Chemorheology of Thermosetting Resins. II. Effect of Particulates on the Chemorheology and Curing Kinetics of Unsaturated Polyester Resin

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Synopsis

The effect of particulates on both the rheological properties during cure and the curing kinetics of unsaturated resin has been investigated. For the investigation, a general-purpose unsaturated polyester resin was used, with calcium carbonate and clay as inorganic particulates and high-density polyethylene powder as organic particulates. It has been found that, as the particulate content increases, the resin/particulate mixture gives rise to shear-thinning behavior and the rate of cure increases. It has also been found that the $CaCO_3$ particles helped control shrinkage during cure when the material was subjected to steady shear deformation and that the gel time t_{η_∞} is shorter for mixtures of resin and particulates than for the neat resin alone. Differential scanning calorimetry (DSC) is found useful for determining the curing kinetics of resin/particulate mixtures. We have combined rheological and DSC measurements to obtain a correlation between viscosity and the degree of cure during isothermal curing operations.

INTRODUCTION

In general, the addition of particulates aids the dimensional stability of the molded parts of reinforced thermosetting composite materials over a wide range of service conditions. The nature of the reinforcing fibers and their surface characteristics strongly affect both the processing conditions required and end-use properties of the molded parts, although the nature of the polymer matrix itself is equally important.

Inorganic fillers are used in thermosetting resins as a heat sink to achieve a better temperature control across a molded part during cure. They are also used to reduce the amount of resin to be used, the overall shrinkage, and the cost. Poor temperature control during cure often gives rise to one, or several, of the following defects: warpage, sink, shrinkage, motley surface resulting from overcure, and blisters resulting from undercure.

In particulate-filled thermosetting composites, the resin matrix is the major load-bearing constituent (although the particulates also bear some load). It is generally accepted that interfacial adhesion between the resin matrix and the particulates is the basic requirement for the improvement of the end-use properties of the material at service conditions. In order to promote interfacial adhesion between the resin matrix and the particulates, it is a common practice to treat the particulates with an organic additive, often referred to as a "coupling agent."[1,2] The coupling agent, when chosen correctly, often helps improve the dispersion of the particulates in the resin matrix, which is very important to the preparation of molding compounds.

LEM AND HAN

Earlier, Han and Lem[3–5] investigated the effect of particulates ($CaCO_3$, clay, milled glass fibers, HDPE powders) on the rheological behavior of an unsaturated polyester resin *without* curing taking place. The study was aimed at enhancing our understanding of the role that particulates play in controlling the viscosity of the suspension, with and without a viscosity thickener, because the uniform dispersion of particulates and the control of the viscosity level in the preparation of polyester premix molding compounds greatly influence the subsequent molding operation. In their study,[3] Han and Lem have found that the viscosity of a suspension was increased as either the particulate concentration was increased or the size of particulates was decreased and that concentrated suspensions exhibited shear-thinning behavior. These observations are in agreement with those reported in the literature.[6,7] Han and Lem[3] have found further that when inorganic particulates (i.e., $CaCO_3$, clay, and milled glass fibers) were added, the viscosity of the resulting suspensions was affected by the surface treatment of the particulates with a coupling agent, and yet no measurable normal stress was observed. However, when organic particulates (i.e., HDPE powders) were added to unsaturated polyester resin, Lem and Han[5] have found that the resulting suspensions gave rise to *negative* normal stresses at and above a certain critical concentration of HDPE powders, over a certain range of shear rates (1–10 s^{-1}).

In Paper I of this series,[8] we have investigated the rheological behavior of a general-purpose unsaturated polyester resin during cure, subjected to steady shearing flow, or oscillatory shearing flow, under isothermal conditions, and, also, the isothermal curing behavior of the resin. In spite of the fact that reinforced thermosetting polyester composites of commercial interest contain a large quantity of inorganic particulates as filler, very little information is available in the literature, discussing the role(s) that particulates play in controlling the chemorheology and curing behavior of particulate-filled unsaturated polyester resins. Kubota[9] appears to be one of the few investigators who studied the effect of particulates on the curing behavior of polyester premix molding compounds. He reported that, as the amount of particulates was increased, the curing starts at a lower temperature, and the total heat generated during cure was decreased (i.e., the final degree of conversion was decreased). Dutta and Ryan[10] investigated the effect of particulates on the curing reaction of an epoxy resin, using DSC measurements.

In the present paper, the second of this series, we report the effects of particulates on both the rheological behavior during cure and the curing kinetics of unsaturated polyester resin.

EXPERIMENTAL

Material

A general-purpose unsaturated polyester resin (Aropol 7030, Ashland Chemical Co.) was used for the study. 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. Three different types of particulates were used: (a) calcium carbonate ($CaCO_3$) (Camel-Wite, A Flintkote Co.); (b) clay, hydrous aluminum silicate (ASP 400P,

TABLE I
Sample Codes and Materials Used

Sample code	Material[a]	t_{η_∞} (min)
Neat resin	Resin/peroxide/promoter[b]	2.9
Fluid 1	Resin/25 wt % CaCO$_3$/peroxide/promoter	1.8
Fluid 2	Resin/50 wt % CaCO$_3$/peroxide/promoter	1.6
Fluid 3	Resin/45 wt % clay/peroxide/promoter	2.4
Fluid 4	Resin/10 wt % HDPE/peroxide/promoter	2.3
Fluid 5	Resin/20 wt % HDPE/peroxide/promoter	2.7
Fluid 6	Resin/30 wt % HDPE/peroxide/promoter	2.9

[a] The amount (wt %) of particulates added is based on the resin.
[b] On weight basis, resin/peroxide/promoter = 60/2.0/1.2.

Englehard Minerals and Chemicals Corp.); (c) high-density polyethylene (HDPE) powders (Arco Polymer Inc., SDP 860). The CaCO$_3$ particles have an average particle diameter of 3.0 μm. The clay particles were in the form of thin flat and laminated plates, and their average size, as equivalent spheres, was 4.8 μm. Both the CaCO$_3$ and clay particles were treated with 1.0 wt % of a silane coupling agent, γ-methacryloxyl propyltrimethoxysilane (Union Carbide Corp., A174). The HDPE powders have an average particle diameter of 40 μm and are recommended by the manufacturer for use in the shrinkage control of polyester compounds.

Apparatus and Experimental Procedure

Both rheological and DSC measurements were conducted, using the apparatuses described in Paper I of this series.[8] All the rheological measurements were conducted at 60°C, and the DSC measurements were made under isothermal conditions, at various temperatures.

The procedure used for the preparation of samples containing the initiator and promoter was the same as that described in Paper I of this series,[8] except for the addition of particulates. In the use of particulates, we used two concentrations of CaCO$_3$, 25 wt % and 50 wt %; one concentration of clay, 45 wt %; and three concentrations of HDPE powders, 10 wt %, 20 wt %, and 30 wt %. Table I gives sample codes and the compositions of the samples used.

