

# Chemorheology of Thermosetting Resins. III. Effect of Low-Profile Additive on the Chemorheology and Curing Kinetics of Unsaturated Polyester Resin

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## Synopsis

An experimental study was conducted to investigate the effect of low-profile thermoplastic additives on the rheological behavior during cure and the curing kinetics of unsaturated polyester resin. For the study, a general-purpose polyester resin was used and two different types of thermoplastic additive, poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA), were used as low-profile additives. It has been found that, during cure, the resin/PMMA system exhibits shear-thinning behavior even before the cure time reaches the critical value  $t_{n,c}$ , whereas the resin/PVAc system does not. Also, both PVAc and PMMA help reduce the shrinkage of the resin during cure. However, our study shows that shrinkage control becomes effective only when the shear rate is greater than a certain critical value. The curing behavior determined with the aid of differential scanning calorimetry (DSC) shows that the rate of cure and the final degree of cure are decreased when the amount of low-profile additive is increased.

## INTRODUCTION

During the last two decades, much effort has been spent on developing zero- or low-shrink fiber-reinforced thermosetting polyester resins, commonly referred to as "low-profile" resins. The objective was to produce molded parts having smooth surfaces and dimensional stability at service conditions. In the formulation of these resins, one adds a certain amount of thermoplastic additives (commonly referred to as low-profile additives) to unsaturated polyester resins. With the development of "low-profile" resins in recent years, thermosetting polyester composites have received increasing attention from industry, especially from the automotive and aerospace industries.

Without low-profile thermoplastic additive, molded parts made of fiber-reinforced unsaturated polyester composites suffer from poor appearance resulting from a wavy surface, warpage, internal cracks, and voids, and deep sink marks.<sup>1-7</sup> With the development of low-profile thermoplastic additives, much of the problem has been alleviated, and it is now possible to obtain the desired products with relatively little shrinkage.

In spite of the technological importance of low-profile resins, the mechanism(s) whereby low-profile additives reduce shrinkage in molded parts of thermosetting polyester compounds is still not clearly understood today. In the literature,<sup>5</sup> three mechanisms have been proposed: (1) optical heterogeneity and boiling monomer; (2) strain relief through stress cracking; (3) thermoplastic expansion.

Bartkus and Kroekel<sup>1</sup> have proposed the mechanism of "optical heterogeneity

and boiling monomer," based on their findings that: (1) when mixed well, a mixture of unsaturated polyester resin and low-profile additive formed two "optically heterogeneous" phases, in which the continuous phase contains the unsaturated polyester and styrene, and the dispersed phase contains thermoplastic additive and styrene; (2) when the mixture was put into a molding operation, the continuous phase crosslinked more rapidly than the dispersed phase, because the styrene radical has a high propensity to react with fumarate groups in the polyester, and formed gels earlier and released considerable amounts of heat; (3) the monomer (i.e., styrene) dissolved in the dispersed (droplet) phase, which reacts at a slower rate than the continuous phase, tended to boil during the exothermic reaction of the continuous phase and, hence, generated an internal pressure to compensate for the shrinkage of the continuous phase during cure. Consequently, foamlike occlusions were observed in the thermoplastic phase, dispersed in the styrene-crosslinked polymer matrix.

However, the mechanism proposed by Bartkus and Kroekel<sup>1</sup> fails to account for the elimination of warpage in the molded parts and the low shrinkage observed in single-phase systems (i.e., a low-profile resin, in which the thermoplastic additive is compatible with the polyester before cure begins). In view of this deficiency, Pattison et al.<sup>2-4</sup> have proposed the mechanism of "strain relief through stress cracking," in which they stipulate that the unreacted styrene monomer thermally expands to compensate for the loss of volume due to polymerization shrinkage. At the same time, as the cure progresses, shrinkage causes strain to develop in the system, and it increases to such an extent that cracks are formed to relieve it. Such stress cracking will propagate through the weakest part of the material, being either in the thermoplastic additive phase or at the interface between the dispersed phase and the continuous phase, and consequently forming voids to compensate for the loss of volume due to polymerization shrinkage.

Neither mechanism discussed above, however, addresses the question of the effectiveness of various types of thermoplastic resin when used as low-profile additive. Atkins<sup>5</sup> has asserted that the ability of various types of thermoplastic resin to control shrinkage is closely related to their thermal expansion coefficient. He observed that the effectiveness of a low-profile additive increases with increasing values of its thermal expansion coefficient. Atkins noted further that, in order for a thermoplastic resin to function effectively as a low-profile additive, it must be incompatible, during cure, with the styrene-crosslinked polyester matrix.

Although the thermoplastic additives currently used in industry appear to perform reasonably well in certain applications, one always searches for new additives that might function for more than just shrinkage control. As a matter of fact, in recent years work has already begun toward the development of elastomeric low-profile additives for producing *toughened* unsaturated polyester resins.<sup>8,9</sup>

In our previous papers,<sup>10,11</sup> we have reported the effect of some thermoplastic additives, namely, poly(methyl methacrylate) (PMMA) dissolved in styrene, poly(vinyl acetate) (PVAc) dissolved in styrene, and polyethylene powders, on the rheological behavior of unsaturated polyester resin, *without* curing taking place. The purpose of the study was to enhance our understanding of the role that thermoplastic additives play in controlling the rheological properties of polyester premix-molding compounds. We have reported that each of the three

TABLE I  
Sample Code and Materials Investigated

Sample code	Material <sup>a</sup>	$t_{\eta_{\infty}}$ (min)
Control sample	Resin/peroxide/promoter	2.9
Fluid 1	Resin/10 wt % PVAc/peroxide/promoter	3.1
Fluid 2	Resin/20 wt % PVAc/peroxide/promoter	4.3
Fluid 3	Resin/10 wt % PMMA/peroxide/promoter	4.2
Fluid 4	Resin/20 wt % PMMA/peroxide/promoter	5.6

<sup>a</sup> The amount of the solution of thermoplastic additive used is based on resin.

thermoplastic additives used gives rise to quite different effects on the rheological behavior of unsaturated polyester resin.

In this paper, the third of this series, we report the effects of thermoplastic additives (namely, PMMA in styrene and PVAc in styrene) on the rheological behavior of unsaturated polyester resin during cure, and the rate of cure. Emphasis will be placed on discussing the effect of the type and amount of thermoplastic additive used on the extent of shrinkage control during the cure of unsaturated polyester resin, as determined by normal force measurements made with a cone-and-plate rheometer.

