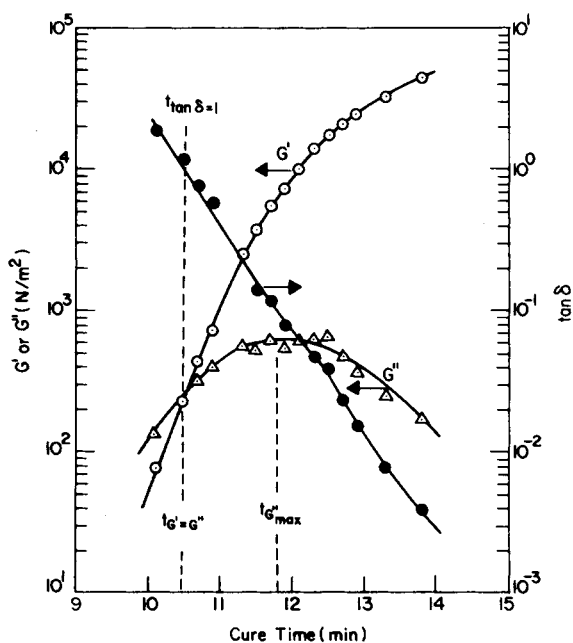


Fig. 10.  $G'$ ,  $G''$ , and  $\tan \delta$  vs. cure time at  $\omega = 1.89$  rad/s ( $T = 30^{\circ}\text{C}$ ): ( $\circ$ )  $G'$ ; ( $\Delta$ )  $G''$ ; ( $\bullet$ )  $\tan \delta$ .

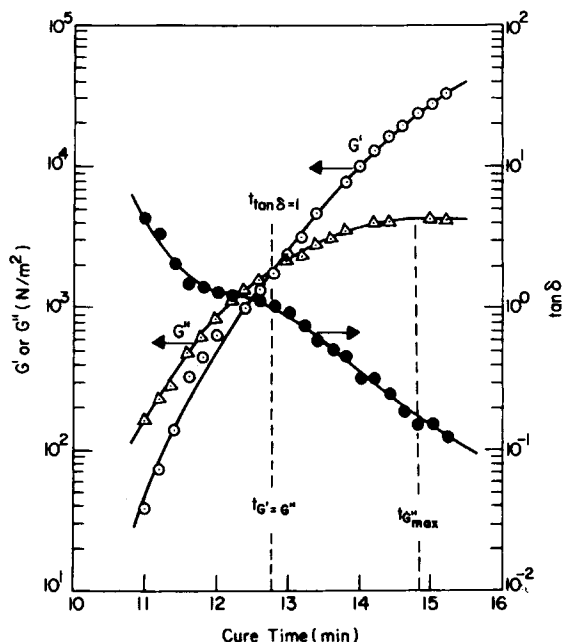


Fig. 11.  $G'$ ,  $G''$ , and  $\tan \delta$  vs. cure time at  $\omega = 29.94$  rad/s ( $T = 30^\circ\text{C}$ ). Symbols are the same as in Figure 10.

$10^\circ\text{C}/\text{min}$  and the amount of the heat released, termed hereafter as “residual heat,” was recorded. Thus, the total amount of heat generated by the curing reaction is the sum of the heat generated during the isothermal cure and the residual heat.

## RESULTS

### Steady Shearing Flow Behavior

Figure 1 gives plots of shear viscosity vs. cure time of the fluid sample at  $30^\circ\text{C}$ , with shear rate as parameter. Similar plots, obtained at other temperatures, are given in Figures 2–4. Several things are worth noting in these plots.

At an early stage of curing, the viscosity increases slowly, but then increases very rapidly, tending to approach a very large value as cure progresses. After the viscosity begins to increase very rapidly, the rate of increase in viscosity starts to diminish at a critical value of cure time. As a matter of fact, when this happened during our experiment, we noticed irregular torque output signals and also observed the exudation of material from the gap between the cone and plate, indicating that the flow had become unstable. Therefore, from the point of view of rigor, the values of viscosity shown on the right-hand side of the vertical line in Figures 1–4 have *little* rheological significance. It is of interest to note in Figures 1 and 2 that, at low temperatures, the time at which the viscosity approaches a very large value (i.e.,  $t_{\eta_\infty}$ ) shows a dependency on shear rate, whereas at higher temperatures (see Figs. 3 and 4)  $t_{\eta_\infty}$  becomes independent of shear rate. Perhaps, the observed shear dependency of  $t_{\eta_\infty}$  at low temperatures might have

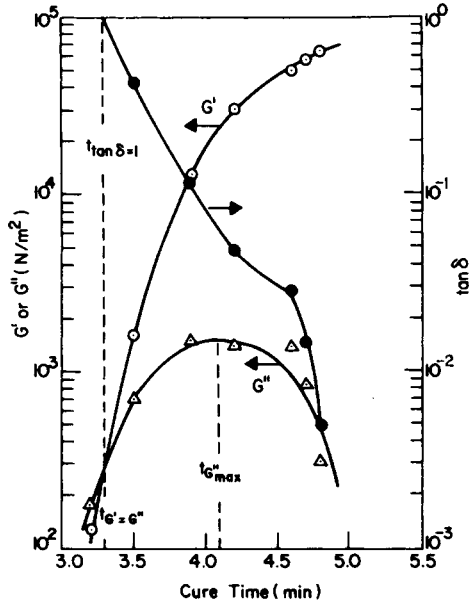


Fig. 12.  $G'$ ,  $G''$ , and  $\tan \delta$  vs. cure time at  $\omega = 1.89$  rad/s ( $T = 50^\circ\text{C}$ ). Symbols are the same as in Figure 10.

been due to experimental error in accurately determining the time at which the curing reaction begins (i.e.,  $t = 0$ ) at a desired temperature. Note further in Figures 3 and 4 that the value of viscosity which starts to deviate from the vertical line *decreases* as shear rate *increases*. This is illustrated schematically in Figure 5.

