Rheology of Unsaturated Polyester Resins. III. Effects of Filler and Low-Profile Additive on the Thickening Behavior of Unsaturated Polyester Resin

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Synopsis

An investigation was made of the rheological behavior of unsaturated polyester resin during thickening in the presence of filler or low-profile additive alone and, also, in the presence of both filler and low-profile additive. For the study, two different types of filler (CaCO$_3$ and clay) and two different types of low-profile additive (PMMA and PVAc) were evaluated. Compared to the resin/thickener system, the resin/filler/thickener system exhibits shear-thinning behavior as thickening progresses, and gives rise to smaller normal stress effects. On the other hand, the resin/low-profile additive/thickener system exhibits two distinct Newtonian regimes in the viscosity-shear stress curves and gives rise to larger normal stress effects. The viscosity behavior of the resin/filler/low-profile additive/thickener system was found to be very similar to that of the resin/low-profile additive/thickener system. In all cases, when the first normal stress difference was plotted against the shear stress, a correlation was obtained which was independent of thickening period. This behavior was exactly the same as for thickening polyester resin alone, as discussed in Part II of this series.

INTRODUCTION

In a previous paper,[1] we have attempted to elucidate the mechanism(s) of the thickening behavior of unsaturated polyester resin. The purpose of the study was to establish a basis on which we could interpret the thickening behavior of polyester premix molding compounds that consist of resin, filler, glass fiber; low-profile additive, viscosity thickener, catalyst (high-temperature curing agent), and mold release agent. Catalyst and mold release agent do not contribute to a better understanding of the rheological behavior of polyester premix molding compounds during thickening, because the amount of these ingredients present is relatively small compared to other ingredients and because they are commonly inactive while thickening takes place. Therefore, we have decided to investigate the effects of only filler and low-profile additive on the thickening behavior of unsaturated polyester resin.

The present study was conducted in order to answer the following two fundamental questions: (1) Will the presence of fillers, which in general increases the viscosity of polyester resin, retard, or accelerate the rate of thickening? (2) Will the presence of low-profile additive, which in general comes as liquid (e.g., PMMA or PVAc dissolved in styrene), complicate thickening behavior? We shall report the highlights of our findings.

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TABLE I
Sample Codes and Materials Used

Sample code	Material
(i) *Polyester resin/filler/thickener system*	
Fluid 1	Resin/CaCO$_3$[a]/MgO[b]
Fluid 2	Resin/clay[c]/MgO
(ii) *Polyester resin/low-profile additive/thickener system*	
Fluid 3	Resin/PMMA[d]/MgO
Fluid 4	Resin/PVAc[e]/MgO
(iii) *Polyester resin/filler/low-profile additive/thickener system*	
Fluid 5	Resin/CaCO$_3$/PMMA/MgO
Fluid 6	Resin/CaCO$_3$/PVAc/MgO

[a] 50 wt % Camel-Wite on the basis of the resin/thickener material.

[b] 1 mol MgO for each mole of prepolymer.

[c] 45 wt % Engelhardt ASP 400 on the basis of the resin/thickener material.

[d] 20 wt % on the basis of the resin/thickener material; Owens-Corning P-701 (33 wt % of PMMA in styrene).

[e] 20 wt % on the basis of the resin/thickener material; Union Carbide LP-40A (40 wt % of PVAc in styrene).

EXPERIMENTAL

The apparatus used is the same as in the previous study,[1] namely two Weissenberg rheogoniometers. All rheological measurements were conducted at 30°C.

The resin used was a general purpose unsaturated polyester supplied to us by Ashland Chemicals Company (Aropol 7030). The fillers (CaCO$_3$ and clay treated with a coupling agent) and the low-profile additives (PMMA and PVAc solution) used are the same, as described in Part I of this series.[2] Table I gives sample codes and the compositions of the samples that were used. The samples were prepared as follows. First, a large batch of material consisting of resin and thickener was prepared, and then the material was divided into several small samples. Various additives, one at a time, were added to each of the latter.

The experimental procedure used was essentially the same as described in Part II of this series,[1] except that in the present study we did not determine the acid number of the samples during thickening.

RESULTS AND DISCUSSION

Rheological Behavior during Thickening in the Presence of Filler

Figure 1 gives plots of viscosity η vs. shear stress τ_w at various periods during thickening for fluid 1, which contains CaCO$_3$ particles as filler. Readers are advised to examine the viscosity curves of resin/CaCO$_3$ suspensions that were given in Figure 2 in Part I of this series,[2] and the viscosity curves of the polyester resin at various thickening period that were given in Figure 6 in Part II of this series.[1] Little evidence is seen in Figure 1, of this paper, to suggest that the presence of CaCO$_3$ affects the thickening behavior of unsaturated polyester resin, except that CaCO$_3$ particles increase the level of viscosities of the resin.