## EXPERIMENTAL

For the study, a general-purpose unsaturated polyester resin (Ashland Chemical, Aropol 7030) was used, together with benzoyl peroxide in granular form (Cadox BFF-60 WET, Noury Chemical Corp.) as initiator and a solution

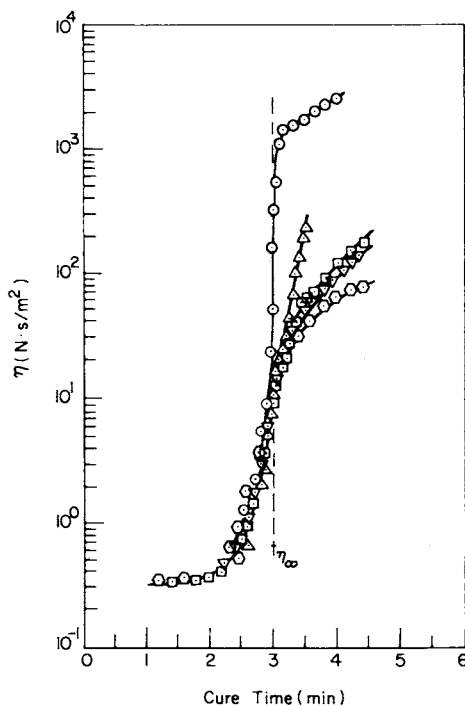


Fig. 1. Viscosity vs. cure time ( $T = 60^{\circ}\text{C}$ ) for Fluid 1 at various shear rates ( $\text{s}^{-1}$ ): ( $\odot$ ) 0.27; ( $\Delta$ ) 2.69; ( $\square$ ) 6.77; ( $\nabla$ ) 10.7; ( $\diamond$ ) 17.0.

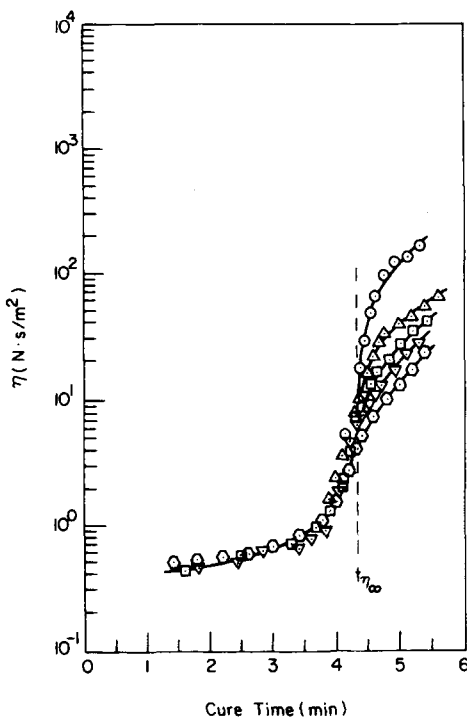


Fig. 2. Viscosity vs. cure time ( $T = 60^{\circ}\text{C}$ ) for Fluid 2 at various shear rates ( $\text{s}^{-1}$ ): Symbols are the same as in Figure 1.

of 5 wt % *N,N*-dimethylaniline (Aldrich Chemical Co.) dissolved in styrene as promoter. In addition, we used two different types of low-profile additive: (a) a solution of 40 wt % poly(vinyl acetate) (PVAc) in styrene (Union Carbide, LP-40A); (b) a solution of 33 wt % poly(methyl methacrylate) (PMMA) in styrene (Owens-Corning, P-701). The procedure employed for preparing test samples containing the initiator and promoter is the same as that described in Paper II of this series.<sup>12</sup> The formulation used was resin/initiator/promoter = 60/2.0/1.2 (parts by weight). We prepared four test samples, and Table I gives sample codes and the compositions of the samples used.

The apparatuses used are the same as in Paper I of this series,<sup>13</sup> namely, a cone-and-plate rheometer and a differential scanning calorimeter (DSC). All rheological measurements were conducted at  $60^{\circ}\text{C}$ , and DSC measurements were conducted at several isothermal cure temperatures. The procedure employed for analyzing the DSC data is the same as that described in Part I of this series.<sup>13</sup>

## RESULTS

### Viscosity Variation during Cure

Figure 1 describes the viscosity variation with cure time at various shear rates for Fluid 1, and Figure 2 for Fluid 2. It is seen that, as the amount of PVAc solution added to the mixture is increased from 10 to 20%,  $t_{\eta_{\infty}}$  is increased from 3.1

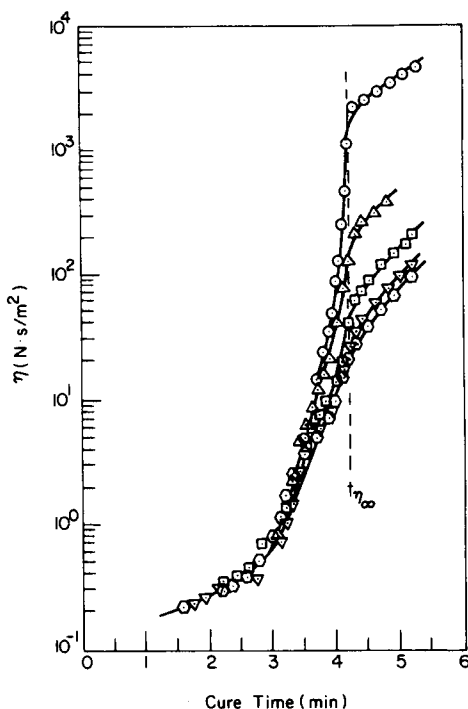


Fig. 3. Viscosity vs. cure time ( $T = 60^{\circ}\text{C}$ ) for Fluid 3 at various shear rates ( $\text{s}^{-1}$ ): Symbols are the same as in Figure 1.

to 4.3 min, indicating that the presence of low-profile additive reduces the rate of cure. Note that  $t_{\eta_{\infty}}$  for neat resin (i.e., control sample) at  $60^{\circ}\text{C}$  is 2.9 min. Note in Figures 1 and 2 that the rate of viscosity increase is slowed down as the amount of PVAc solution added is increased. This is attributed to the fact that since the PVAc solution contains 60 wt % styrene, increasing the amount of PVAc solution makes more styrene available in the mixture, thus diluting the peroxide and promoter contents, and consequently slowing down the curing reaction.