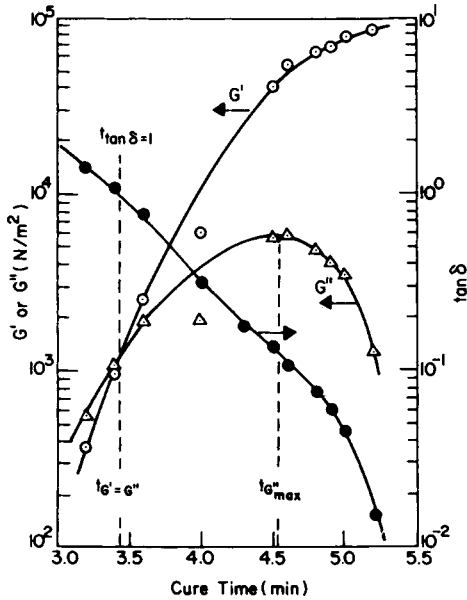


Fig. 13.  $G'$ ,  $G''$ , and  $\tan \delta$  vs. cure time at  $\omega = 29.94$  rad/s ( $T = 50^\circ\text{C}$ ). Symbols are the same as in Figure 10.

TABLE II  
Summary of Characteristic Cure Time Determined from Oscillatory Shearing Flow Measurement

Frequency (rad/s)	$t_{\tan \delta=1}$ (min)	$t_{G''_{max}}$ (min)
(i) At $T = 30^\circ\text{C}$		
1.19	12.9	13.8
1.89	10.5	11.8
2.99	11.4	13.2
4.74	11.4	12.8
7.52	13.1	14.3
11.92	12.4	14.0
29.94	12.8	14.8
(ii) At $T = 50^\circ\text{C}$		
1.89	3.3	4.1
2.99	3.6	4.4
4.74	3.6	4.8
7.52	3.5	4.2
11.92	3.7	5.1
18.89	3.8	4.8
29.94	3.4	4.6

In view of the fact that fluid elasticity develops as the curing reaction progresses (i.e., as the size of the molecules becomes larger due to polymerization reactions) and that the fluid elasticity increases with shear rate, the deviation from the vertical line in the viscosity–cure time curve at cure time  $t_{\eta_{\infty}}$  (see Figs. 3 and 4) may be attributable to the *onset* of flow instability due to fluid elasticity.

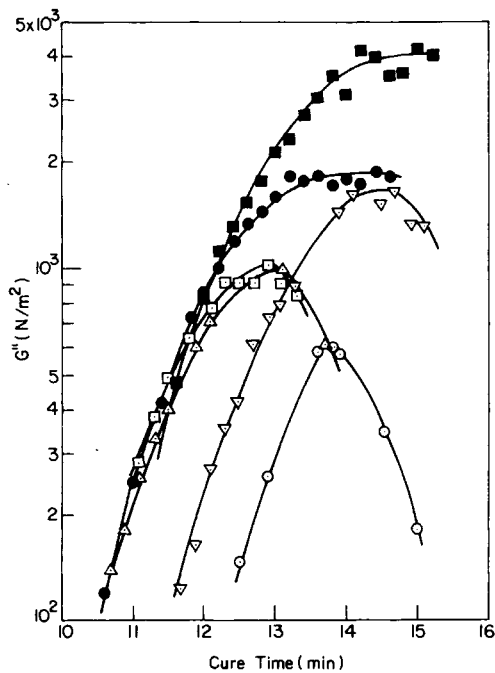


Fig. 14.  $G''$  vs. cure time ( $T = 30^\circ\text{C}$ ) at various angular frequencies (rad/s): ( $\odot$ ) 1.19; ( $\Delta$ ) 2.99; ( $\square$ ) 4.74; ( $\nabla$ ) 7.52; ( $\bullet$ ) 11.92; ( $\blacksquare$ ) 29.94.

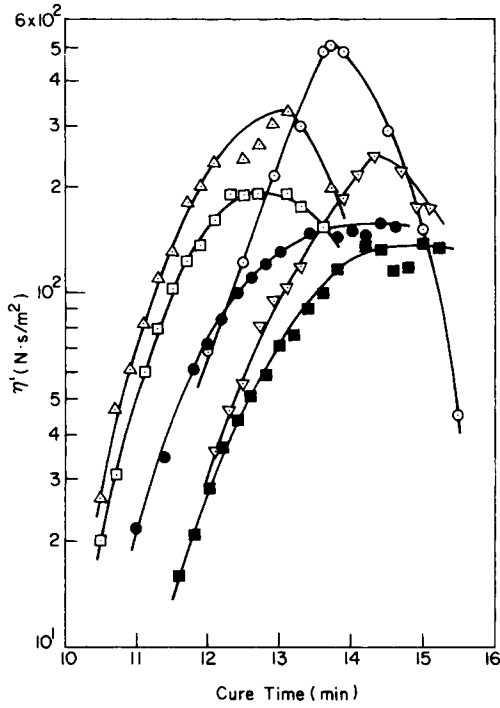


Fig. 15.  $\eta'$  vs. cure time ( $T = 30^\circ\text{C}$ ) at various angular frequencies (rad/s). Symbols are the same as in Figure 14.

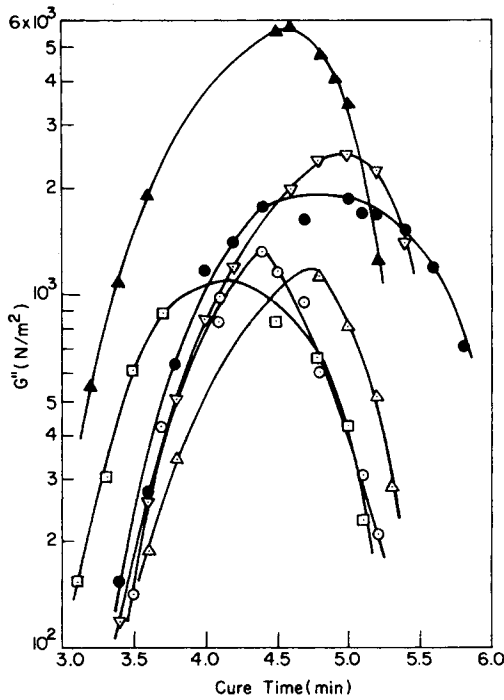


Fig. 16.  $G''$  vs. cure time ( $T = 50^\circ\text{C}$ ) at various angular frequencies (rad/s): ( $\circ$ ) 2.99; ( $\Delta$ ) 4.74; ( $\square$ ) 7.52; ( $\nabla$ ) 11.92; ( $\bullet$ ) 18.89; ( $\blacktriangle$ ) 29.95.