Figure 2 gives plots of η vs. τ_w at various periods during thickening for fluid
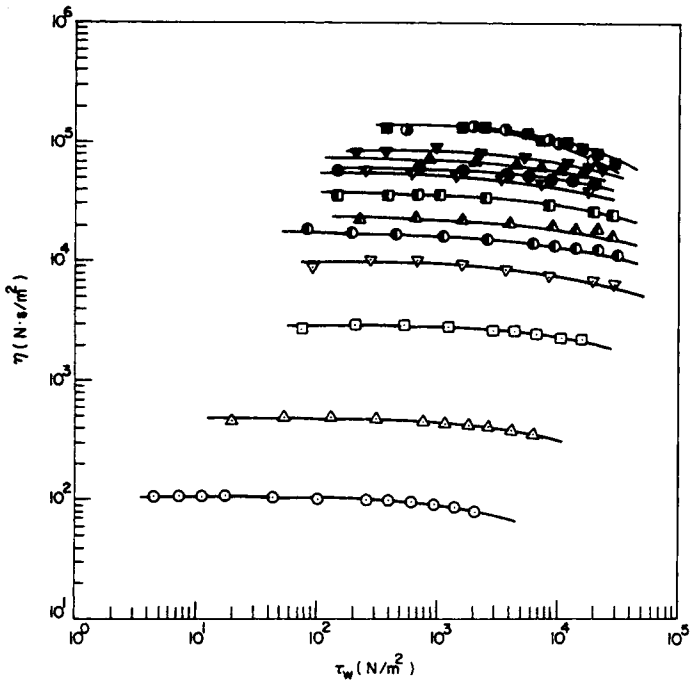
Fig. 1. Viscosity vs. shear stress for fluid 1 at various periods after thickening began (h): (⊙) 5.7; (△) 10.9; (▣) 26.1; (▽) 50.3; (◐) 77.7; (▲) 96.4; (▩) 126.5; (▼) 150.2; (●) 173.5; (▲) 194.3; (■) 316.8; (▼) 363.6; (◑) 459.6.
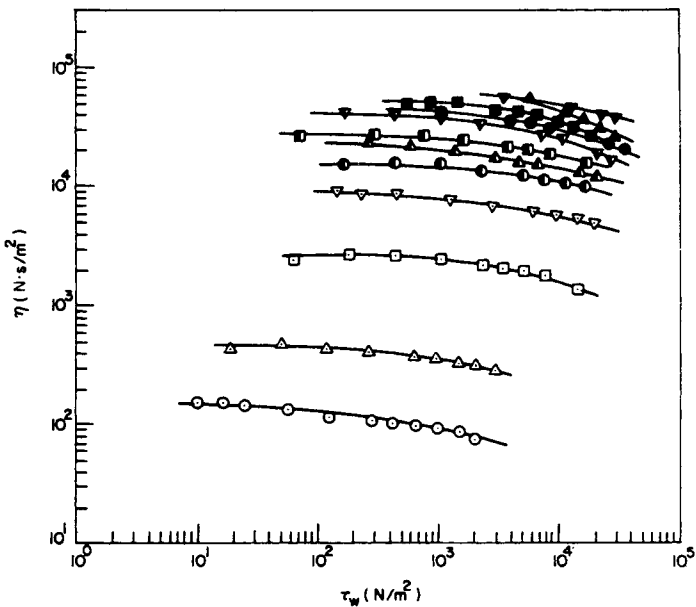

Fig. 2. Viscosity vs. shear stress for fluid 2 at various periods after thickening began (h): (⊙) 6.2; (△) 11.6; (▣) 27.9; (▽) 51.0; (◐) 80.9; (▲) 100.4; (▩) 127.8; (▼) 151.1; (●) 124.4; (▲) 318.3; (■) 364.7; (▼) 461.2.
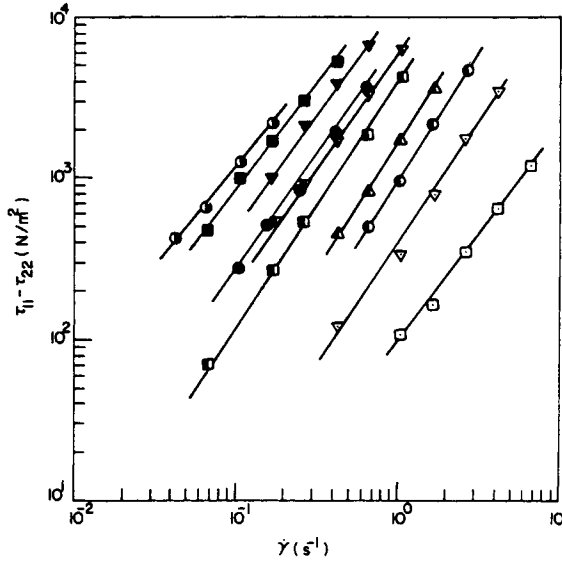
Fig. 3. First normal stress difference vs. shear rate for fluid 1 at various periods after thickening began. Symbols are the same as in Figure 1.