In the present study, we only measured the steady shearing flow properties, namely, shear viscosity and normal stresses. In the analysis of DSC data for obtaining information on curing kinetics, we have used the *ultimate* heat of reaction in calculating the degree of cure. The procedure used for the analysis of DSC data is the same as that described in Paper I of this series.[8]

RESULTS

Rheological Measurement

Table I presents the sample code and the type and amount of particulates for six different combinations. These are identified as Fluids 1–6. Figure 1 gives plots of viscosity (η) vs. cure time for Fluid 1 at various shear rates ($\dot{\gamma}$). Similar plots are given in Figure 2 for Fluid 2, in Figure 3 for Fluid 3, and in Figures 4–6
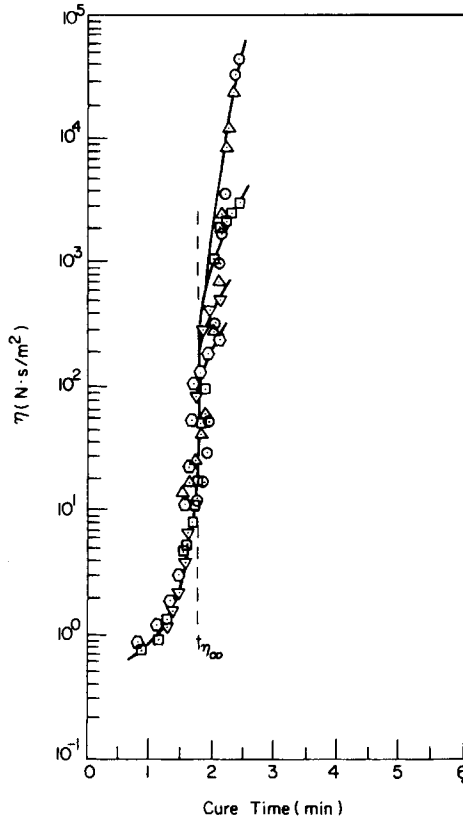
Fig. 1. Viscosity vs. cure time for Fluid 1 at various shear rates (s^{-1}): ($\odot$) 0.03; ($\triangle$) 0.11; ($\square$) 1.07; ($\triangledown$) 6.77; ($\circ$) 17.0.

for Fluids 4–6.   There are some common features in the figures shown above that are worth noting.

At low concentrations of particulates, namely Fluid 1 (see Fig. 1) and Fluid 4 (see Fig. 4), the increase in viscosity with cure time is seen to be independent of shear rate.   On the other hand, at higher concentrations of particulates (see Figs. 2, 3, and 6), the viscosity, while increasing as cure progresses, decreases with increasing shear rate.   The dependency of η on $\dot{\gamma}$ (i.e., shear-thinning behavior) for concentrated suspensions has been discussed in the literature,[6,7] using phenomenological explanations.   Since the particulates used in our study are *not* reactive with the resin, we believe that the shear-thinning behavior observed in Figures 2, 4, and 6 is attributable to the breakage of the agglomerates (or lumps) of particles as the shear rate was increased.

As cure progresses in steady shearing flow, as may be seen in Figures 1–6, the cure time reaches the point, hereafter referred to as t_{η_∞}, at which the rate of viscosity increase begins to decrease.   During cure, however, the molecules grow bigger, eventually forming a three-dimensional network, and thus the viscosity of the system is expected to increase rapidly, approaching infinity.   During our rheological measurements, however, we noticed that, at t_{η_∞}, material was exuded from the gap between the cone and plate.   Therefore, as pointed out in Paper I of this series,[8] from the point of view of rigor, the viscosity data at and beyond
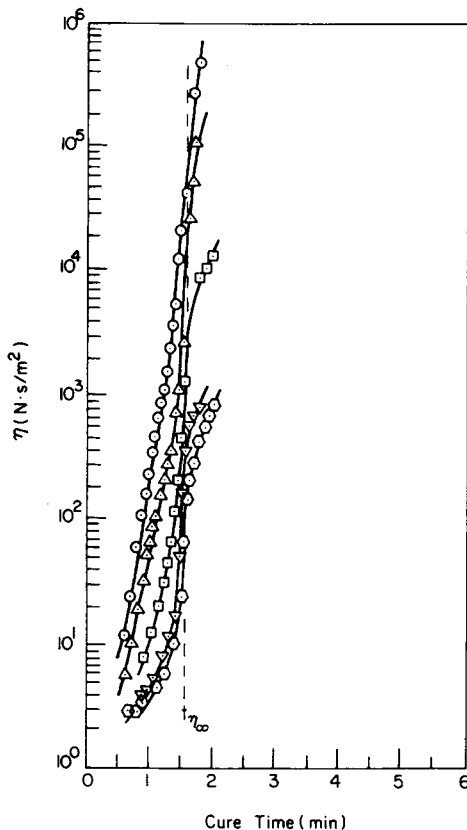
Fig. 2. Viscosity vs. cure time for Fluid 2 at various shear rates (s^{-1}): (⊙) 0.03; (▲) 0.11; (▫) 1.07; (▽) 6.77; (⊙) 17.0.

t_{η_∞} may be of little rheological significance. Since the onset of flow instability occurred at a value of viscosity that was still measurable, it may not be correct to call t_{η_∞} the "gel time."

Figure 7 gives schematically a summary of the viscosity variation with cure time, observed in Figures 1–6, and Table I gives a summary of t_{η_∞} values. It is seen in Table I that t_{η_∞} is *decreased* as the concentration of $CaCO_3$ is increased, whereas t_{η_∞} is *increased* as the concentration of HDPE powder is increased. Note that t_{η_∞} for the neat resin itself is 2.9 min at 60°C. This clearly indicates that $CaCO_3$ particles and HDPE powders play different roles in influencing the curing behavior of unsaturated polyester resin. We will elaborate further on this when we present the DSC results of curing kinetics.

Figures 8 and 9 describe the variation in normal stress difference, $\tau_{11} - \tau_{22}$, with cure time for Fluids 1 and 2, respectively. Figure 10 describes similar information of Fluid 3, and Figures 11–13 for Fluids 4, 5, and 6 (i.e., the resin/HDPE powder systems containing varying amounts of particulate loading), respectively. It is seen in Figures 8–13 that, when the material was at rest (i.e., $\dot\gamma = 0$), a *negative* normal force was generated, indicating that shrinkage occurred during cure. However, as the shear rate is increased, *positive* normal forces develop. Note that similar observations have been made with neat resin, as reported in Paper I of this series.[8]
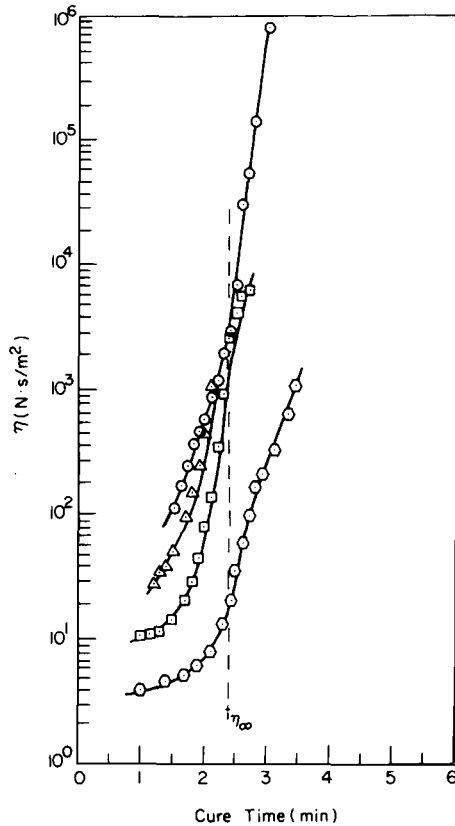
Fig. 3. Viscosity vs. cure time for Fluid 3 at various shear rates (s^{-1}): (⊙) 0.03; (△) 0.27; (□) 1.07; (⊙) 17.0.

A close examination of Figures 8 and 9 reveals some interesting observations: (1) the addition of CaCO$_3$ particles to resin help reduce shrinkage because a *positive* $\tau_{11} - \tau_{22}$ develops at $\dot{\gamma} = 1.07$ s^{-1}, whereas, with neat resin, the *negative* $\tau_{11} - \tau_{22}$ still persists even at higher shear rates, say at $\dot{\gamma} = 2.69$ s^{-1} [see Fig. 9(b) in Paper I of this series]; (2) once $\tau_{11} - \tau_{22}$ becomes positive, the rate of increase in $\tau_{11} - \tau_{22}$ is greater with the resin/CaCO$_3$ system than with neat resin. Similar observations may be made on the role of clay, insofar as the variation in $\tau_{11} - \tau_{22}$ with cure time is concerned.