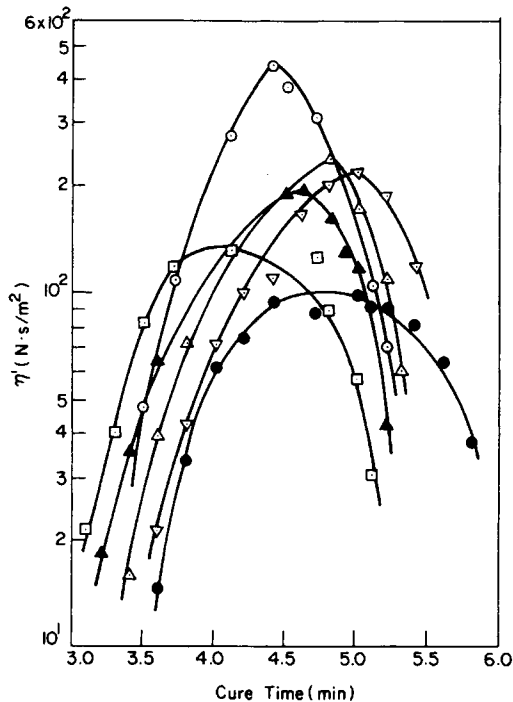


Fig. 17.  $\eta'$  vs. cure time ( $T = 50^\circ\text{C}$ ) at various angular frequencies (rad/s). Symbols are the same as in Figure 16.

Figure 6 describes the dependency of viscosity on cure temperature. It is seen that, as the isothermal cure temperature is increased, the value of  $t_{\eta_\infty}$  is decreased, which is also summarized in Table I. This is understandable, because the rate of curing reaction increases as the temperature increases. More quantitative statements will be made below when we present the experimental results of curing kinetics.

In the past, it has been suggested that  $t_{\eta_\infty}$  may indicate the time at which gel formation begins. However, directly demonstrating the formation of gels at  $t_{\eta_\infty}$  is not a trivial matter. Later, we will discuss more about the time at which gel formation may start, commonly referred to as "gel point," when we present the experimental results of dynamic shearing flow measurements.

When a sample was placed in the rheometer at the rest position (i.e., no flow), we observed that the plates were *pulled together*, which, we believe, is attributable to the shrinkage of the material. The normal forces ( $F$ ) measured were used to calculate the first normal stress difference  $\tau_{11} - \tau_{22}$  using the expression,  $-(\tau_{11} - \tau_{22}) = [2F/\pi R^2]_{\dot{\gamma}=0}$ , in which  $R$  is the radius of the plate and the *negative* sign refers to the direction in which the plates are *pulled together*. Note that the sign of  $\tau_{11} - \tau_{22}$  is *positive* when the plates move *apart* from each other.

Figure 7 gives plots of  $\tau_{11} - \tau_{22}$  vs. cure time for the fluid at *rest*, at different values of isothermal cure temperature. The slope of the linear portion of the curves shown in Figure 7 increases with temperature, following the Arrhenius relationship shown in Figure 8. It can be observed in Figure 9 that, when a test sample is subjected to steady shearing flow at high shear rates, the normal stresses



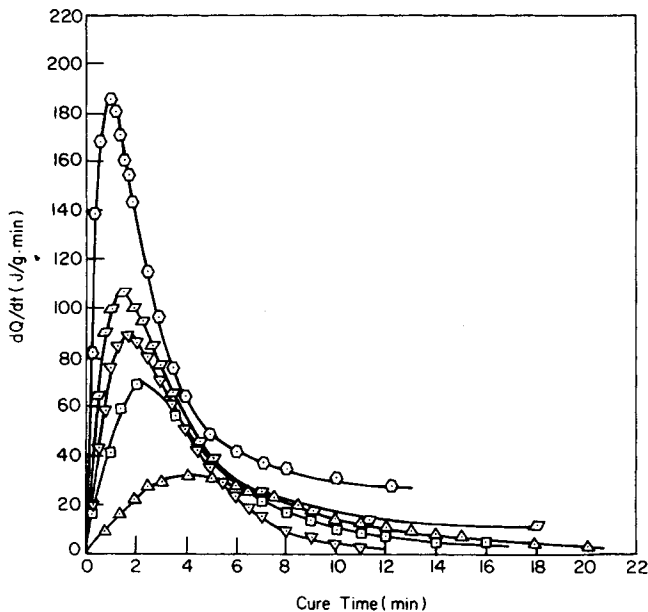


Fig. 18.  $dQ/dt$  vs. cure time at various temperatures ( $^{\circ}\text{C}$ ): ( $\Delta$ ) 40; ( $\square$ ) 45; ( $\nabla$ ) 50; ( $\triangle$ ) 55; ( $\circ$ ) 60.

generated by the motion of the fluid can overcome the shrinkage stress, and therefore the values of  $\tau_{11} - \tau_{22}$  increase very rapidly with cure time, giving rise to positive values.

It should again be mentioned that, from the point of view of rigor, the values of  $\tau_{11} - \tau_{22}$  calculated from the expression  $\tau_{11} - \tau_{22} = 2F/\pi R^2$ , and displayed in Figures 7-9, when the fluid undergoes shrinkage during flow, is of little rheological significance. This is because some of the assumptions made<sup>48</sup> in deriving

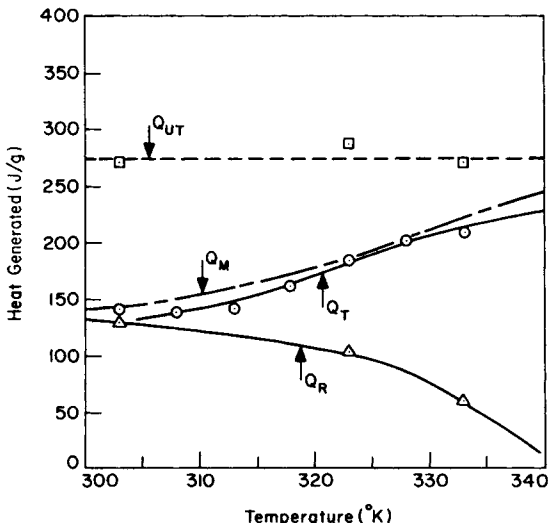


Fig. 19. Heat generated by curing reaction at various isothermal cure temperatures: ( $\circ$ )  $Q_T$ ; ( $\Delta$ )  $Q_R$ ; ( $\square$ )  $Q_{TOT}$ .