2, which contains clay particles as fillers. Again, readers are advised to examine the viscosity curves of resin/clay suspensions that were given in Figure 4 in Part I of this series,[2] and the viscosity curves of the polyester resin at various thickening periods that were given in Figure 6 in Part II of this series.[1] It is of interest to note that the strong shear-thinning behavior that existed in the resin/clay system without a thickening agent (see Fig. 4 in Part I of this series) disappears with the addition of thickening agent.
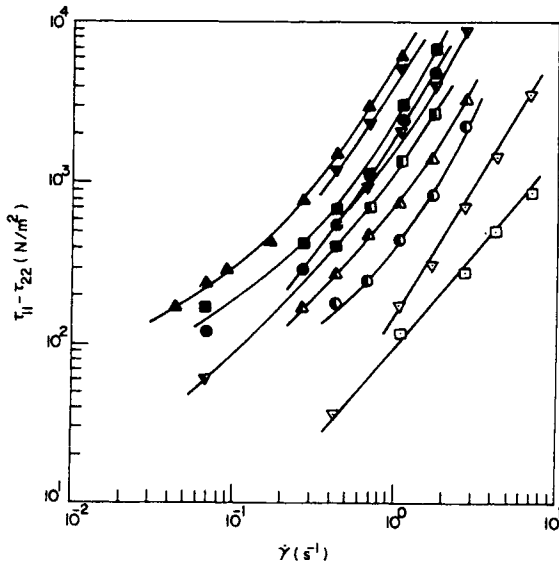

Fig. 4. First normal stress difference vs. shear rate for fluid 2 at various periods after thickening began. Symbols are the same as in Figure 2.
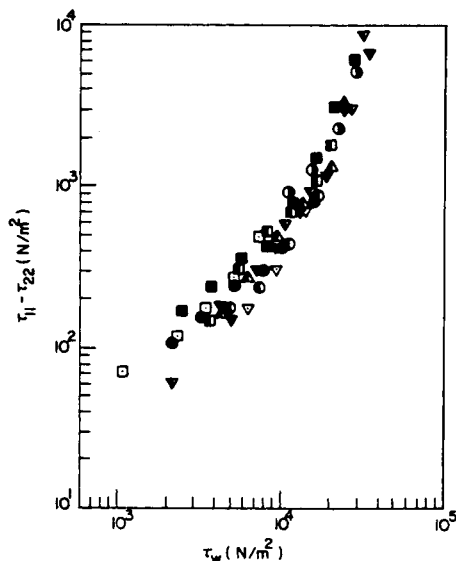
Fig. 5. First normal stress difference vs. shear stress for fluid 1 at various periods after thickening began. Symbols are the same as in Figure 1.

Figure 3 gives plots of the first normal stress difference $\tau_{11}-\tau_{22}$ vs. the shear rate $\dot{\gamma}$ at various periods during thickening for fluid 1, and Figure 4 for fluid 2. It is seen that, in both systems, $\tau_{11}-\tau_{22}$ increases with $\dot{\gamma}$ and as thickening progresses. However, when $\tau_{11}-\tau_{22}$ is plotted against τ_w, one obtains a correlation, which is independent of the thickening period, as shown in Figures 5 and 6. Note that the correlation given in Figures 5 and 6 (for the resin/$CaCO_3$ system and resin/clay system, respectively) is exactly the same as that in the thickening of
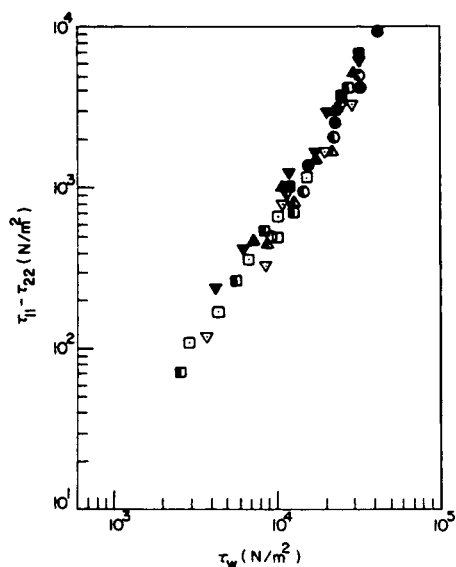

Fig. 6. First normal stress difference vs. shear stress for fluid 2 at various periods after thickening began. Symbols are the same as in Figure 2.

polyester resin alone (see Fig. 11 in Part II of the series). It is worth noting in Figures 5 and 6 that, at a given value of τ_w, the values of $\tau_{11}-\tau_{22}$ for the resin/$CaCO_3$/thickener system are the same as those for the resin/clay/thickener system. This is not surprising because, without a viscosity thickener, neither the resin/$CaCO_3$ system nor the resin/clay system exhibit normal stress effects (see Part I of this series).