We observe from Figures 11–13 that the addition of HDPE powders to resin, also, helps reduce shrinkage, very similar to the addition of CaCO$_3$ and clay particles. We also observe that shrinkage control is improved by increasing the concentration of HDPE powder from 10 to 30 wt %. This observation is based on the fact that a *positive* $\tau_{11} - \tau_{22}$ develops at $\dot{\gamma} = 0.27$ s^{-1} when 30 wt % of HDPE powder is added, whereas a *negative* $\tau_{11} - \tau_{22}$ develops at the same shear rate when 10 wt % HDPE powder is added. It should be pointed out, however, that as the amount of particulates added is increased, less resin will be available, and therefore less overall shrinkage is expected. On the other hand, a decrease in the amount of resin used also decreases the fluid elasticity that is generated from the crosslinking reaction. Therefore, at a fixed cure time, the overall effect
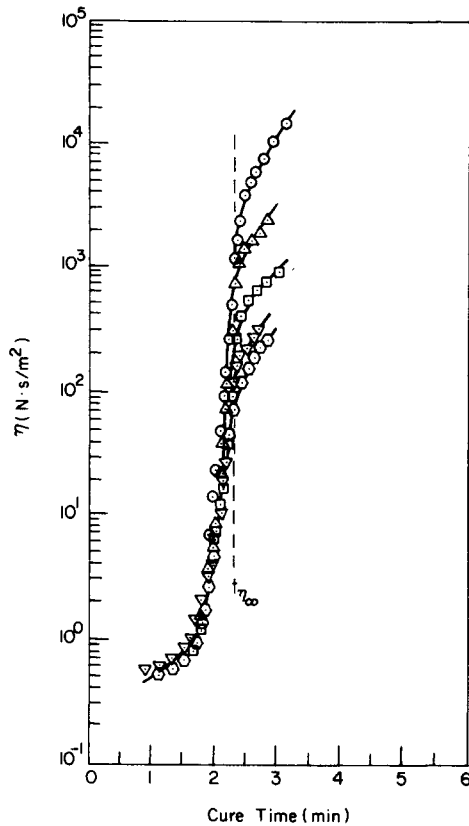
Fig. 4. Viscosity vs. cure time for Fluid 4 at various shear rates (s^{-1}): ($\odot$) 0.27; ($\triangle$) 1.07; ($\square$) 2.69; ($\triangledown$) 6.77; ($\odot$) 17.0.

of the addition of particulates on the variation of normal stresses may be nullified. Nevertheless, the dilution of resin by the addition of particulates, cannot alone explain the experimentally observed normal stress behavior.

DSC Measurement

Figure 14 gives plots of the rate of heat generated, dQ/dt, versus cure time for Fluid 1, and Figure 15 for Fluid 2, at various isothermal curing temperatures. It is seen that, at an identical isothermal curing temperature, an increase in the amount of $CaCO_3$ from 25 to 50 wt % has increased the value of dQ/dt, and that the peak in dQ/dt occurs sooner with 50 wt % $CaCO_3$ than with 25 wt % $CaCO_3$. This leads us to conclude that the rate of cure increases as the amount of $CaCO_3$ is increased from 25 to 50 wt %. This observation is consistent with that made from independent viscosity measurements (see Figs. 1 and 2, and Table II).

Figure 16 describes the heat generated during the cure of Fluid 2, at various isothermal temperatures. It is seen that the total heat Q_{TOT}, based on the amount of resin used, is fairly constant. Q_{TOT} is the sum of the heat (Q_T) generated during isothermal curing and the heat (Q_R) evolved when the sample was heated at 10°C/min to 200°C followed by the isothermal cure. The scatter of

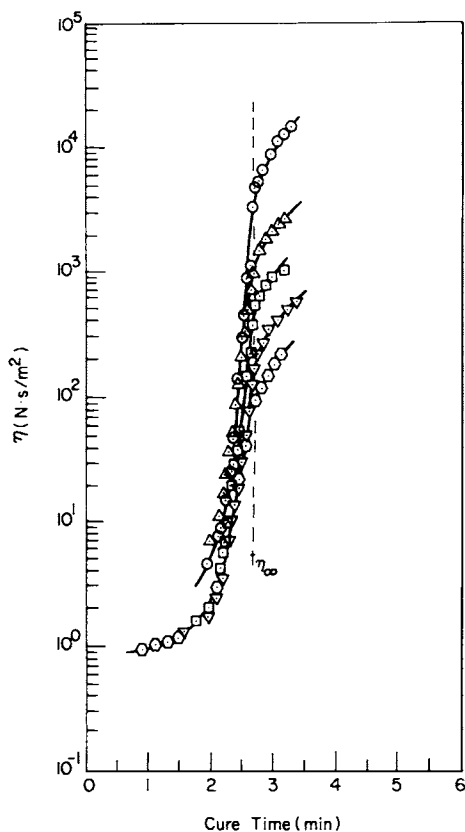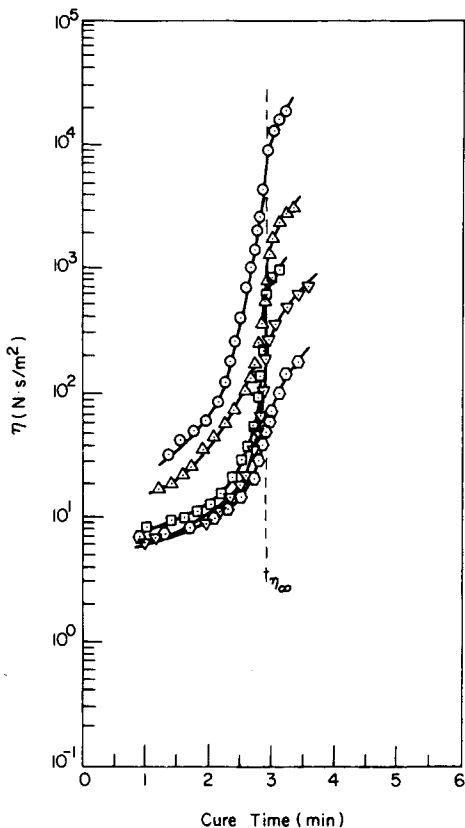Fig. 5. Viscosity vs. cure time for Fluid 5 at various shear rates (s^{-1}): (⊙) 0.27; (▲) 1.07; (▣) 2.69; (▼) 6.77; (⊙) 17.0.