Figure 3 describes the viscosity variation with cure time at various shear rates for Fluid 3, and similar information is given in Figure 4 for Fluid 4. Two things are worth mentioning. First,  $t_{\eta_{\infty}}$  is increased from 4.2 to 5.6 min as the amount of PMMA solution added is increased from 10% to 20%. The value of  $t_{\eta_{\infty}}$  for the resin/PMMA mixture is greater than that for the resin/PVAc mixture, for approximately the same amount of styrene available. Therefore, the observed difference in  $t_{\eta_{\infty}}$  between the resin/PVAc and resin/PMMA mixtures must have its origin in the nature of the compatibility of the respective low-profile additives with the unsaturated polyester resin. Second, it is seen in Figures 3 and 4 that as cure progresses, the viscosity of resin/PMMA mixture exhibits shear-thinning behavior (i.e., the viscosity decreases with increasing shear rate). The shear-thinning behavior observed appears to suggest that, even before cure begins, the PMMA forms a separate phase in the form of small droplets. This speculation is based on the experimental observations<sup>10,14</sup> that a two-phase emulsion can show shear-thinning behavior when either the aggregates of droplets are broken up or the individual droplets deform when the emulsion is subjected to intensive shearing motion. Therefore, a slower rate of viscosity increase for the resin/

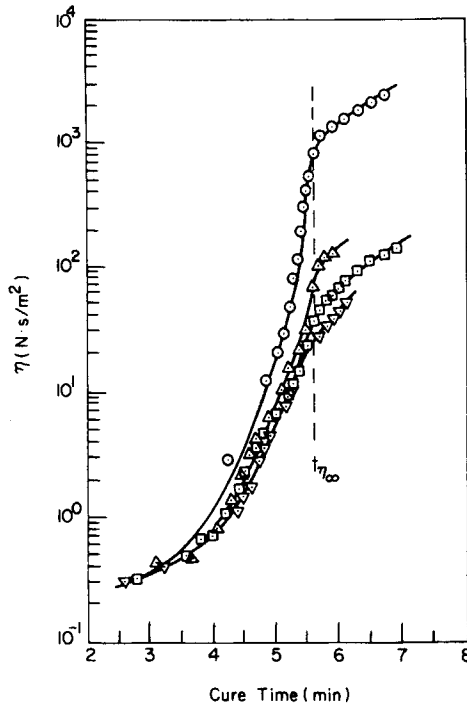


Fig. 4. Viscosity vs. cure time ( $T = 60^{\circ}\text{C}$ ) for Fluid 4 at various shear rates ( $\text{s}^{-1}$ ): Symbols are the same as in Figure 1.

PMMA system, compared to that for the resin/PVAc system, may be attributable to the formation of a PMMA/styrene droplet phase in the resin/PMMA mixture. Part of the promoter ( $N,N$ -dimethylaniline) and peroxide might have been occluded in the PMMA/styrene droplets, consequently decreasing the rate of cure.

### Normal Stress Response during Cure

The normal stress response ( $\tau_{11} - \tau_{22}$ ) during the cure of Fluid 1 is given in Figure 5, and similar results are given in Figure 6 for Fluid 2. As observed with neat resin<sup>13</sup> and with particulate-filled resins,<sup>12</sup> as cure progresses, *negative* normal stresses develop when the fluid is at rest (i.e.,  $\dot{\gamma} = 0$ ) or at low shear rates, and *positive* normal stresses develop at high shear rates. It is seen in Figures 5 and 6 that shrinkage control (i.e., development of *positive* normal stresses) is improved as the amount of PVAc solution added is increased from 10% to 20%. Figure 7 describes the normal stress response during the cure of Fluid 3, and similar information is given in Figure 8 for Fluid 4. Similar observations may be made on the effectiveness of shrinkage control by PMMA.

Figure 9 describes the normal stress response of neat resin *with* and *without* low-profile additive when the fluid is at rest (i.e.,  $\dot{\gamma} = 0$ ). It is seen that the addition of low-profile additive does not help reduce the shrinkage of the resin at rest. However, as shown in Figure 10, when the fluid is subjected to steady

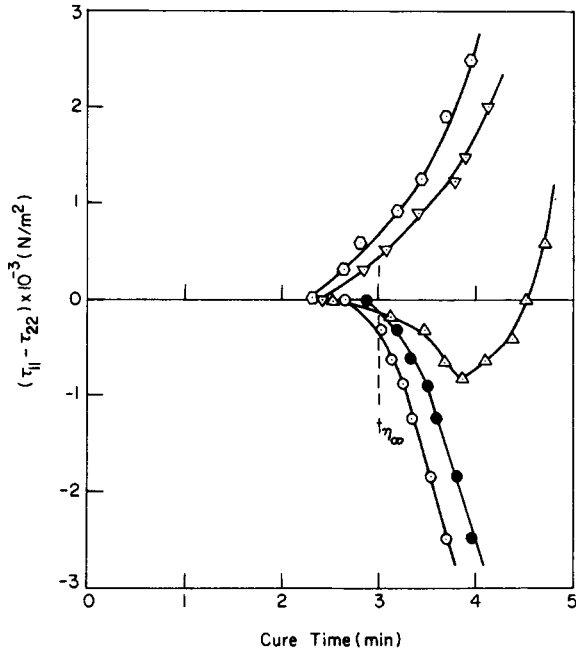


Fig. 5.  $\tau_{11} - \tau_{22}$  vs. cure time ( $T = 60^\circ\text{C}$ ) for Fluid 1 at various shear rates ( $\text{s}^{-1}$ ): (●) 0.00; (○) 0.27; (△) 2.69; (▽) 10.7; (◻) 17.0.

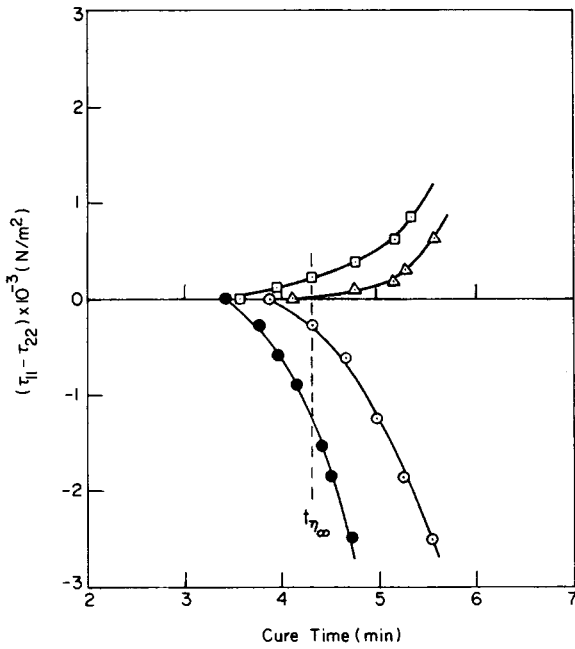


Fig. 6.  $\tau_{11} - \tau_{22}$  vs. cure time ( $T = 60^\circ\text{C}$ ) for Fluid 2 at various shear rates ( $\text{s}^{-1}$ ): (●) 0.00; (○) 0.27; (△) 2.69; (◻) 6.77.