Comparing Figure 11 in Part II of this series with Figures 5 and 6 presented in this paper, we observe that the magnitude of $\tau_{11}-\tau_{22}$ in the resin/thickener system is decreased in the presence of filler particles. This is understandable from the point of view that the filler particles increase the system's viscosity, but contribute nothing to its normal stresses, thus giving rise to smaller values of $\tau_{11}-\tau_{22}$ for the same value of τ_w. It can then be concluded that filler particles seem to have little influence on the thickening behavior of unsaturated polyester systems. It should be mentioned that, in our previous paper,[1] we already proposed a thickening mechanism for unsaturated polyester resins.

It should be noted that, due to the presence of solid particles in a liquid system, τ_w, instead of $\dot{\gamma}$, must be used to correlate with $\tau_{11}-\tau_{22}$ (see Part I of this series).

Rheological Behavior during Thickening in the Presence of Low-Profile Additive

Figures 7 and 8 give plots of η vs. τ_w, at various periods of thickening, for fluids 3 and 4, containing PMMA solution and PVAc solution, respectively, as low-profile additive. It is seen in Figure 7 that the addition of PMMA solution to the resin/thickener system gives rise to viscosity curves having two Newtonian
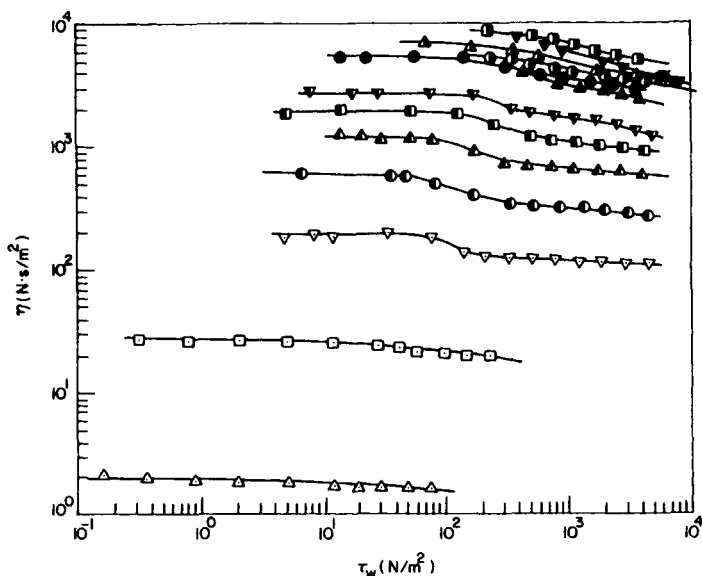

Fig. 7. Viscosity vs. shear stress for fluid 3 at various periods after thickening began (h): (△) 11.2; (▫) 30.7; (▽) 51.9; (◉) 81.8; (▲) 101.6; (▪) 128.8; (▼) 152.6; (●) 175.2; (▲) 197.0; (▼) 288.1; (◐) 338.0; (▲) 386.6; (▪) 486.5.
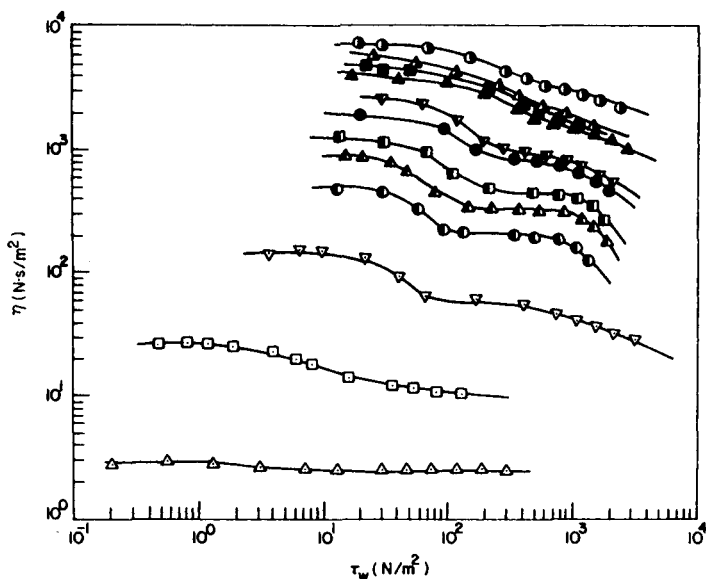
Fig. 8. Viscosity vs. shear stress for fluid 4 at various periods after thickening began (h): (△) 12.5; (□) 29.5; (▽) 52.6; (◑) 82.7; (▲) 102.5; (■) 130.4; (▼) 154.0; (●) 176.5; (▲) 197.0; (■) 246.0; (◐) 339.8; (▲) 385.7.