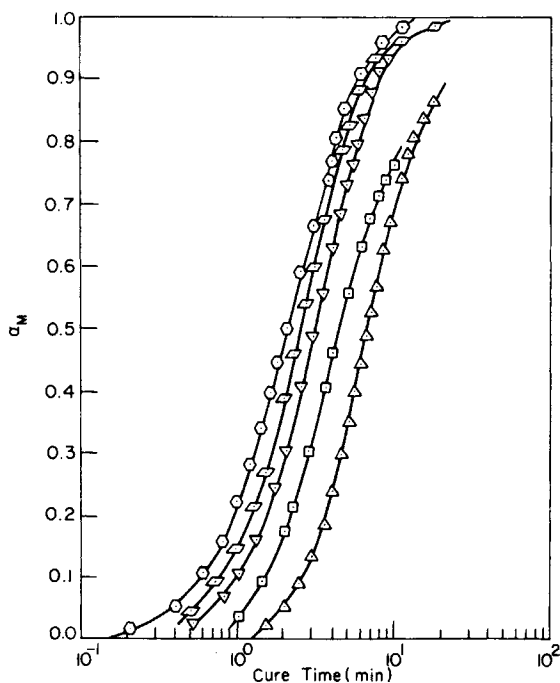


Fig. 20.  $\alpha_M$  vs. cure time at various isothermal cure temperatures (K): ( $\Delta$ ) 313; ( $\square$ ) 318; ( $\nabla$ ) 323; ( $\square$ ) 328; ( $\circ$ ) 333.

the expression  $\tau_{11} - \tau_{22} = 2F/\pi R^2$  from the equations of motion are violated. For instance, the available surface area and, also, the volume of the fluid undergoing the steady shearing deformation become time-dependent when shrinkage occurs. This, therefore, affects both the boundary conditions and the shape of the fluid at the rim (i.e., the meniscus).

### Dynamic Shearing Flow Behavior

Figure 10 gives the results of dynamic measurement taken at 30°C, at angular frequency  $\omega = 1.89$  rad/s, and Figure 11 gives similar results at  $\omega = 29.94$  rad/s. It is seen that the storage modulus ( $G'$ ) monotonically increases with cure time, whereas the loss modulus ( $G''$ ) goes through a maximum at low frequency ( $\omega = 1.89$ ). Furthermore,  $G''$  approaches a constant value at high frequency ( $\omega = 29.94$ ), as cure progresses. Figures 12 and 13 give the results of dynamic measurement taken at 50°C, at angular frequencies,  $\omega = 1.89$  rad/s and  $\omega = 29.94$  rad/s, respectively. It is seen that  $G''$  goes through a maximum at both low and high frequencies. Earlier, Imai<sup>6</sup> reported results similar to those shown in Figures 10–13 during the cure of unsaturated polyester resins.

Whereas *steady-state* shearing flow measurements only characterize the rheological properties of a material in the *liquid state*, oscillatory shearing flow measurements are also useful for characterizing the rheological properties of a material in both the *rubbery* and *glassy* states, implying that it can be used after the material enters the gelation stage (beyond the gel point). With this technique, however, it is not easy, in general, to discern the gel point. Very recently,

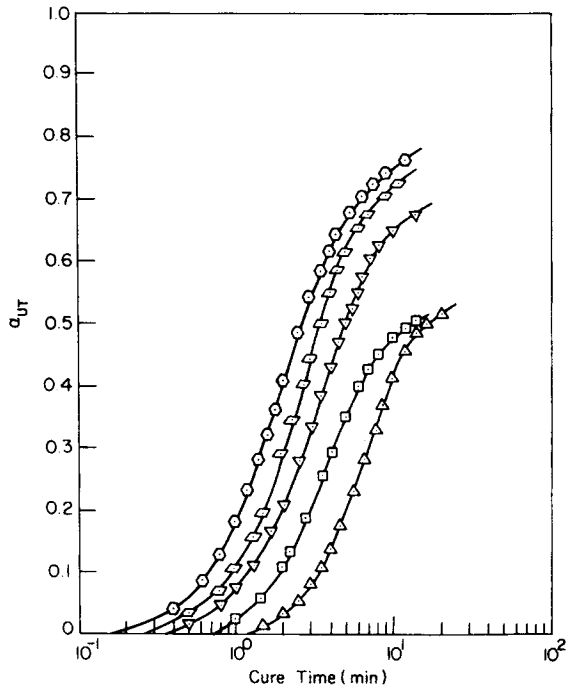


Fig. 21.  $\alpha_{UT}$  vs. cure time at various isothermal cure temperatures ( $^{\circ}\text{K}$ ). Symbols are the same as in Figure 20.

Tung and Dynes<sup>13</sup> reported that the time at which the crossover of  $G'$  and  $G''$  occurs (i.e.,  $t_{\tan \delta=1}$ ) during the isothermal cure of epoxy resins coincides with the gel time independently measured by the standard gel time test (ASTM D2471-72).

Our results (see Figures 1-4 and 10-13) tend to agree with the results of Tung and Dynes,<sup>13</sup> when the test fluid was cured at low temperatures (e.g.,  $30^{\circ}\text{C}$ ) or at a low rate of cure. However, at high temperatures (e.g.,  $50^{\circ}\text{C}$ ) it appears that the time at which the maximum in  $G''$  occurs (i.e.,  $t_{G''_{\max}}$ ) coincides with the value of  $t_{\eta_{\infty}}$ , determined from steady shearing flow measurements, and that the time at which the crossover of  $G'$  and  $G''$  occurs (i.e.,  $t_{\tan \delta=1}$ ) is shorter than  $t_{G''_{\max}}$ . Table I gives a summary of  $t_{\eta_{\infty}}$  at various cure temperatures, and Table II gives a summary of the comparison between  $t_{\tan \delta=1}$  and  $t_{G''_{\max}}$  for the unsaturated polyester resin investigated at two different values of isothermal cure temperature. This observation is in agreement with that made independently by Yap and Williams,<sup>8</sup> who employed the dynamic spring analysis (DSA) technique during the cure of an unsaturated polyester resin.