TABLE II
Thermokinetic Parameters Evaluated for the Fluid Systems Investigated

Temp (K)	k_1 (min^{-1})	k_2 (min^{-1})	m	n	α_p	$\dot{\alpha}_p$ (min^{-1})	t_p (min)
(a) Neat resin							
313	0.0048	0.203	0.29	1.71	0.140	0.118	4.0
318	0.0131	0.351	0.23	1.77	0.109	0.254	2.0
323	0.0278	0.793	0.35	1.65	0.166	0.325	1.7
333	0.0924	1.570	0.40	1.60	0.183	0.678	1.0
(b) Fluid 1							
308	0.0103	0.190	0.31	1.69	0.143	0.088	9.5
313	0.0153	0.381	0.31	1.69	0.146	0.154	5.4
318	0.0137	0.439	0.39	1.61	0.186	0.190	3.5
323	0.0276	0.796	0.43	1.57	0.204	0.269	3.0
328	0.0285	0.897	0.47	1.53	0.224	0.371	1.9
333	0.0740	1.490	0.55	1.50	0.232	0.513	1.6
(c) Fluid 2							
308	0.0029	0.666	0.30	1.70	0.149	0.119	4.2
318	0.0160	0.398	0.31	1.69	0.146	0.205	1.8
323	0.0373	0.808	0.33	1.67	0.154	0.354	1.5
328	0.0537	1.470	0.41	1.59	0.194	0.500	1.0
333	0.0883	1.540	0.41	1.59	0.188	0.556	0.85
338	0.1040	2.050	0.49	1.51	0.227	0.785	0.75
348	0.2570	2.700	0.48	1.52	0.208	1.020	0.50

Fig. 6. Viscosity vs. cure time for Fluid 6 at various shear rates (s^{-1}): (⊙) 0.27; (▲) 1.07; (□) 2.69; (▼) 6.77; (◉) 17.0.

the data in Figure 16 may be attributable to the variation of the number of filler particles in the *minute* sample size (mg), used for DSC measurements. The *ultimate* heat Q_{UT} used in Figure 16 is defined as the average value of several measurements of Q_{TOT}, taken at various cure temperatures. Using the procedure described in Paper I of this series,[8] we have computed the rate of change of the degree of cure $(d\alpha/dt)$ and the degree of cure (α), and the results are given in Figure 17 for Fluid 1 and in Figure 18 for Fluid 2. It should be mentioned that
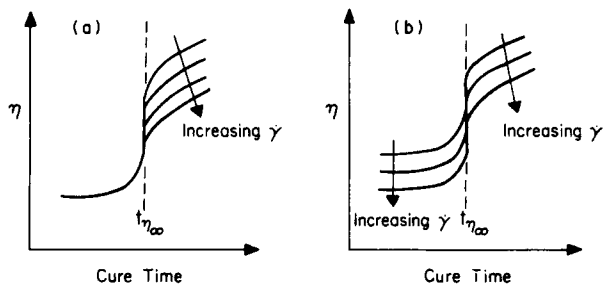
Fig. 7. Schematic depicting the viscosity vs. cure time plot at various shear rates for: (a) suspension of low filler concentration; (b) suspension of high filler concentration.
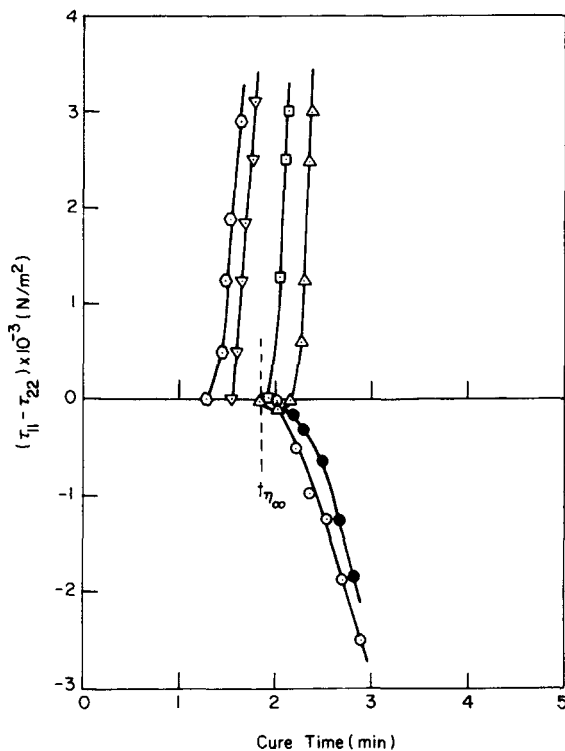
Fig. 8. $\tau_{11} - \tau_{22}$ vs. cure time for Fluid 1 at various shear rates (s^{-1}): ($\bullet$) 0.0; ($\odot$) 0.03; ($\triangle$) 0.11; ($\square$) 1.07; ($\triangledown$) 6.77; ($\circleddash$) 17.0.

the values of α and $d\alpha/dt$ given in Figures 17 and 18 are obtained using the *ultimate* heat Q_{UT}.

Using the following empirical rate expression,

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

suggested by Kamal and co-workers[11,12] and the experimental results given in Figures 17 and 18, we have calculated the kinetic parameters k_1, k_2, m, and n, and the results are summarized in Table II. It is seen in Table III that the activation energy of the rate constant k_2 is decreased from 49.0 to 30.5 kJ/mol as the concentration of CaCO$_3$ is increased from 25 to 50 wt %. The decrease in the activation energy of the curing reaction also implies an increase in the rate of cure, $d\alpha/dt$ (compare Fig. 17 with Fig. 18). It should be pointed out that, in

TABLE III
Activation Energy for the Fluid Systems Investigated

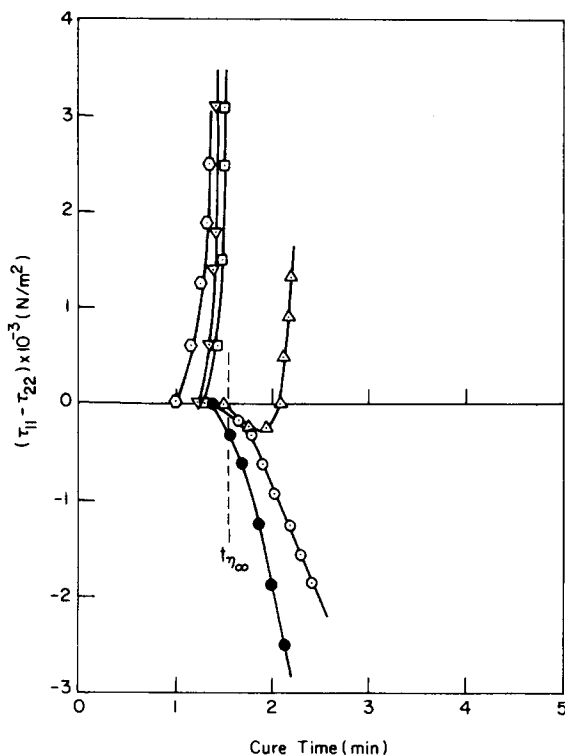| Material	Activation energy (kJ/g · mol)			
	k_1	k_2	$\dot{\alpha}_p$	α_p
Neat resin	99.3	62.8	83.0	62.1
Fluid 1	48.5	49.0	58.9	63.5
Fluid 2	70.3	30.5	37.5	37.2

Fig. 9. $\tau_{11} - \tau_{22}$ vs. cure time for Fluid 2 at various shear rates (s^{-1}): (●) 0.0; (⊙) 0.03; (△) 0.11; (□) 1.07; (▽) 6.77; (⊘) 17.0.

determining the kinetic parameters appearing in eq. (1), we have assumed a second-order reaction and used the method suggested by Ryan and Dutta.[13]

Figure 19 gives plots of the degree of cure α vs. cure time for Fluid 1, and Figure 20 for Fluid 2, at various isothermal cure temperatures. It is seen that, as the isothermal cure temperature is increased, α is increased accordingly, and that cure starts sooner with Fluid 2 than with Fluid 1. It should be noted that, as the concentration of filler is increased, it reduces the number of the reactive double bonds per unit volume of the mixture, resulting in lower values of α. It should be remembered that, as the concentration of filler is increased, the viscosity of the mixture of resin and filler is increased accordingly (see Figs. 1 and 2).

Having obtained information on both the variations in viscosity (η) and the degree of cure (α) with cure time, we have constructed plots of η vs. α, as shown in Figure 21 for Fluid 1 and in Figure 22 for Fluid 2. Due to the fact that the viscosity of Fluid 2 follows shear-thinning behavior (see Fig. 2), a series of curves are shown in Figure 22, showing the dependency on the applied shear rate.