regimes as thickening progresses and then a non-Newtonian shear-thinning regime as thickening levels off. It is seen in Figure 8 that the addition of PVAc solution to the resin/thickener system gives rise to viscosity curves having two Newtonian regimes, as well as a non-Newtonian shear-thinning regime at high values of τ_w, as thickening progresses and, then, a typical non-Newtonian regime as thickening levels off. Note that, without low-profile additive, viscosity curves of unsaturated polyester resin follow Newtonian behavior very closely, as shown in Figure 6 in Part II of this series.[1] Hence one can conclude that the presence of low-profile additive appears to significantly influence the thickening behavior of unsaturated polyester resin.

In light of the viscosity curves of the resin/PVAc system and the resin/PMMA system presented in Figures 6 and 7 in Part I of this series,[2] a close examination of Figures 7 and 8 appears to indicate that, during the course of thickening, PVAc forms a discrete phase (i.e., droplets) in the presence of a viscosity thickener in the mixture. This speculation is based on the display of strong shear-thinning behavior in the resin/PVAc/thickener system. One would not expect to observe shear-thinning behavior in liquid mixtures forming homogeneous solutions. Note that mixtures of resin and PVAc solution form homogeneous solutions and exhibit Newtonian behavior, as demonstrated in Figure 6 in Part I of this series.[2] This observation is of practical significance, because the phase separation of PVAc from the polyester premix molding compound during thickening, if it occurs, will influence the degree of shrinkage of the molded products. Ideally, an effective thermoplastic additive should be compatible with the molding compound at the uncured stage in order to avoid exudation during the aging and storage period, but it should be totally incompatible with the resin during cure.

In our previous paper,[2] we pointed out that mixtures of resin and PMMA solution form two phases. Therefore, the shear-thinning behavior of the resin/PMMA/thickener system observed in Figure 7 does not surprise us. The really important, unanswered, question then is whether one should choose a low-profile additive that is miscible or immiscible with the resin, in order to minimize mold shrinkage. In a forthcoming paper, we plan to answer this important question after we will have conducted molding experiments with different types of low-profile additive.

Figure 9 gives plots of $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$ at various periods of thickening for fluid 3 (containing PMMA solution) and Figure 10 for fluid 4 (containing PVAc solution). It is seen that $\tau_{11}-\tau_{22}$ increases with $\dot{\gamma}$ as thickening progresses. However, when $\tau_{11}-\tau_{22}$ is plotted against τ_w, we obtain a correlation, shown in Figures 11 and 12, which, again, is independent of the period of thickening. Note that, as thickening progresses, τ_w also increases, and therefore, in the plots of $\tau_{11}-\tau_{22}$ vs. τ_w, an increase in τ_w indirectly implies an increase in the period of thickening.

Comparing Figure 11 in Part II of this series with Figures 11 and 12 presented here, we observe that the magnitude of $\tau_{11}-\tau_{22}$ in the resin/low-profile additive/thickener system is much greater than that in the resin/thickener system. In other words, during the course of thickening, the low-profile additives (PMMA solution or PVAc solution) increased the normal stress effects of the mixtures of polyester resin and viscosity thickener. The observed increase in the normal stress effects may be attributable to the formation of the droplet phase that has resulted from the presence of low-profile additive. It should be pointed out that, when PVAc solution is mixed with the polyester resin, forming a homogeneous solution, $\tau_{11}-\tau_{22}$ is negligibly small, as we already have discussed in our previous paper (see Fig. 12 in Part I of this series). Note further that mixtures of resin and PMMA solution, forming heterogeneous mixtures, give rise to large normal
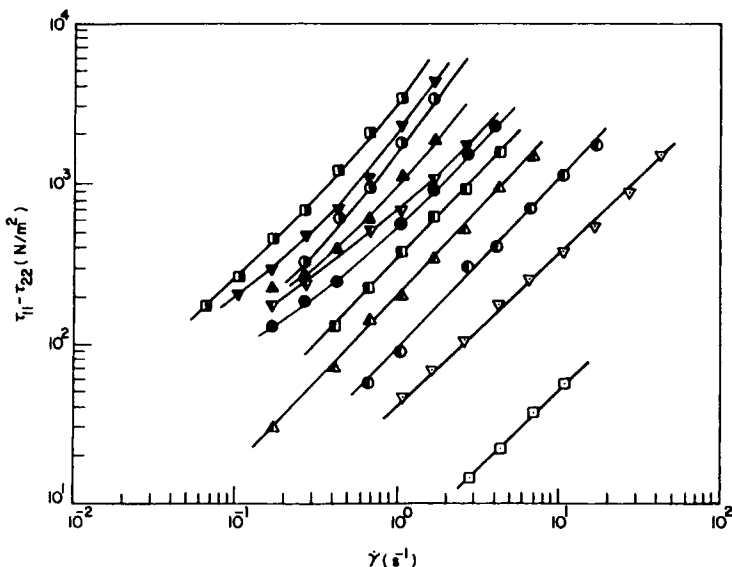