Figure 14 describes the dependency of  $G''$  on  $\omega$ , and Figure 15 describes the dependency of dynamic viscosity ( $\eta'$ ) on  $\omega$ , for the unsaturated polyester resin investigated at  $30^{\circ}\text{C}$ . Similar plots are given in Figures 16 and 17 for the same material at  $50^{\circ}\text{C}$ . Note that  $\eta'$  is the quantity derived from  $G''$  using the relationship  $\eta' = G''/\omega$ . It is seen that not only the magnitude of  $G''$  (and  $\eta'$ ), but also the shape of the  $G''$  curve (and  $\eta'$  curve) are strongly dependent upon the frequency ( $\omega$ ) imposed on the fluid. More specifically stated: (1) at a given cure time,  $G''$  increases with increasing  $\omega$ , whereas  $\eta'$  decreases with increasing  $\omega$ ; (2)

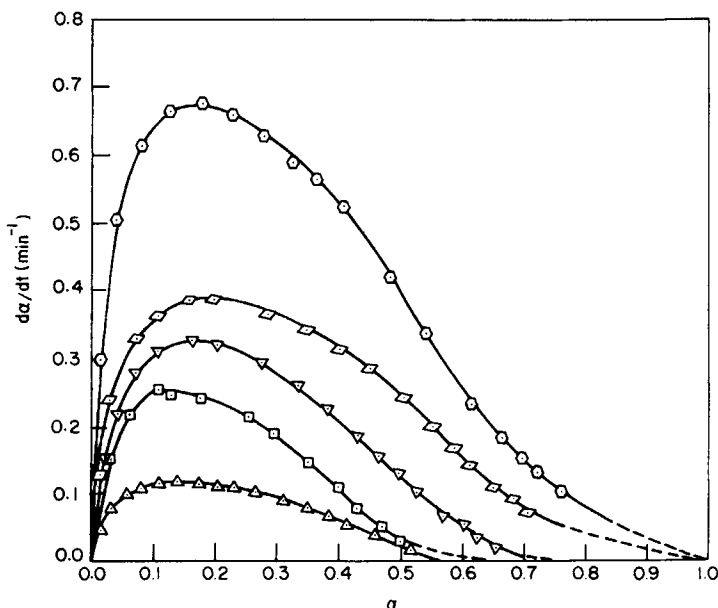


Fig. 22.  $d\alpha/dt$  vs.  $\alpha$  at various isothermal cure temperatures (K). Symbols are the same as in Figure 20.

at low temperatures,  $G''$  and  $\eta'$  go through a maximum as cure progresses at low frequencies, but, at high frequencies,  $G''$  and  $\eta'$  increase initially and then level off as cure progresses; (3) at high temperatures,  $G''$  and  $\eta'$  go through a maximum as cure progresses, at all the frequencies investigated.

### DSC Measurement

Figure 18 gives plots of the rate of heat generated ( $dQ/dt$ ) vs. cure time ( $t$ ) for isothermal DSC runs at various temperatures. It is seen that  $dQ/dt$  increases with increasing temperature, as expected intuitively for exothermic chemical reactions.

Figure 19 shows: (1) the measured heat generated ( $Q_T$ ) during the isothermal DSC runs; (2) the heat of the curing reaction ( $Q_M$ ) under isothermal conditions, as calculated by curve fitting the experimental data to the following quadratic expression:

$$Q_M(T) = C_0 + C_1T + C_2T^2 \quad (4)$$

following the suggestion of Kamal and co-workers<sup>28,29</sup>; (3) the residual heat ( $Q_R$ ) that was released when the sample was heated to 200°C, upon the completion of an isothermal curing reaction, at the rate of 10°C/min; (4) the total heat of the curing reaction ( $Q_{TOT}$ ), given by:

$$Q_{TOT} = Q_T + Q_R \quad (5)$$

(It is of great interest to note in Fig. 19 that the value of  $Q_{TOT}$  turns out to be a constant, almost independent of the temperature chosen for isothermal cure); (5) the ultimate heat of the curing reaction ( $Q_{UT}$ ), the average of the several

TABLE III  
Summary of Kinetic Parameters Appearing in Eq. (3) for the Unsaturated Polyester Resin Investigated

Temp (K)	Kinetic parameters			
	$k_1$ (min <sup>-1</sup> )	$k_2$ (min <sup>-1</sup> )	$m$	$n$
313	0.0048	0.203	0.29	1.71
318	0.0131	0.351	0.23	1.77
323	0.0278	0.793	0.35	1.65
328	0.0607	1.110	0.43	1.57
333	0.0924	1.570	0.40	1.60

values of  $Q_{TOT}$ , taken at various isothermal cure temperatures. It should be remembered that  $Q_T$  in Figure 19 is the cumulative heat generated during isothermal cure, which was obtained by integrating the curve,  $dQ/dt$  vs.  $t$ , given in Figure 18.

Following the assumption made by previous investigators<sup>28-36</sup> that the amount of heat generated by the curing reaction is directly proportional to the degree of cure (or the extent of reaction) of the sample at that time, one can now define

$$\alpha_M = Q_i(T)/Q_M(T) \quad (6)$$

and

$$\alpha_{UT} = Q_i(T)/Q_{UT} \quad (7)$$

depending upon the choice of the total heat generated,  $Q_M(T)$  or  $Q_{UT}$ . Note that  $Q_i(T)$  refers to the heat generated at a particular time  $t$  at an isothermal curing temperature  $T$ .

Figure 20 gives plots of  $\alpha_M$  vs. cure time, and Figure 21 plots of  $\alpha_{UT}$  vs. cure time, for the unsaturated polyester resin investigated at various values of isothermal cure temperature. It is seen that very high values of the degree of cure (approaching  $\alpha_M = 1$ ) are obtained with  $\alpha_M$ , compared to those obtained with  $\alpha_{UT}$ . We know that the curing reaction cannot approach completion at such low temperatures, say at 50°C, because the ratio of the residual heat ( $Q_R$ ) to the ultimate heat ( $Q_{UT}$ ) is fairly large, i.e., 0.376 (see Fig. 19). Therefore we believe that  $\alpha_{UT}$ , rather than  $\alpha_M$ , yields more realistic values for the degree of cure. For this reason, we have chosen to use  $\alpha_{UT}$  (hereafter the subscript  $UT$  will be deleted) in constructing the plots of the rate of cure ( $d\alpha/dt$ ) vs. the degree of cure ( $\alpha$ ), given in Figure 22. Note that the plots given in Figure 22 may be obtained by graphically (or numerically) differentiating the plots given in Figure 21. Alternatively, one can obtain  $d\alpha/dt$  from the expression

$$\frac{d\alpha}{dt} = \frac{1}{Q_{UT}} \left( \frac{dQ}{dt} \right)_T \quad (8)$$

with the aid of  $(dQ/dt)_T$ , determined experimentally (see Fig. 18).