DISCUSSION

Rheological Behavior of Particulate-Filled Unsaturated Polyester Resin during Cure

Little has been published in the literature that discusses the effect of particulates on the rheological behavior, during curing, of mixtures of unsaturated
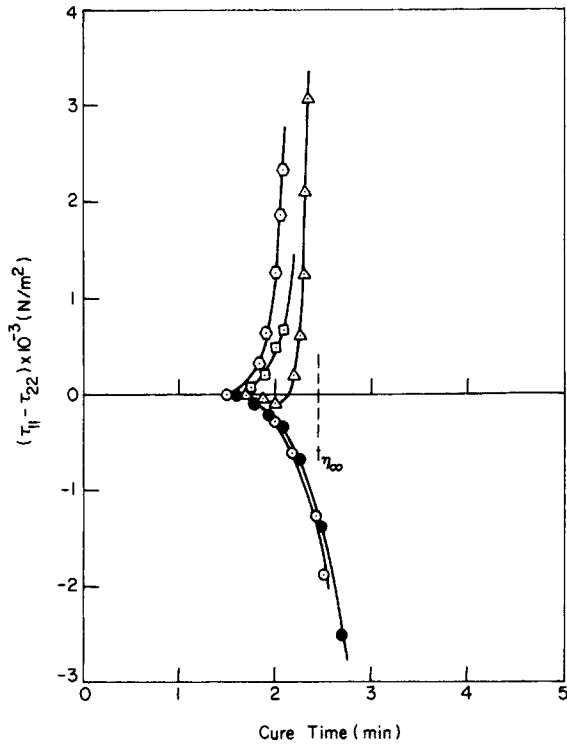
Fig. 10. $\tau_{11} - \tau_{22}$ vs. cure time for Fluid 3 at various shear rates (s^{-1}): (●) 0.0, (☉) 0.03; (△) 0.27; (▣) 1.07; (⊙) 6.77.
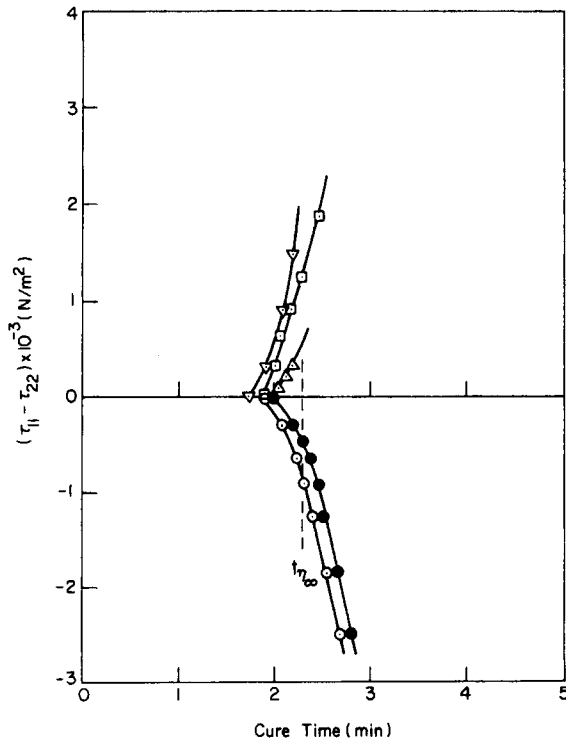

Fig. 11. $\tau_{11} - \tau_{22}$ vs. cure time for Fluid 4 at various shear rates (s^{-1}): (●) 0.0; (☉) 0.27; (△) 1.07; (▣) 2.69; (▽) 6.77.
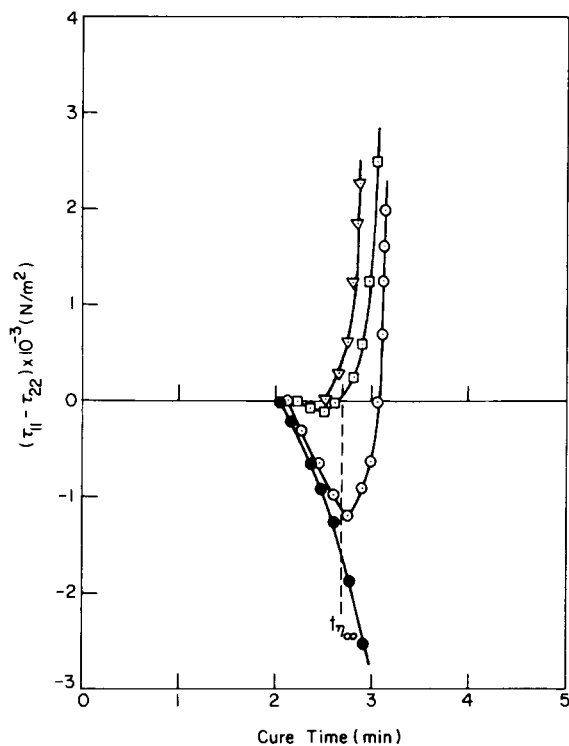
Fig. 12. $\tau_{11} - \tau_{22}$ vs. cure time for Fluid 5 at various shear rates (s^{-1}): (●) 0.0; (⊙) 0.27; (△) 1.07; (▣) 2.69; (▽) 6.77.
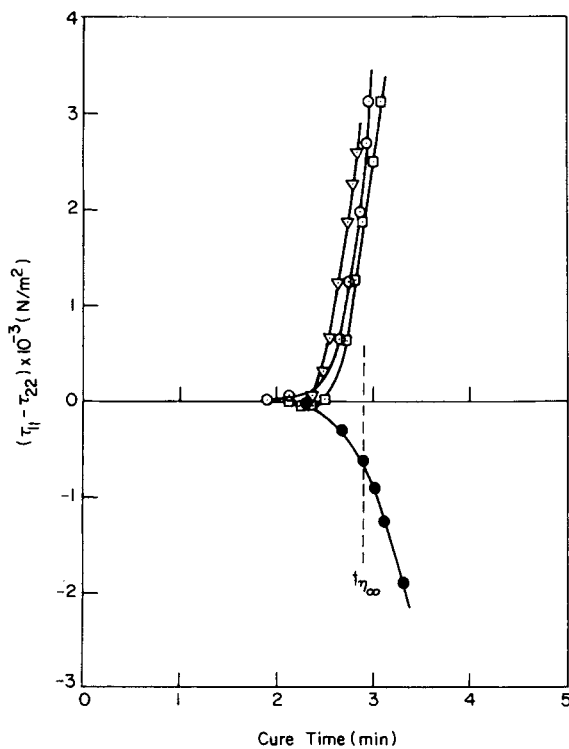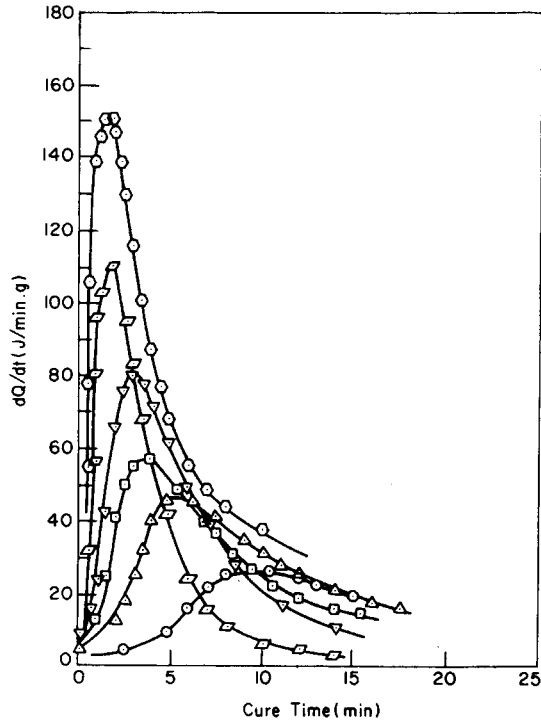

Fig. 13. $\tau_{11} - \tau_{22}$ vs. cure time for Fluid 6 at various shear rates (s^{-1}): (●) 0.0; (⊙) 0.27; (△) 1.07; (▣) 2.69; (▽) 6.77.