Fig. 9. First normal stress difference vs. shear rate for fluid 3 at various periods after thickening began. Symbols are the same as in Figure 7.
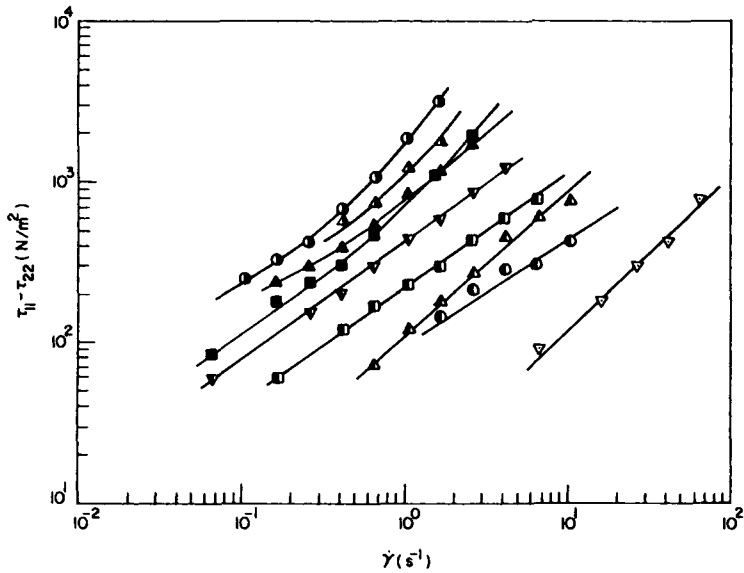
Fig. 10. First normal stress difference vs. shear rate for fluid 4 at various periods after thickening began. Symbols are the same as in Figure 8.

stress effects, compared to the mixtures of resin and PVAc solution, which form homogeneous solutions. And yet, when a thickening agent is added to each system, the magnitudes of $\tau_{11}-\tau_{22}$ in the two systems become almost the same. This is further evidence, though indirect, supporting the view presented above that PVAc forms a separate phase during the course of the thickening of unsaturated polyester resin, although mixtures of resin and PVAc solution without a thickening agent form homogeneous solutions.

From the point of view of processing, we have yet to demonstrate whether or not the normal stresses in polyester molding compounds have any practical significance in controlling the degree of shrinkage of the molded products. In a future paper, we intend to address this question.

Rheological Behavior during Thickening in the Presence of Both Filler and Low-Profile Additive

Figure 13 gives plots of η vs. τ_w, at various periods of thickening, for fluid 5 (containing both $CaCO_3$ particles and PMMA solution), and Figure 14 for fluid 6 (containing both $CaCO_3$ particles and PVAc solution). It is seen that the shape of the viscosity curves is very similar in the two systems. Note that thickening of the unsaturated polyester resin occurs in the presence of both filler particles and droplets of low-profile additive suspended in the resin. Undoubtedly, the state of dispersion is very complex, as discussed in Part I of this series.[2] Note further that the viscosity behavior of these systems very much resembles that of the resin/PVAc/thickener system, shown in Figure 8.

Figure 15 gives plots of $\tau_{11}-\tau_{22}$ vs. $\dot{\gamma}$, at various periods of thickening, for fluid 5, and Figure 16 for fluid 6. It is seen that $\tau_{11}-\tau_{22}$ increases with $\dot{\gamma}$, and as thickening progresses. However, when $\tau_{11}-\tau_{22}$ is plotted against τ_w as given
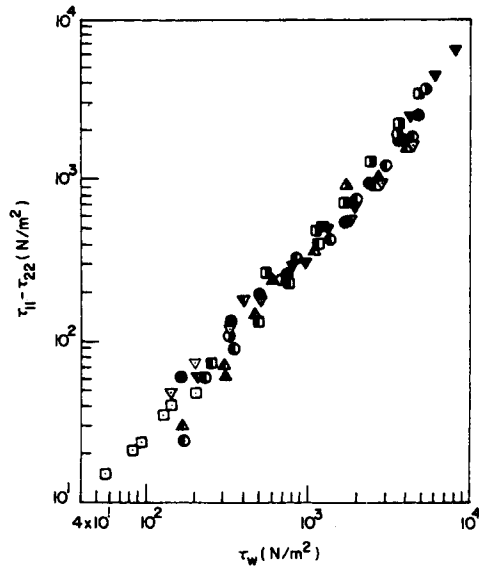
Fig. 11. First normal stress difference vs. shear stress for fluid 3 at various periods after thickening began. Symbols are the same as in Figure 7.