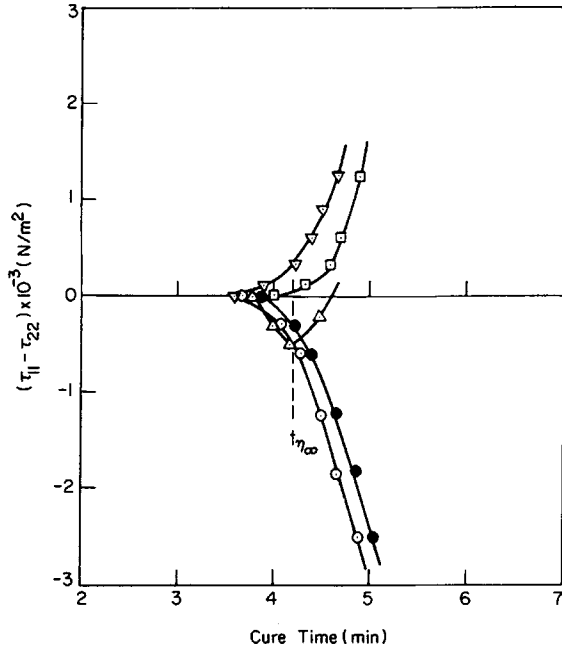


Fig. 7.  $\tau_{11} - \tau_{22}$  vs. cure time ( $T = 60^\circ\text{C}$ ) for Fluid 3 at various shear rates ( $\text{s}^{-1}$ ): (●) 0.00; (○) 0.27; (△) 2.69; (□) 6.77; (▽) 10.7.

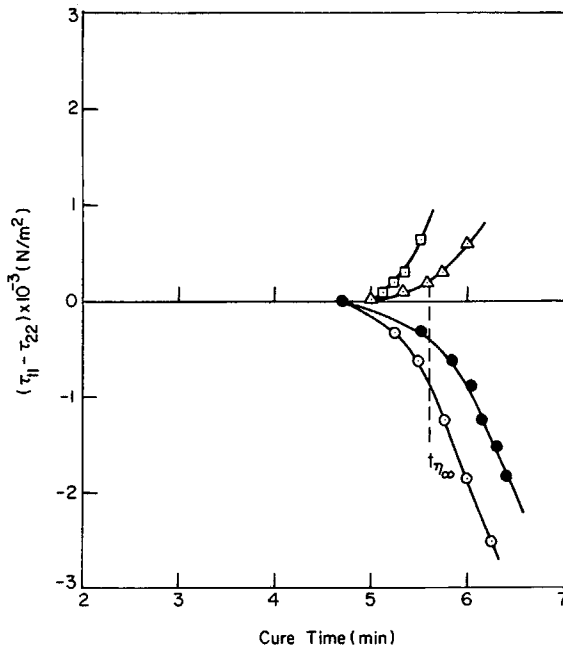


Fig. 8.  $\tau_{11} - \tau_{22}$  vs. cure time ( $T = 60^\circ\text{C}$ ) for Fluid 4 at various shear rates ( $\text{s}^{-1}$ ): (●) 0.00; (○) 0.27; (△) 2.69; (□) 6.77.



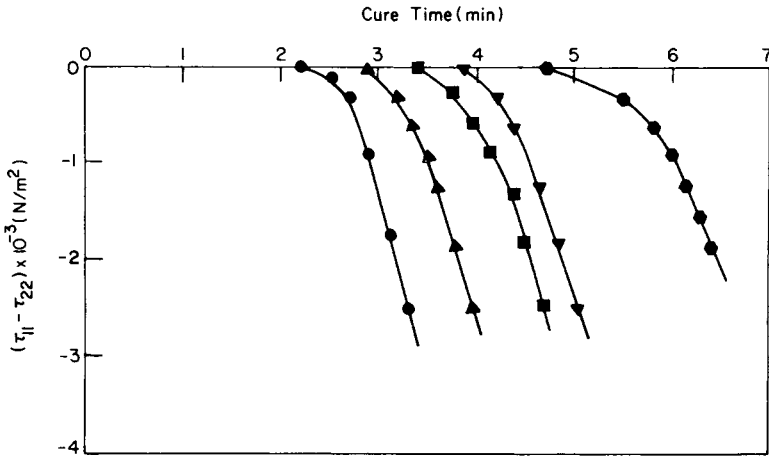


Fig. 9.  $\tau_{11} - \tau_{22}$  vs. cure time ( $T = 60^\circ\text{C}$ ) for various fluids at rest ( $\dot{\gamma} = 0.0 \text{ s}^{-1}$ ): (●) control sample; (▲) Fluid 1; (■) Fluid 2; (▼) Fluid 3; (●) Fluid 4.

shearing deformation, the shrinkage control becomes more effective as the amount of low-profile additive reaches a certain level. It should be noted that less low-profile additive may be needed if the rate of deformation is increased, in order to achieve the same degree of shrinkage control. In other words, there is an interplay between the amount of low-profile additive needed and the rate of deformation imposed in controlling the shrinkage of thermosetting resin during cure. On the basis of the experimental results presented above, it can be concluded that thermosetting resins with low-profile additives must be subjected

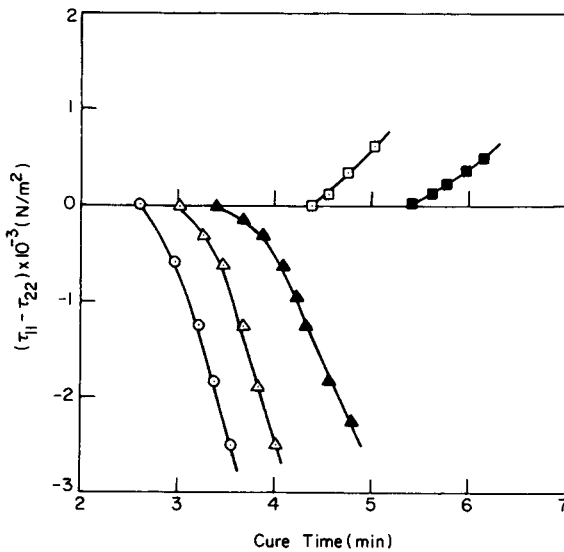


Fig. 10.  $\tau_{11} - \tau_{22}$  vs. cure time ( $T = 60^\circ\text{C}$ ) for various fluids at  $\dot{\gamma} = 1.07 \text{ s}^{-1}$ : (○) control sample; (Δ) Fluid 1; (□) Fluid 2; (▲) Fluid 3; (■) Fluid 4.