Having constructed plots of  $d\alpha/dt$  vs.  $\alpha$ , we have determined the parameters in the kinetic expression, defined by eq. (3), and the results are summarized in Table III. In calculating the kinetic parameters, we assumed a second-order reaction (i.e.,  $m + n = 2$ ) as suggested by Kamal and co-workers,<sup>28,29</sup> and used

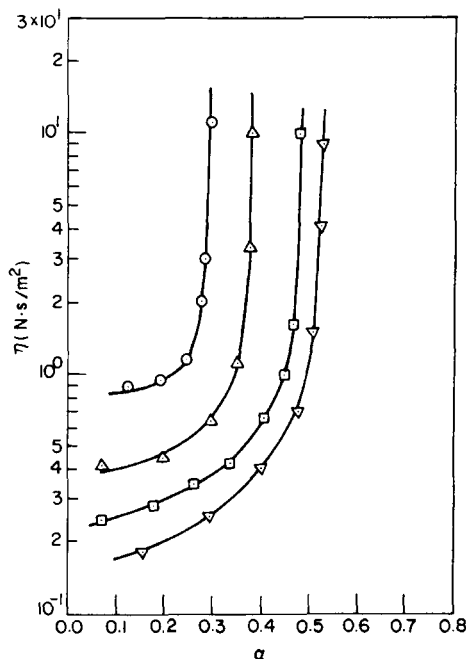


Fig. 23.  $\eta$  vs.  $\alpha$  at various isothermal cure temperatures ( $^{\circ}\text{C}$ ): ( $\odot$ ) 30; ( $\Delta$ ) 40; ( $\square$ ) 50; ( $\nabla$ ) 60.

the procedure suggested by Ryan and Dutta.<sup>47</sup> It is seen in Table III that, over the range of isothermal curing temperatures investigated (i.e., 40–60 $^{\circ}\text{C}$ ), the values of  $m$  and  $n$  are relatively insensitive to temperature, and the values of  $k_1$  and  $k_2$  increase with temperature, following the Arrhenius relationship.

Having obtained data on the viscosity ( $\eta$ ) and the degree of cure ( $\alpha$ ) that vary with cure time (see, for example, Figs. 3 and 21), we have constructed plots describing how  $\eta$  varies with  $\alpha$ , as given in Figure 23. It is seen that, as the temperature increases, one can achieve a higher degree of cure before the viscosity approaches a very large value.

## DISCUSSION

### Rheological Behavior During Cure

The steady shearing flow properties observed during the isothermal cure of an unsaturated polyester resin are summarized schematically in Figure 24. Note that, at and above  $t_{\eta_{\infty}}$ , the increase in  $\eta$  with cure time depends upon the shear rate applied. In the rigorous sense, the significance of  $\eta$  above  $t_{\eta_{\infty}}$  is questionable because the flow is no longer stable. Of particular interest is the normal stress behavior showing that: (1) at low shear rates, *negative* normal forces develop as cure progresses; (2) at intermediate shear rates, *negative* normal forces develop at an early stage of cure, but *positive* normal forces develop as cure progresses further; (3) at high shear rates, *positive* normal forces develop from the beginning of the cure and increase very rapidly as cure progresses further. As mentioned above, *negative* normal forces indicate that, during cure, the cone and plate are

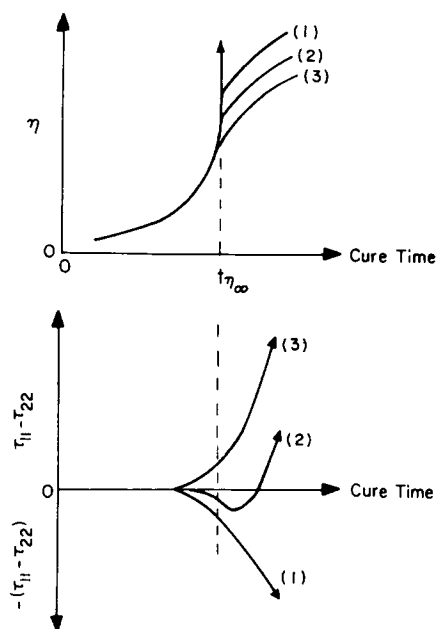


Fig. 24. Schematic of plots of  $\eta$  and  $\tau_{11} - \tau_{22}$  versus cure time, with shear rate as parameter. The shear rate increases from curve (1) to curve (3).

pulled together. The only physical explanation that we can offer is that the material shrinks during cure.

It is worth elaborating on the potential usefulness of the normal force measurements reported above, especially regarding the *negative* values of  $\tau_{11} - \tau_{22}$ . Referring to Figures 7 and 8, we observe that, as the curing temperature increases, the rate of decrease in  $\tau_{11} - \tau_{22}$  [i.e., the slope of the  $-(\tau_{11} - \tau_{22})$  vs. cure time curve] increases. When there is no motion in the fluid at  $\dot{\gamma} = 0$ , the only normal force exerted on the fluid must have come from the shrinkage of the material that was placed between the cone and plate. In view of the fact that the rate of cure (i.e., the rate of polymerization) increases with temperature, one would expect that the rate of shrinkage would also increase with temperature. Therefore, the increase in the slope of the  $-(\tau_{11} - \tau_{22})$  vs. cure time curve with increasing cure temperature, shown in Figure 8, must be attributable to an increase in the rate of shrinkage as the curing temperature is increased.

We have indeed measured the shrinkage of the unsaturated polyester resin at rest (i.e., at  $\dot{\gamma} = 0$ ) during isothermal cure, using a simple dilatometric technique.<sup>49</sup> Figure 25 displays the results of the shrinkage measurements performed at two different temperatures. It is seen in Figure 25 that both the extent of shrinkage and the rate of shrinkage increase as the curing temperature is increased. This observation supports the speculation made above on the origin of the *negative* normal forces (see Figs. 7 and 8).