Fig. 14. dQ/dt vs. cure time for Fluid 1 at various isothermal cure temperatures (K): (⊙) 303; (△) 313; (▣) 318; (▽) 323; (▱) 328; (⊙) 333.
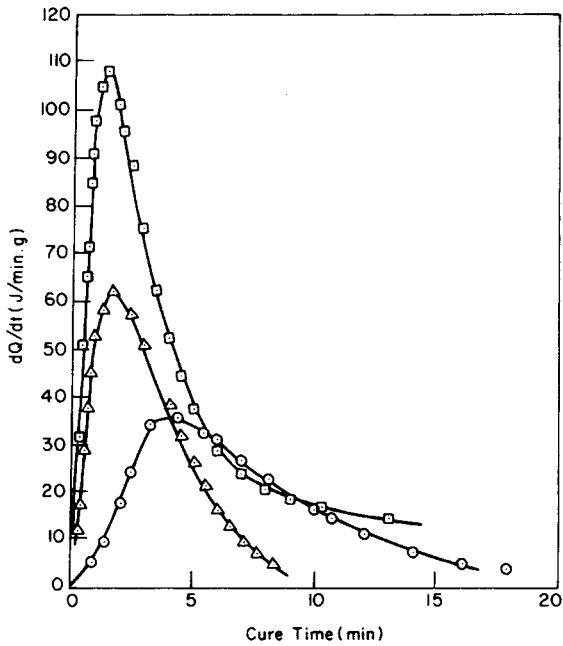

Fig. 15. dQ/dt vs. cure time for Fluid 2 at various isothermal cure temperatures (K): (⊙) 303; (▲) 318; (▣) 323.
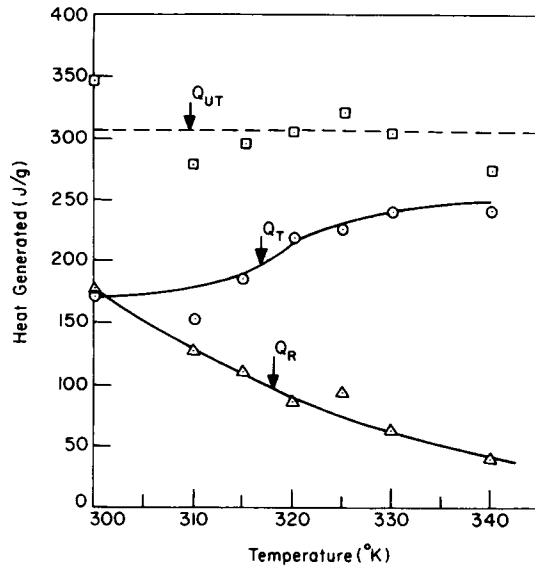
Fig. 16. Heat generated vs. cure temperature for Fluid 2: (⊙) Q_T; (▲) Q_R; (□) Q_{TOT}.

polyester resin and particulates. It has been found in the present study that the addition of inorganic particulates, particularly $CaCO_3$, reduces the gel time t_{η_∞} considerably and that the extent of t_{η_∞} reduction depends on the nature and amount of particulates added. On the basis of the t_{η_∞} values determined (see Table I), the $CaCO_3$ particles appear to have promoted the decomposition of the benzoyl peroxide used as initiator, and hence increased the rate of cure, to an
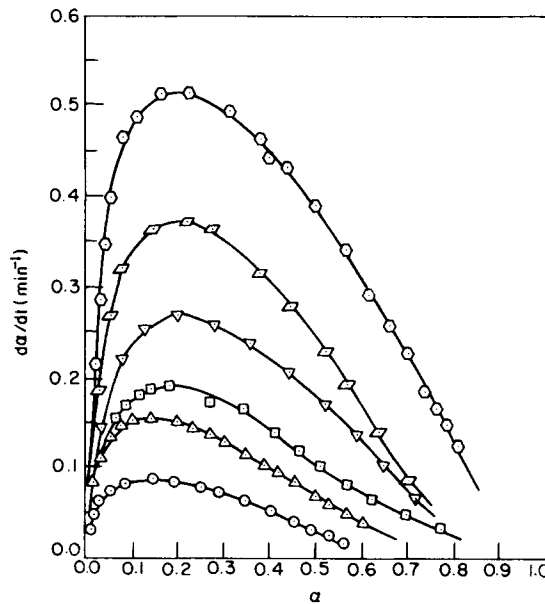

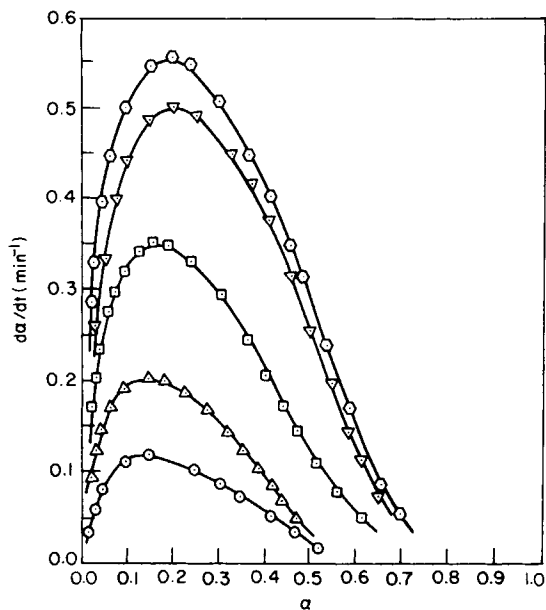Fig. 17. $d\alpha/dt$ vs. α for Fluid 1 at various isothermal cure temperatures. Symbols are the same as in Figure 14.

Fig. 18. $d\alpha/dt$ vs. α for Fluid 2 at various isothermal cure temperatures (K): (⊙) 308; (▲) 318; (▣) 323; (▽) 328; (⊙) 333.
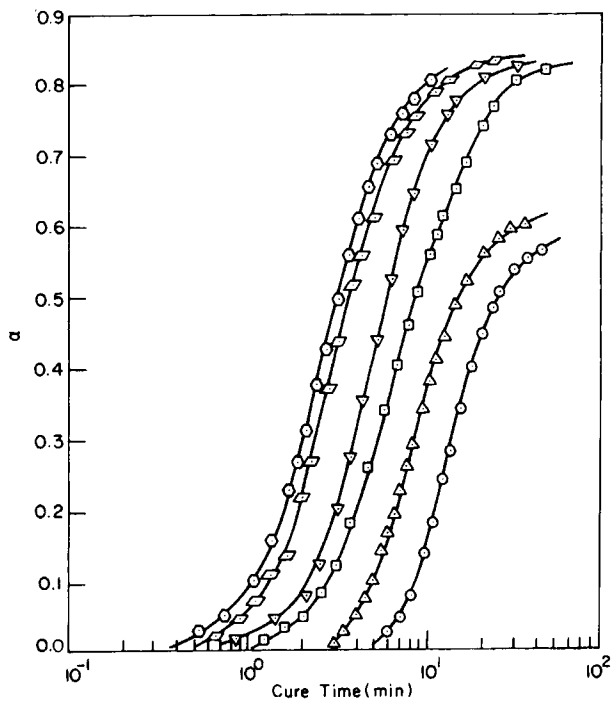

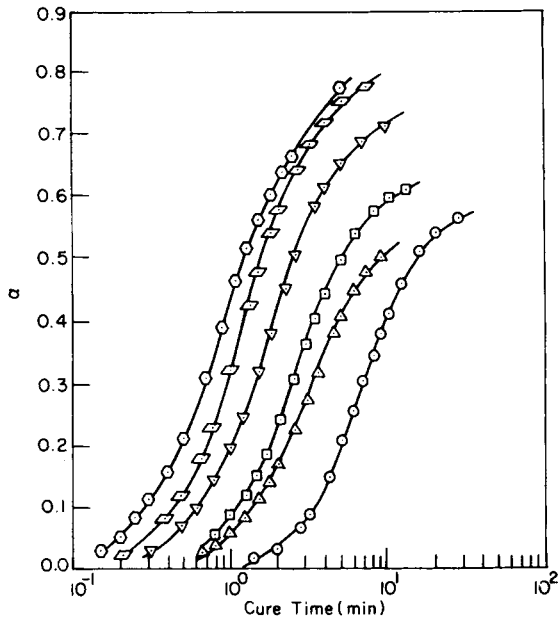Fig. 19. α vs. cure time for Fluid 1 at various isothermal cure temperatures. Symbols are the same as in Figure 14.