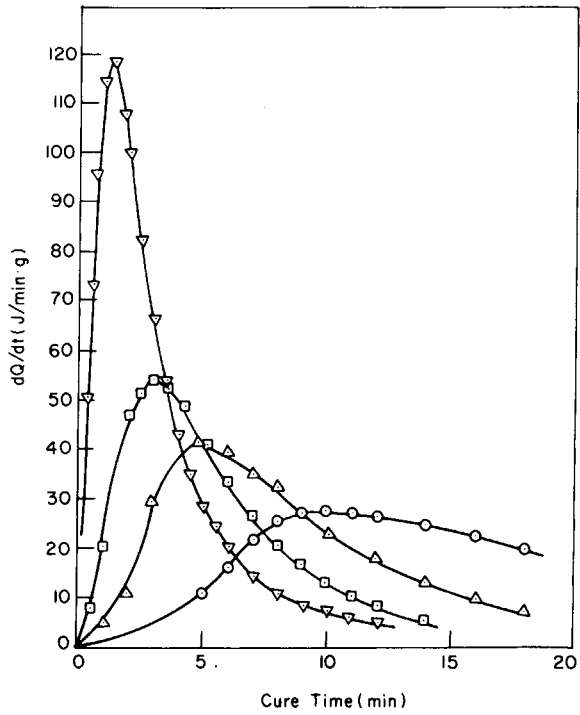


Fig. 11.  $dQ/dt$  vs. cure time for Fluid 1 at various cure temperatures ( $^{\circ}\text{C}$ ): ( $\odot$ ) 35; ( $\Delta$ ) 45; ( $\square$ ) 50; ( $\nabla$ ) 60.

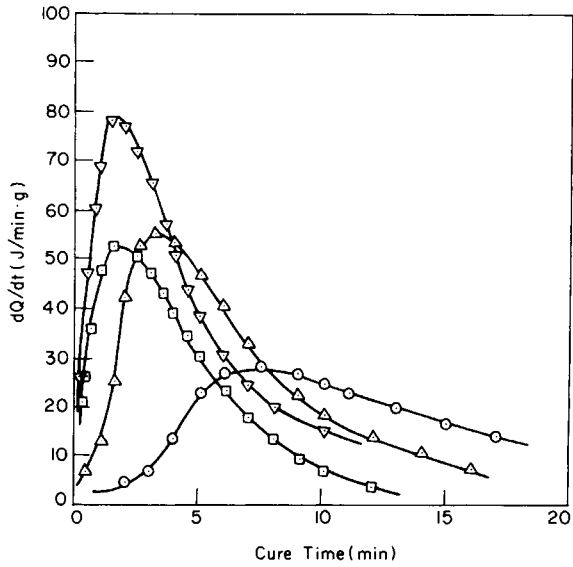


Fig. 12.  $dQ/dt$  vs. cure time for Fluid 2 at various cure temperatures ( $^{\circ}\text{C}$ ): ( $\odot$ ) 45; ( $\Delta$ ) 55; ( $\square$ ) 60; ( $\nabla$ ) 65.

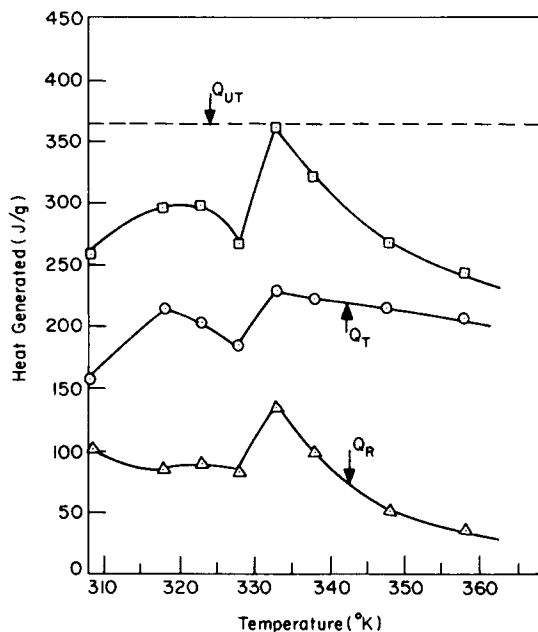


Fig. 13. Heat generated vs. cure temperature for Fluid 1: (○)  $Q_T$ ; (△)  $Q_R$ ; (□)  $Q_{TOT}$ .

to a certain amount of deformation during cure, especially near the incipient gel point, if shrinkage control is going to be effective.

### Curing Kinetics

Figures 11 and 12 describe the rate of heat generated  $dQ/dt$  during the isothermal cure, at various temperatures, for Fluids 1 and 2, respectively. It is seen that as the amount of PVAc solution added is increased from 10 to 20%, the isotherm peak is decreased, indicating that the rate of cure is decreased. Figure 13 gives plots of the heat generated in curing vs. the isothermal cure temperature for Fluid 1. It is seen that the total amount of heat generated  $Q_{TOT}$  changes as the isothermal cure temperature increases. It passes through a maximum at 318K, a minimum at 328K, another maximum at 333K, and then decreases. This behavior is quite different from that observed with neat resin and  $\text{CaCO}_3$ -filled resin, reported respectively in Paper I<sup>13</sup> and Paper II<sup>12</sup> of this series. This is attributable to the phase separation, during cure, of PVAc droplets exuding from the styrene-crosslinked polyester matrix. Indeed we have observed, in a separate experiment,<sup>15</sup> that the PVAc phase exudes during cure from a mixture of neat resin and PVAc solution, which initially formed an optically homogeneous solution.<sup>10</sup> This observation is in consonance with that reported by Pattison et al.<sup>3</sup> and Atkins.<sup>5</sup>

In defining the degree of cure  $\alpha$ , in this paper we have used, as the *ultimate* heat  $Q_{UT}$ , the largest value (362.9 J/g) of  $Q_{TOT}$ , occurring at 333K (see Fig. 13). It should be remembered, however, that in the cure of neat resin and particulate-filled resins, as discussed in Paper I<sup>13</sup> and Paper II<sup>12</sup> of this series, the ultimate heat  $Q_{UT}$  is defined as the average of several values of the total heat  $Q_{TOT}$ ,

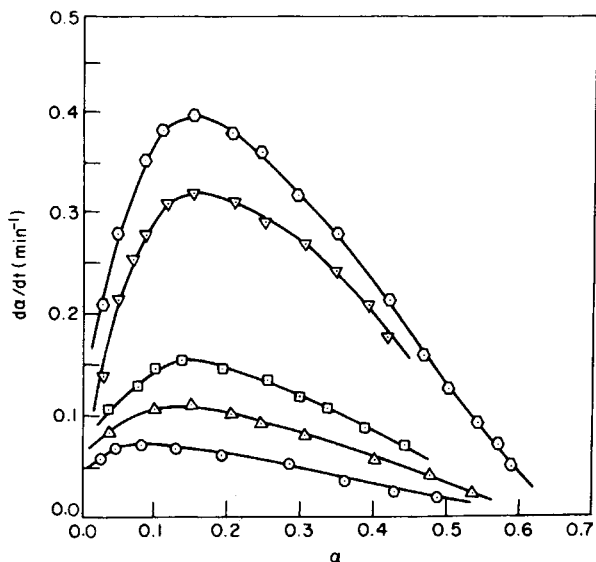


Fig. 14.  $d\alpha/dt$  vs.  $\alpha$  for Fluid 1 at various cure temperatures ( $^{\circ}\text{C}$ ): ( $\odot$ ) 35; ( $\Delta$ ) 45; ( $\square$ ) 55; ( $\nabla$ ) 60; ( $\ominus$ ) 65.

and this turns out to be independent of the isothermal cure temperature employed.