On the basis of the interpretation presented above, we believe that normal force measurements at low shear rates in a cone-and-plate rheometer may be useful in evaluating the extent of shrinkage during the cure of thermosetting resins. This possibility is indeed an exciting one, especially for the development of ef-

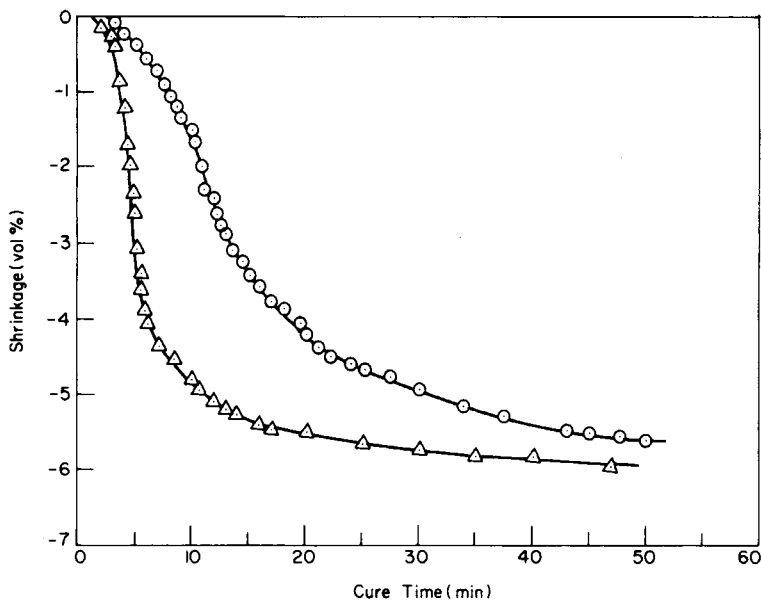


Fig. 25. Volume shrinkage vs. cure time at various isothermal cure temperatures ( $^{\circ}\text{C}$ ): (○) 30; (△) 50.

efficient low-profile additives for the shrinkage control of thermosetting polyester resins.

Oscillatory shearing flow measurement has been used for some time in investigating the rheological behavior of thermosetting resins during cure. The literature indicates that two different suggestions have been made on the determination of gel time from dynamic measurements. These are that the gel time is (1) the time at which both the elastic modulus ( $G'$ ) and loss modulus ( $G''$ ) have the same value, i.e.,  $t_{G'=G''}$  or  $t_{\tan \delta=1}$ ; (2) the time at which the loss modulus has the greatest (or maximum) value, i.e.,  $t_{G''_{\max}}$ . The oscillatory shearing flow properties observed in our experimental investigation are summarized schematically in Figure 26. It is seen in Figure 26 that  $t_{G''_{\max}}$  is greater than  $t_{\tan \delta=1}$ . Over the limited range of low conditions employed in both steady and oscillatory shearing flow experiments, we have found that, at high cure temperatures (say,  $50^{\circ}\text{C}$ )  $t_{G''_{\max}}$  (hence  $t_{\eta'_{\max}}$ ) coincides reasonably well with the  $t_{\eta_{\infty}}$  determined from steady shearing flow experiments. On the other hand, at low cure temperatures (say,  $30^{\circ}\text{C}$ )  $t_{\tan \delta=1}$  agrees fairly well with  $t_{\eta_{\infty}}$ . It appears therefore that both of the above suggestions are applicable, depending upon the processing conditions, under which cure takes place.

Note that, in steady shearing flow at high shear rates, the normal force measurement taken during cure represents the difference between the elastic effect (giving rise to a *positive* normal force) and the shrinkage force (giving rise to a *negative* normal force). Note further that the magnitude of the shrinkage force remains constant at a given curing rate (i.e., cure temperature) and depends upon neither the mode of deformation (i.e., oscillatory or steady shearing flow) nor the intensity of deformation, to which the thermosetting resin is subjected during cure. We are of the opinion that the observed peak in  $G''$  is due to neither the



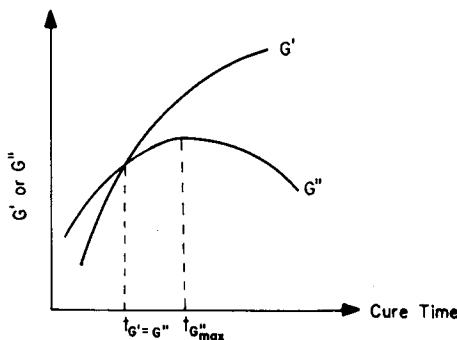


Fig. 26. Schematic of plots of  $G'$  and  $G''$  vs. cure time.

molecular origin nor the network transition, as pointed out by other investigators.<sup>8,17</sup>

### Curing Kinetics of Unsaturated Polyester Resin

The curing kinetics of unsaturated polyester resins have been studied by several investigators.<sup>5,28,29,31-35</sup> Table IV gives a summary of the kinetic parameters reported by the previous investigators, together with the results of our own investigation. Since each group of investigators used different resin formulations, we have also listed those resin formulations in Table IV. Considering the differences in resin formulation, the numerical values of the kinetic parameters given in Table IV may be considered to be in reasonable agreement. Since the degree of cure may be defined in two different ways [i.e.,  $\alpha_{UT}$  using eq. (7) and  $\alpha_M$  using eq. (6)], we have calculated the kinetic parameters, using both definitions,  $\alpha_{UT}$  and  $\alpha_M$ .

It should be mentioned that, when evaluating the kinetic parameters appearing in eq. (3), the results of our DSC measurements (see Table III) give rise to *nonzero* values of  $k_1$ , whereas earlier investigators<sup>28,29,34</sup> reported  $k_1$  values equal to zero. We believe that this can be attributed to a different *rate* of cure, which stems from the fact that in our study, a promoter (*N,N*-dimethylaniline) was used to accelerate the curing reactions at relatively low reaction temperatures, in order to facilitate our rheological measurements. Note that the reaction constant  $k_1$  is determined directly from the DSC thermogram at a cure time equal to zero. It is seen from Figure 18 that, in the presence of promoter, the curing reactions are indeed fast, giving rise to *nonzero* values of the intercept in the DSC thermogram at zero cure time. It is worth noting further that, in the absence of promoter, we have obtained *zero*  $k_1$  values for the same systems cured at low temperatures (i.e., 60°C and lower).

Of particular interest is the relationship between the viscosity  $\eta$  and the degree of cure  $\alpha$ . It is seen in Figure 23 that higher values of  $\alpha$  are achieved as the cure temperature is increased, before  $\eta$  approaches a very large value. Similar observation was reported earlier by Ryan,<sup>5</sup> who also investigated the rheological behavior of thermosetting polyester resins during isothermal cure, using a cone-and-plate rheometer. According to the theory advanced by Flory,<sup>50</sup> one would expect to observe the same value of  $\alpha$  at the incipient gel point, regardless of the temperature at which curing takes place.