Fig. 20. α vs. cure time for Fluid 2 at various isothermal cure temperatures (K): (⊙) 308; (△) 318; (▣) 323; (▽) 328; (▱) 338; (◉) 348.
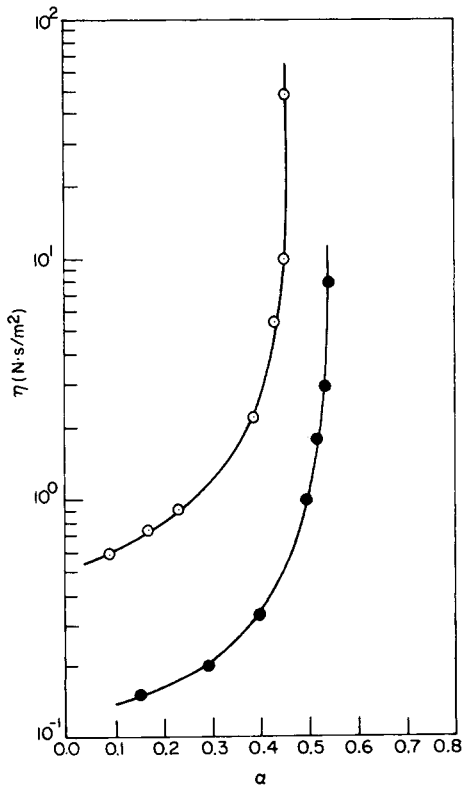

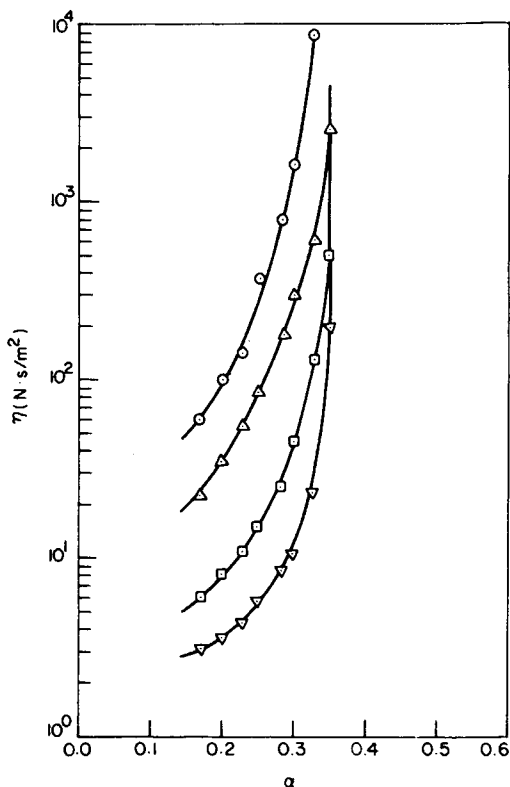Fig. 21. η vs. α for Fluid 1 at 60°C: (●) neat resin; (○) Fluid 1.

Fig. 22. η vs. α for Fluid 2 at 60°C at various shear rates (s^{-1}): (⊙) 0.03; (▲) 0.11; (▢) 1.07; (▼) 6.77.

extent greater than the clay particles did. Note that an increase in the amount of $CaCO_3$ particles added has *decreased* t_{η_∞}, whereas an increase in the amount of HDPE powder has increased t_{η_∞}. Earlier, Cassoni et al.[14] reported that the pot life of $CaCO_3$-filled orthophthalic ester resin was shorter than that of neat resin. They attributed this to the effect of filler pH on the performance of initiator.

It should be pointed out that HDPE powder has been used for the purpose of controlling the shrinkage of thermosetting polyester composites, but not as fillers. There are other thermoplastic materials, which are also used in controlling the shrinkage of thermosetting polyester composites. In the following paper,[16] we will discuss, in greater detail, the role of some of those low-profile thermoplastic additives in influencing the rheology and the curing behavior of unsaturated polyester resin.

One of the drawbacks in using thermosetting resins, especially unsaturated polyester resin, is the shrinkage occurring during cure. Fillers are used primarily to increase the strength and reducing the cost. It has been reported that fillers also contribute to reduce the extent of shrinkage in the thermosetting resin. The present study shows, albeit *qualitatively*, how the shrinkage may be controlled during cure by the type and amount of particulates added to the resin. The method used to determine the extent of shrinkage control in the present study is the normal force measurement, using a cone-and-plate rheometer.
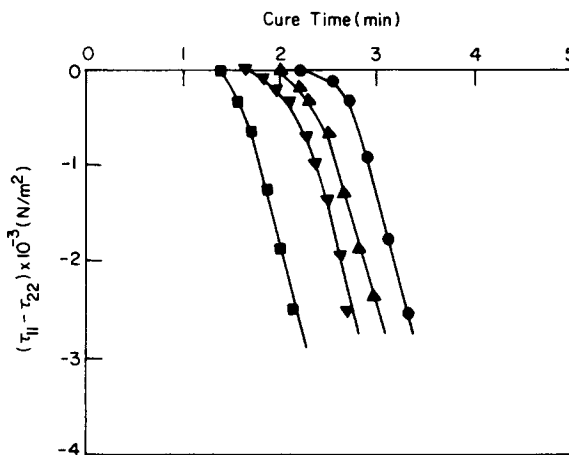
Fig. 23. $\tau_{11} - \tau_{22}$ vs. cure time for suspensions of $CaCO_3$ and clay at rest: (●) neat resin; (▲) Fluid 1; (■) Fluid 2; (▼) Fluid 3.

It should be emphasized that the polymerization shrinkage forces, exerted on the material during cure, are 3-dimensional in nature. As pointed out in Paper I of this series,[8] when a thermosetting resin (e.g., unsaturated polyester resin, epoxy resin) is subjected to steady shearing deformation during cure, it shrinks in every direction and, thus, the measurements of normal force, whether acting in the positive or negative direction, cannot be interpreted as "elastic effects," from the point of view of rigor. Therefore, in the strict sense, the calculations of $\tau_{11} - \tau_{22}$, presented in Figures 8–13, are *not* correct, except for the case of high shear rates and very low curing rates, where the shrinkage forces may be negligibly small compared to the normal forces generated by the fluid elasticity. This is because, in the calculations of $\tau_{11} - \tau_{22}$, we have used a theoretical expression that is valid only for fluid systems which do *not* undergo shrinkage (see Paper I of this series for more details[8]).