Figures 14 and 15 describe how the rate of cure ( $d\alpha/dt$ ) varies with the degree of cure ( $\alpha$ ) for Fluids 1 and 2, respectively, and Figures 16 and 17 describe how  $\alpha$  varies with cure time for Fluids 1 and 2, respectively. It is seen that, at the same value of  $\alpha$ ,  $d\alpha/dt$  decreases with an increase in the amount of PVAc solution added, and that in achieving the same value of  $\alpha$ , a longer cure time is required

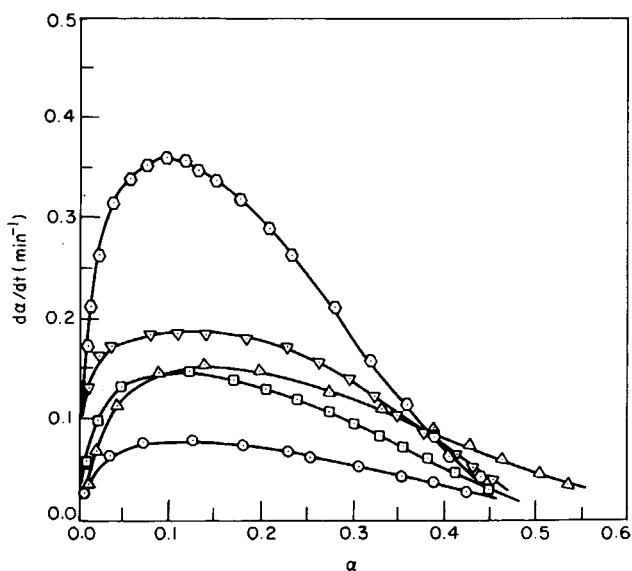


Fig. 15.  $d\alpha/dt$  vs.  $\alpha$  for Fluid 2 at various cure temperatures ( $^{\circ}\text{C}$ ): ( $\odot$ ) 45; ( $\Delta$ ) 55; ( $\square$ ) 60; ( $\nabla$ ) 65; ( $\ominus$ ) 80.

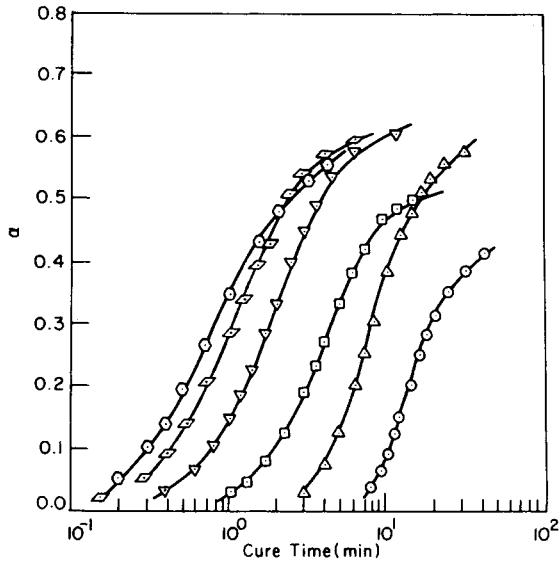


Fig. 16.  $\alpha$  vs. cure time for Fluid 1 at various cure temperatures ( $^{\circ}\text{C}$ ): ( $\odot$ ) 35; ( $\Delta$ ) 45; ( $\square$ ) 55; ( $\nabla$ ) 65; ( $\diamond$ ) 75; ( $\circ$ ) 85.

with 20% PVAc solution than with 10% PVAc solution. This observation is consistent with the observation made when discussing the viscosity variation with cure time (i.e.,  $t_{\eta_{\infty}}$  is greater with Fluid 2 than with Fluid 1). It is of interest to note in Figures 16 and 17 that the final degree of cure is *not* necessarily increased by increasing the cure temperature, which was the case when curing neat resin *with* and *without* filler.<sup>12,13</sup> In other words, at a certain intermediate cure

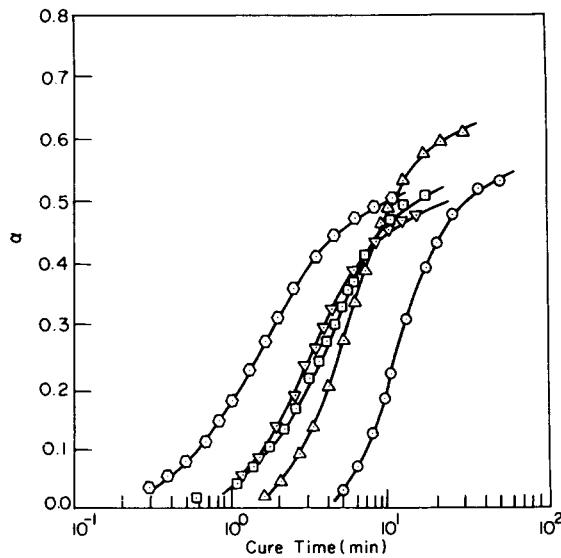


Fig. 17.  $\alpha$  vs. cure time for Fluid 2 at various cure temperatures ( $^{\circ}\text{C}$ ): ( $\odot$ ) 45; ( $\Delta$ ) 55; ( $\square$ ) 60; ( $\nabla$ ) 65; ( $\circ$ ) 80.