in Figures 17 and 18, we obtain a correlation for the resin/filler/low-profile additive/thickener system, very similar to that obtained for the resin/low-profile additive/thickener system (see Figs. 11 and 12), and for the resin/filler/thickener system (see Figs. 5 and 6). The practical usefulness of the experimental corre-
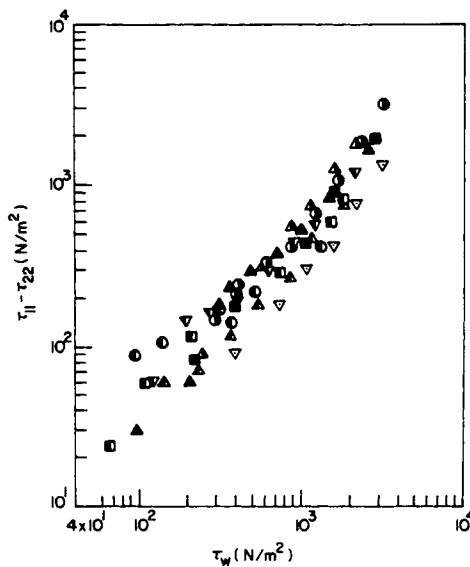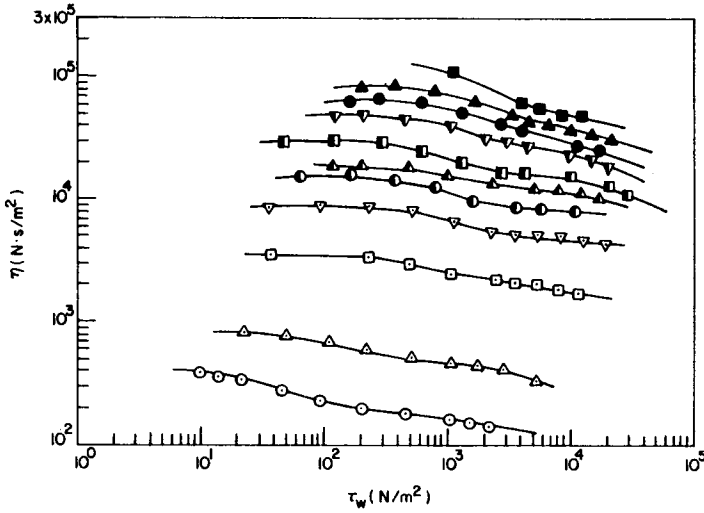

Fig. 12. First normal stress difference vs. shear stress for fluid 4 at various periods after thickening began. Symbols are the same as in Figure 8.

Fig. 13. Viscosity vs. shear stress for fluid 5 at various periods after thickenig began (h): (⊙) 7.3; (▲) 12.3; (▣) 28.8; (▽) 53.3; (◑) 83.3; (▲) 108.3; (▣) 131.0; (▼) 155.0; (●) 178.0; (▲) 198.7; (■) 272.7.

lation, given in Figures 17 and 18, is that, for all intents and purposes, one can construct a power-law relationship.

$$\tau_{11}-\tau_{22} = \alpha(\tau_w)^m \tag{1}$$

in which α and m are constants, characteristic of the material.   Note that the empirical expression, eq. (1), is valid over the entire period of thickening, and would also be independent of the temperature at which thickening takes place. Earlier, Han and co-workers[3–7] and White and co-workers[8,9] demonstrated that plots of $\tau_{11}-\tau_{22}$ vs. τ_w give rise to a correlation, which is independent of tem-
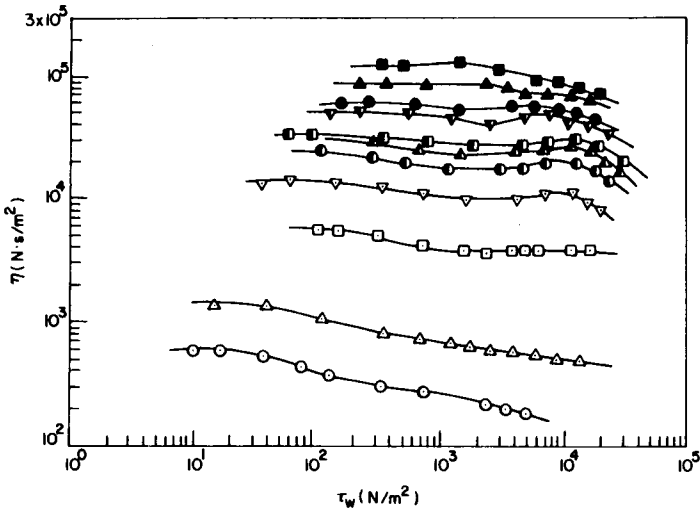