Figure 23 describes, in a *qualitative* sense, the rate of shrinkage occurring during cure when fluids containing inorganic fillers ($CaCO_3$ and clay) are at rest. Figure 24 gives similar plots when HDPE powder is used. It is seen that both the inorganic fillers, $CaCO_3$ and clay, and HDPE powder are *not* effective at all in controlling shrinkage, because the shrinkage rate [i.e., the slope of the linear portion of the curve of $-(\tau_{11} - \tau_{22})$ vs. cure time] is almost the same whether an inorganic filler or HDPE powder is used. However, when the fluid was subjected to steady shearing deformation, the difference in the normal stress response among the various particulates employed becomes pronounced, as shown in Figure 25. It can be concluded from Figure 25 that, among the particulates employed, $CaCO_3$ is most effective in controlling shrinkage during the cure of unsaturated polyester resin.

It should be mentioned at this juncture that the temperature chosen for cure in the present study is quite low (60°C), compared to that commonly practiced in processing polyester premix molding compounds (say, 120–150°C). According to the shrinkage control mechanism advanced by Atkins,[15] thermoplastic additives (in the present study, HDPE powder) expand at elevated temperatures, compensating for the volume loss due to the shrinkage of the matrix resin (in the
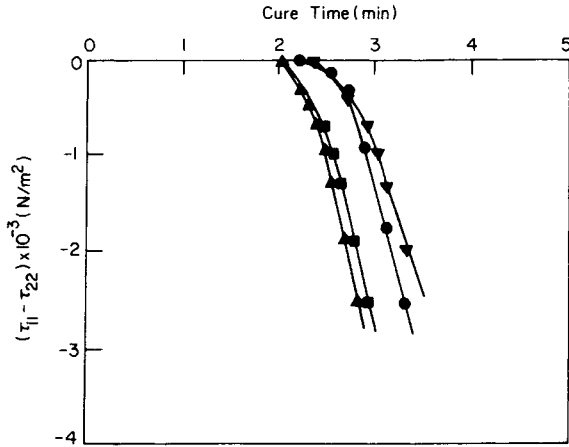
· Fig. 24. $\tau_{11} - \tau_{22}$ vs. cure time for suspensions of HDPE powders at rest: (●) neat resin; (▲) Fluid 4; (■) Fluid 5; (▼) Fluid 6.

present study, polyester resin). If this is true, the measurement of normal forces of mixtures of resin and HDPE at 60°C, conducted in the present investigation, is not adequate for describing the effectiveness of shrinkage control of HDPE powder.
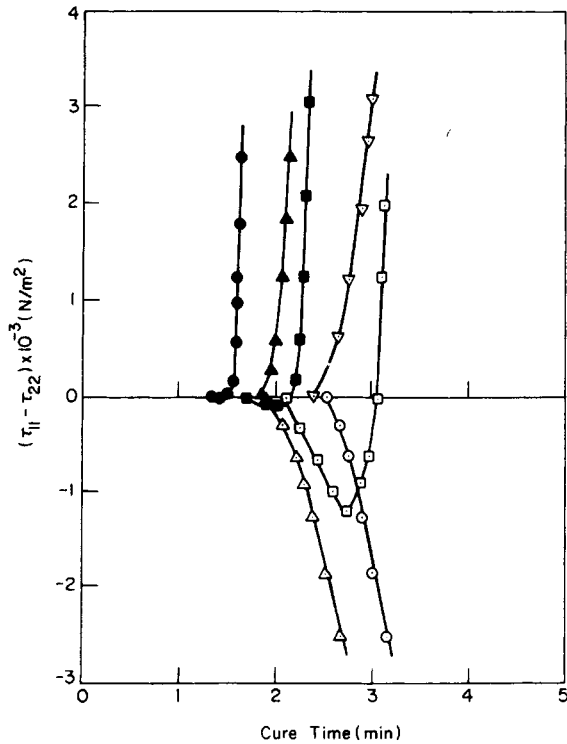

Fig. 25. $\tau_{11} - \tau_{22}$ vs. cure time for various fluids investigated at $\dot{\gamma} = 0.27$ s^{-1}: (⊙) neat resin; (▲) Fluid 1; (●) Fluid 2; (■) Fluid 3; (△) Fluid 4; (□) Fluid 5; (▽) Fluid 6.

In the following paper,[16] we will discuss findings from our investigation of the effects of various thermoplastic additives on the rheological behavior, during curing, of unsaturated polyester resins, subjected to steady shearing flow.

Curing Kinetics of Particulate-Filled Unsaturated Polyester Resin

Kubota[9] appears to be the only one so far, who was reported on the effects of inorganic fillers on the curing kinetics of unsaturated polyester resin. Our findings in the present investigation are in general agreement with those of Kubota. However, we have carried our data analysis far beyond what Kubota did.

In Table II, we have presented the values of the peak $(\dot{\alpha}_p)$, the time (t_p) at which the peak occurs, and the degree of cure (α_p) up to the cure time t_p for both Fluids 1 and 2. It is seen in Table II that $\dot{\alpha}_p$ increases and t_p decreases, with increasing amounts of $CaCO_3$ added. This information clearly reveals that the rate of cure is increased in the presence of filler. Note that fillers increase the viscosity, which in turn decreases the rate of the termination reaction between the growing radicals and, thus, increases the rate of cure.

In determining the kinetic parameters appearing in eq. (1), we have found that both rate constants k_1 and k_2 and, also α_p and $\dot{\alpha}_p$ follow the Arrhenius relationship. As shown in Table III, the activation energies determined for k_1 and k_2 are comparable in their magnitude.

CONCLUDING REMARKS

Based on the results presented above, it is concluded that an unsaturated polyester resin filled with particulates, subjected to steady shearing flow during cure, may exhibit shear-thinning behavior before t_{η_∞} is reached (see Figures 2, 3, and 5.) The observed shear-thinning behavior is attributable to breakage of the particle agglomerates as the shear rate is increased, behavior which is typical of concentrated suspensions. On the other hand, the shear-thinning behavior observed at and beyond t_{η_∞}, similar to that reported in Paper I of the series,[8] is attributable to two sources: (1) the deformation of large molecules formed from crosslinking reactions in the unsaturated polyester resin; (2) the breakage of agglomerates of particles under shearing motion.

Note in Figures 1 and 4 that, when the concentration of particulates is low, no shear-thinning behavior is observed until the cure time reaches a critical value t_{η_∞}. For such fluid systems, the shear-thinning behavior observed at and beyond t_{η_∞} is attributable primarily to the deformation of large molecules formed by polymerization reactions in the resin. The fact that the viscosity does not approach an infinitely large value at t_{η_∞} (see Figs. 1 and 4) seems to suggest two possibilities: (a) no "true" gelation, forming 3-dimensional networks, occurs at t_{η_∞}; (b) steady shearing flow does not prevail at and beyond t_{η_∞}. Indeed, during our experiment, we have observed material exuding from the gap between the platens as the cure time proceeded beyond t_{η_∞}. Again, we have discussed this subject in greater detail in our previous paper.[8] The value of viscosity, at t_{η_∞} at which flow instability occurs, depends on the type and amount of particulates added.

When a particulate-filled unsaturated polyester resin, placed in a cone-end-plate rheometer, was at rest, we have observed *negative* normal stress effects, which we believe originated from polymerization shrinkage. The type and amount of particulates used are found to have little influence on this behavior, as long as the fluid is at rest. However, when a fluid is subjected to steady shearing deformation, the normal stress response is found to vary greatly among the various particulates investigated. In the absence of a rigorous theoretical development at the present time, the normal force measurements taken provide only *qualitative* information on the shrinkage behavior of the fluid systems investigated.

The experimental results of the curing kinetics of particulate-filled unsaturated polyester resin, determined by DSC, reveal that the presence of particulates increases the rate of cure. Of the various fillers investigated, calcium carbonate was found to be most effective.

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