TABLE II  
Kinetic Parameters Evaluated for the Fluid Systems Investigated

Temp (K)	$k_1$ (min <sup>-1</sup> )	$k_2$ (min <sup>-1</sup> )	$m$	$n$
(a) Fluid 1				
318	0.0046	0.228	0.27	1.73
323	0.0064	0.458	0.29	1.71
328	0.0144	0.345	0.27	1.73
333	0.0500	0.780	0.35	1.65
338	0.0599	0.751	0.34	1.66
348	0.1220	1.140	0.33	1.67
(b) Fluid 2				
318	0.0084	0.144	0.27	1.73
328	0.0117	0.270	0.29	1.71
333	0.0264	0.282	0.27	1.73
338	0.0336	0.416	0.24	1.76
358	0.1000	0.577	0.24	1.76
(c) Fluid 3				
313	0.0190	0.170	0.33	1.67
323	0.0273	0.342	0.34	1.66
328	0.0260	0.423	0.30	1.70
333	0.0367	0.736	0.36	1.64
338	0.0775	0.566	0.23	1.77
343	0.1440	0.914	0.28	1.72
(d) Fluid 4				
333	0.0534	0.354	0.28	1.72
338	0.0796	0.576	0.26	1.74
343	0.1050	0.433	0.14	1.86
348	0.1400	0.942	0.32	1.68
353	0.1750	0.836	0.23	1.77

temperature a greater degree of cure can be achieved when PVAc solution is added to the resin.

We have also obtained DSC results for the resin/PMMA system (Fluids 3 and 4), which are very similar to those shown above for the resin/PVAc system (Fluids 1 and 2). Space limitation here does not permit us to present the results.

Having constructed plots of  $d\alpha/dt$  vs.  $\alpha$ , we have determined the kinetic parameters appearing in the empirical rate expression<sup>16,17</sup>

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

by the method suggested by Ryan and Dutta.<sup>18</sup> Table II gives a summary of the kinetic parameters evaluated for the four fluid systems investigated, in which a second-order reaction (i.e.,  $m + n = 2$ ) was assumed. We have found that the rate constants,  $k_1$  and  $k_2$ , follow the Arrhenius relationship.

## DISCUSSION

### Measurement of Shrinkage Control during Cure

Low-profile thermoplastic additives have long been used for controlling the shrinkage of polyester premix molding compounds. Researchers<sup>1-7</sup> have pro-

posed more than one mechanism to explain how thermoplastic additives do this. Besides the efforts spent on explaining the mechanism of shrinkage control, there has so far been no discussion in the literature suggesting how one can measure (or determine) the extent of shrinkage and the rate of shrinkage during cure. If an experimental technique is developed, it will be very useful for evaluating the effectiveness of various thermoplastic additives in the early stage of product development.

In the present study, we have demonstrated that measurement of normal stresses in a cone-and-plate rheometer is very useful for detecting, at least qualitatively, the onset of shrinkage and, also, the rate of shrinkage, of a thermosetting resin or its molding compounds during cure. This experimental technique, however, cannot quantify the amount of shrinkage occurring during cure. At present we are trying to develop a new device for the quantitative measurement of shrinkage when a thermosetting resin or its compound undergoes cure.

The results presented above have led us to speculate that polymerization shrinkage can be reduced considerably when the material is subjected to intensive shearing deformation. It should be mentioned at this juncture that the temperature chosen (60°C) for cure in the present study is quite low, compared to that (say, 120–150°C) commonly practiced in the processing of polyester premix molding compounds. Furthermore, all the shrinkage control mechanisms proposed so far (i.e., optical heterogeneity and boiling monomer; strain relief through stress cracking; thermoplastics expansion) refer to the situation where the resins are cured at high temperatures (say, at 150°C). Nevertheless, the results presented here are still useful for certain applications, because not all thermosetting polyester compounds are fabricated at high temperatures.

The choice among the commercially available processes for the fabrication of thermosetting resins and composites is dictated by several factors, such as the nature of the resin system, the size and shape of the parts to be molded, production rate, and types of reinforcement used. Although many thermosetting composites are fabricated at high temperatures through matched molding (e.g., compression molding, transfer molding, and injection molding), low-temperature molding compounds are also found to be useful in cold molding (e.g., stamping) and contact molding (e.g., hand lay-up and spray-up for making boats, tanks, and building panels).

### The Effect of Thermoplastic Additive on Curing Kinetics

Kubota<sup>19</sup> appears to be the only one so far to investigate the effect of thermoplastic additives on the curing behavior of unsaturated polyester resins, by making DSC measurements. Our results presented above are quite extensive and quantitative, compared to Kubota's investigation, and the low-profile additives used in our study are different from those Kubota used.

It has been shown above that the addition of low-profile additive slows down the rate of cure because of the dilution of the resin and initiator by additional styrene, originally present in the solution of low-profile additive. Note that our independent rheological measurements show that the PMMA solution increases  $t_{\eta_{\infty}}$  of the resin more than PVAc solution does, and this trend increases with the concentration of low-profile additive in the resin. We attribute this to the phase separation of PMMA/styrene from the mixture of resin, PMMA, and styrene,

which forms a two-phase system even before cure begins.<sup>10</sup> When the PMMA/styrene forms a separate phase from the mixture, both promoter and peroxide may be absorbed (or occluded) in the PMMA/styrene droplets, causing a decrease in the actual concentration of promoter and peroxide available for copolymerization of styrene with polyester resin in the continuous phase. This will then decrease the rate of cure.

On the other hand, the effect of different types of low-profile additive on the values of the reaction rate constants  $k_1$  and  $k_2$  is not that simple to interpret. Table II shows, for instance, that with 10 wt % of low-profile additive, the values of  $k_2$  for Fluid 1 (containing PVAc) are greater than those for Fluid 3 (containing PMMA), whereas with 20 wt % of low-profile additive the opposite trend seems to prevail. Also, the effect of isothermal cure temperature on the reaction rate constants  $k_1$  and  $k_2$  appears to be very complicated, as may also be seen in Table II. The complexity mentioned above seems to have resulted from two primary sources: (1) the complex morphological state of the exuded droplets of low-profile additive in the matrix resin undergoing curing; (2) the possible variation in the amount of low-profile additive present in the samples (mg) used for obtaining DSC measurements.

The curing of unsaturated polyester resin is believed to occur by virtue of free-radical copolymerization between an unsaturated acid in the polyester resin and a reactive diluent (in our case, styrene). Therefore, the mole ratio of styrene to the unsaturated acid influences the rate of cure. Thus, the additional amount of styrene that becomes available when a low-profile additive (40 wt % PVAc in styrene; 33 wt % PMMA in styrene) is added, will increase the mole ratio of styrene to the unsaturated acid, decreasing the rate of cure and, also, the final degree of cure by changing the ratio of resin to initiator/promoter. On the other hand, a thermoplastic additive is needed to control shrinkage of the resin during cure. Therefore, one must determine an optimum amount of low-profile additive to be added that will minimize the sacrifice of the rate of cure and yet maximize the shrinkage control. It should be emphasized once again that the effectiveness of shrinkage control depends, also, on the rate of deformation that may be imposed, during processing, on the resin system. Our study shows that a large rate of deformation, especially near the gel point, is very effective for shrinkage control.