TABLE IV  
Summary of Isothermal Curing Study on Conventional Unsaturated Polyester Resins by Various Investigators

	Horie et al. <sup>35</sup>	Kamal and Sourour <sup>29</sup>	Kamal et al. <sup>28</sup>	Pusatcioglu et al. <sup>34</sup>	Present study
		(i) Formulation of resin			
Styrene (wt %)	varied	30.0	40.0	28.0	36.3
Nature of peroxide	benzoyl peroxide (BP)	60% MEKPO in DMP	60% MEKPO in DMP	60% MEKPO in DMP	60% BP in phthalate plasticizer
Amount of peroxide (wt %)	2.42	0.99	0.99	0.70	3.16
Nature of promoter	—	—	—	—	5 wt % DMA
Amount of promoter (wt %)	—	—	—	—	1.9
		(ii) Thermal analysis			
Total heat of cure (J/g)	—	305.0	347.2	309.2	275.0
		(iii) Kinetic parameters <sup>a</sup> appearing in eq. (3)			
Activation energy for $k_1$ (kJ/g-mol)	—	—	—	—	99.3 (102.7)
Activation energy for $k_2$ (kJ/g-mol)	77.4	(78.2)	(72.8)	71.1	62.8 (78.9)
$m$	—	(0.25)	(0.33)	0.45	0.34 (0.49)
$n$	—	(1.75)	(1.67)	1.55	1.66 (1.51)

<sup>a</sup> The numbers *without* the bracket are based on  $\alpha_{UT}$ , and the numbers *with* the bracket are based on  $\alpha_M$ .

According to Gillham and co-workers,<sup>24,25</sup> vitrification can occur before gelation when the cure is carried out at a temperature below  $T_{gg}$ , the temperature at which gelation and vitrification can occur simultaneously. In view of the fact that the  $T_{g\infty}$  (i.e., the glass transition temperature  $T_g$  for the fully cured polymer) of the polyester resin employed is about 110°C,<sup>51</sup> which is much higher than the isothermal cure temperatures (30–60°C) chosen in the present investigation, one is very much tempted to explain the observed temperature dependence of the  $\eta$ - $\alpha$  relationship (see Fig. 23) by invoking the theory of vitrification and gelation advanced by Gillham and co-workers.<sup>24,25</sup>

It should be pointed out, however, that, as shown in Figures 3 and 4,  $\eta$  still increases *without* approaching an infinitely large value as cure time increases beyond  $t_{\eta\infty}$ , and, moreover,  $\eta$  exhibits shear-thinning behavior as cure time increases beyond  $t_{\eta\infty}$ . Therefore we are of the opinion that, in our experiment, vitrification could *not* have occurred at  $t_{\eta\infty}$ , before gelation. We speculate that the following mechanisms might explain the experimentally observed  $\eta$ -cure time curves shown in Figures 3 and 4: (1) Some gel particles might have been formed at  $t_{\eta\infty}$  and thus the specimen, subjected to steady shearing flow, might have behaved like a suspension (i.e., a two-phase system) at cure times beyond  $t_{\eta\infty}$ . (2) As cure progresses beyond  $t_{\eta\infty}$ , the molecular weight of the resin has increased sufficiently to exhibit non-Newtonian (i.e., shear-thinning) viscoelastic behavior, although the flow might have been unstable at cure times beyond  $t_{\eta\infty}$ .

Ammon et al.<sup>52</sup> have reported that crosslinked polyester resins form a heter-

ogeneous network structure, and Funke<sup>53</sup> has observed that an increase in the cure temperature of styrene-unsaturated polyester systems reduces the degree of heterogeneity of the final three-dimensional networks. Independently, Imai<sup>6</sup> has observed that, in order to obtain the same values of viscoelastic properties (using dynamic measurements), a polyester resin cured at a high polymerization rate (i.e., high cure temperature) required a greater portion of the unsaturated polyester resin converted to gels than one cured at a low polymerization rate (i.e., low cure temperature). These investigations, then, appear to support our view that: (1) during the cure of an unsaturated polyester resin, gel particles may be formed even at a low cure rate (because of the high functionality for cross-linking), giving rise to a heterogeneous phase as cure progresses beyond  $t_{\eta_{\infty}}$ ; (2) the observed shear-thinning behavior at cure times beyond  $t_{\eta_{\infty}}$  is due in part to the presence of gel particles giving rise to suspensions, and is largely attributable to the macromolecules formed during cure; (3) the observed increase in the degree of cure with increasing cure temperature is not due to the occurrence of vitrification before gelation, but is characteristic of styrene-unsaturated polyester systems giving rise to heterogeneous network structure containing gel particles.

### CONCLUDING REMARKS

The following conclusions may be made on the basis of the results presented above: (1) When an unsaturated polyester resin is subjected to steady shearing flow during cure, its viscosity exhibits shear-thinning behavior at and above  $t_{\eta_{\infty}}$ , which is attributable to the formation of large molecules. (2) The normal force response of the thermosetting polyester resin during cure, subjected to steady shearing flow, depends on the intensity of deformation (i.e., the shear rate). More specifically, at low shear rates, especially when the fluid is at rest, *negative* normal forces develop as cure progresses, which is attributable to the polymerization shrinkage during cure. But at high shear rates, the shrinkage force is overtaken by the *elastic* normal forces which are generated by the deformation of macromolecules, thus giving rise to *positive* normal forces. (3) When an unsaturated polyester resin is subjected to oscillatory shearing flow during cure at low temperatures,  $G''$  and  $\eta'$  increase initially and level off at high frequencies as cure progresses. On the other hand,  $G''$  and  $\eta'$  go through a maximum as cure progresses, either when the resin is cured at high temperature and at all frequencies or when the resin is cured at low temperature and at low frequencies. (4) The time required for the onset of gel formation depends on the rate of the crosslinking reaction (i.e., the cure temperature). We have found that  $t_{\tan \delta=1}$ , determined from dynamic measurements, agrees fairly well with  $t_{\eta_{\infty}}$ , determined from steady shearing measurements, for the thermosetting polyester resin cured at slow rates (i.e., at low temperatures). On the other hand,  $t_{G''_{\max}}$  determined from dynamic measurements agrees reasonably well with  $t_{\eta_{\infty}}$  for the resin cured at fast rates (i.e., at high temperatures). (5) The curing kinetics of an unsaturated polyester resin determined by DSC are in good agreement with those reported in the literature. (6) By combining the results of DSC and rheological measurements, we have been able to construct plots of viscosity vs. the degree of cure, at various isothermal cure temperatures.

It should be remembered that, in the present investigation, the chemorheology

and curing kinetics of an unsaturated polyester resin were studied under *isothermal* conditions. In a future publication, we will discuss the results of the nonisothermal curing of unsaturated polyester resins.

This study was supported in part by the National Science Foundation under Grant CPE-8211426 and Owens-Corning Fiberglas Corp., for which the authors are very grateful.

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Received February 25, 1983

Accepted May 16, 1983