On the basis of the curing kinetics reported above (see Table II), there are some differences in the final degree of cure between the resin/PVAc system and the resin/PMMA system. With 10 wt % of low-profile additive, the activation energy of the rate constant  $k_2$  for the resin/PVAc system is very close to that for the

TABLE III  
Activation Energy of Fluid Systems Investigated

Sample code	Activation energy (kJ/g-mol)	
	$k_1$	$k_2$
Control sample	99.3	62.8
Fluid 1	56.2	50.1
Fluid 2	69.1	32.0
Fluid 3	29.0	50.8
Fluid 4	59.6	70.3



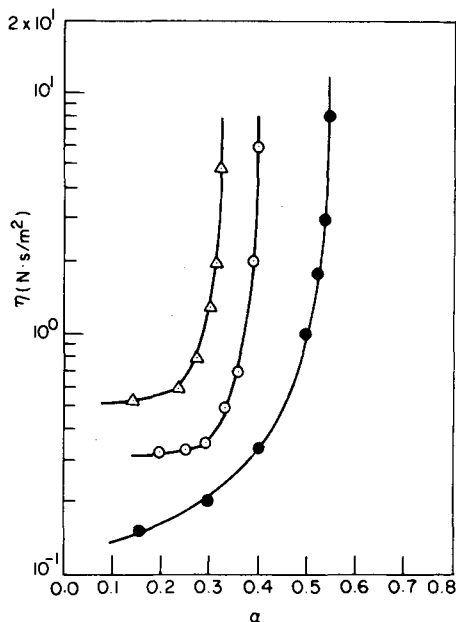


Fig. 18.  $\eta$  vs.  $\alpha$  ( $T = 60^\circ\text{C}$ ) at  $\dot{\gamma} = 17.0 \text{ s}^{-1}$ : (●) control sample; (○) Fluid 1; (Δ) Fluid 2.

resin/PMMA system, and the degree of cure  $\alpha$  up to gel time  $t_{\eta_\infty}$  is approximately the same in the two systems, as shown in Figures 16 and 17 and, also, in Table III. However, as the amount of low-profile additive is increased from 10% to 20%, the activation energy of the rate constant  $k_2$  is decreased for the resin/PVAc system, whereas it is increased for the resin/PMMA system. This seems to indicate that there is a substantial difference in the roles that the two low-profile additives play during cure. Note that in the curing of a resin/low-profile additive mixture, a decrease in the activation energy of reaction does not necessarily imply an increase in the rate of cure, because the degree of cure (also, the rate of cure) is decreased as the amount of low-profile additive is increased (see Figs. 18 and 19). We speculate that the observed decrease in the activation energy of reaction may be attributable to the difference between the structure and morphology of the styrene-crosslinked polyester network of the resin/PVAc/styrene system and that of the resin/PMMA/styrene system.

With reference to the variation of viscosity with cure time, we already have pointed out that PMMA separates from the resin/PMMA mixture even before cure begins.<sup>10</sup> The rate of phase separation of PMMA is expected to increase as the amount of low-profile additive is increased. After a close examination of the rheological measurements presented above for the resin/PVAc system (see Figs. 1 and 2) and resin/PMMA system (Figs. 3 and 4), together with the fact that the resin/PVAc system does not exhibit shear-thinning behavior *before*  $t_{\eta_\infty}$  is reached, we speculate that, in the resin/PVAc system, phase separation occurs *only* at and beyond  $t_{\eta_\infty}$ . On the other hand, shear-thinning behavior, which is typical for concentrated emulsions at high shear rates, is observed with the resin/PMMA system (see Figs. 3 and 4).

When a separate phase of low-profile additive is formed, some of the reactive

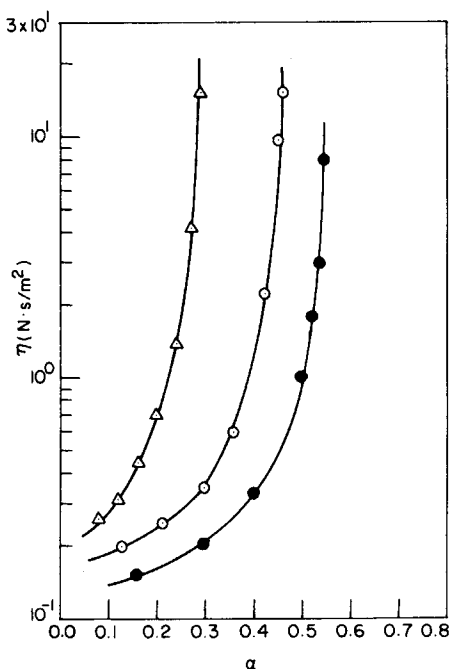


Fig. 19.  $\eta$  vs.  $\alpha$  ( $T = 60^\circ\text{C}$ ) at  $\dot{\gamma} = 17.0 \text{ s}^{-1}$ : (●) control sample; (⊙) Fluid 3; (Δ) Fluid 4.

free radicals, and some of the styrene, can be occluded in the newly formed phase, affecting (in fact, slowing down) the rate of cure and, consequently, decreasing the final degree of cure. It would seem that the morphological state of the exuded phase (PVAc or PMMA) greatly influences the rate of cure and the final degree of cure. We believe that the rate of exudation of low-profile additive depends on its compatibility with the resin, its concentration in the mixture, the curing temperature, the rate of cure, and the rate of deformation which the mixture undergoes during cure. Future research in our laboratory will be directed to finding the relative importance of these factors.

### CONCLUDING REMARKS

We have demonstrated that both the rheological behavior during cure and the curing kinetics, of an unsaturated polyester resin are greatly influenced by the type and amount of low-profile thermoplastic additive used. More specifically, we have found that: (1) the resin/PVAc system, forming an optically homogeneous solution before curing begins, exhibits a phase separation, forming two phases, as curing progresses beyond the incipient gel point; (2) the resin/PMMA system, forming an optically heterogeneous solution before curing begins, exhibits shear-thinning behavior during cure before the incipient gel point is reached; (3) the shrinkage of the resin during cure, judged by the normal stress response in a cone-and-plate rheometer, is decreased by the addition of thermoplastic additive; (4) shrinkage control is found to be more effective when the mixture of resin/thermoplastic additive is subjected to intensive shearing deformation than when the material is at rest; (5) when phase separation of thermoplastic

additive occurs during cure, an optimum cure temperature appears to exist, at which the rate of cure is the greatest.

We conclude from the results presented above that an optimum amount of low-profile additive must be used in order to minimize the sacrifice of the rate of cure and yet maximize the shrinkage control. This is because the addition of low-profile additive decreases the rate of cure of the resin.

In future publications we will discuss the effectiveness of various thermoplastic additives, including the elastomeric thermoplastic resins being developed in industry, in controlling shrinkage of thermosetting polyester resins during cure.

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