Fig. 14. Viscosity vs. shear stress for fluid 6 at various periods after thickening began (h): (⊙) 7.8; (▲) 13.0; (▣) 30.0; (▽) 55.0; (◑) 72.2; (▲) 106.3; (▣) 132.1; (▼) 156.2; (●) 179.6; (▲) 200.5; (■) 389.6.
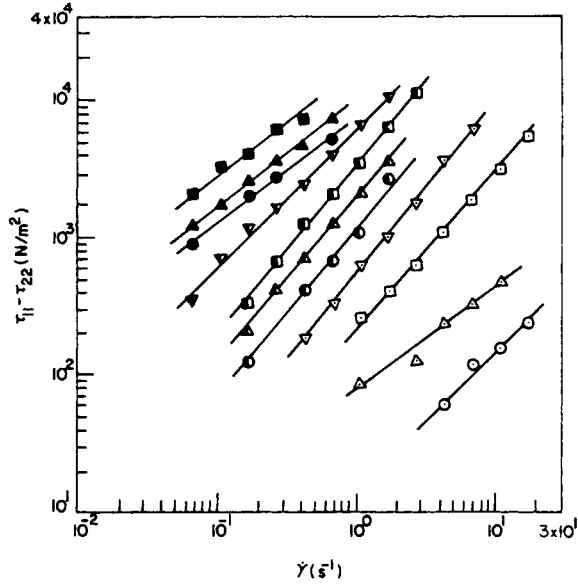
Fig. 15. First normal stress difference vs. shear rate for fluid 5 at various periods after thickening began. Symbols are the same as in Figure 13.

perature. Therefore, eq. (1) may be very useful in predicting (or controlling) the normal stress effects of polyester premix molding compounds during thickening.

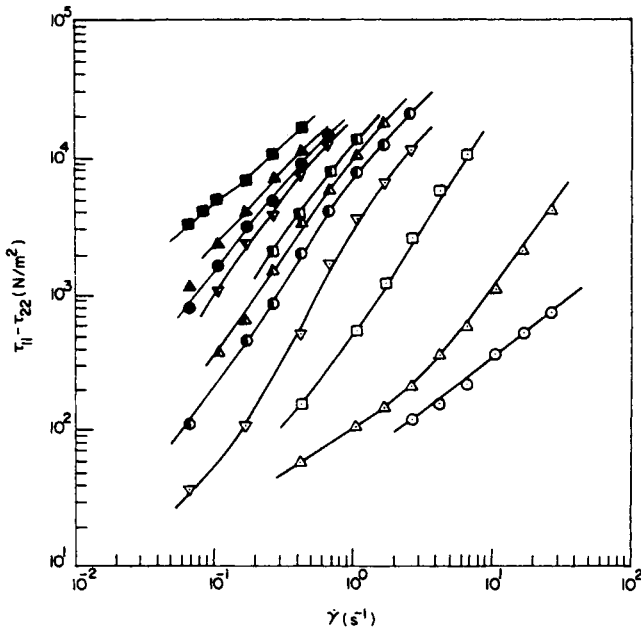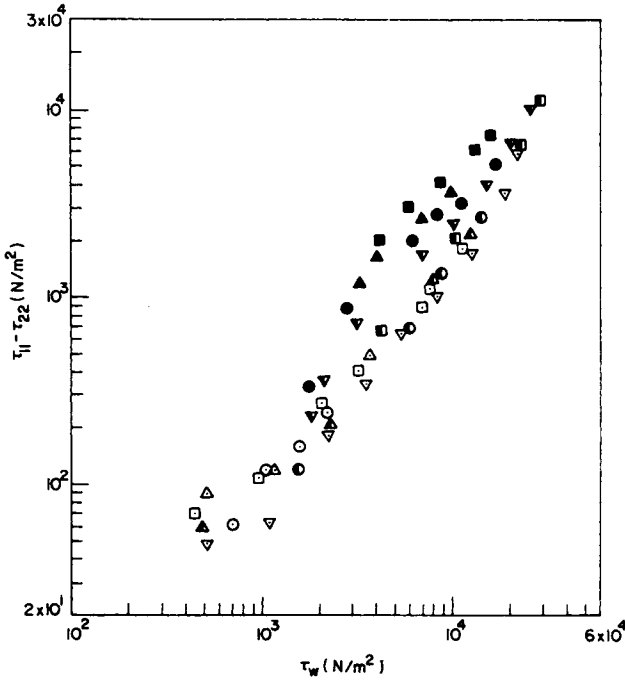Figure 19 gives plots of zero-shear viscosity versus thickening time, in the

Fig. 16. First normal stress difference vs. shear rate for fluid 6 at various periods after thickening began. Symbols are the same as in Figure 14.

Fig. 17. First normal stress difference vs. shear stress for fluid 5 at various periods after thickening began. Symbols are the same as in Figure 13.
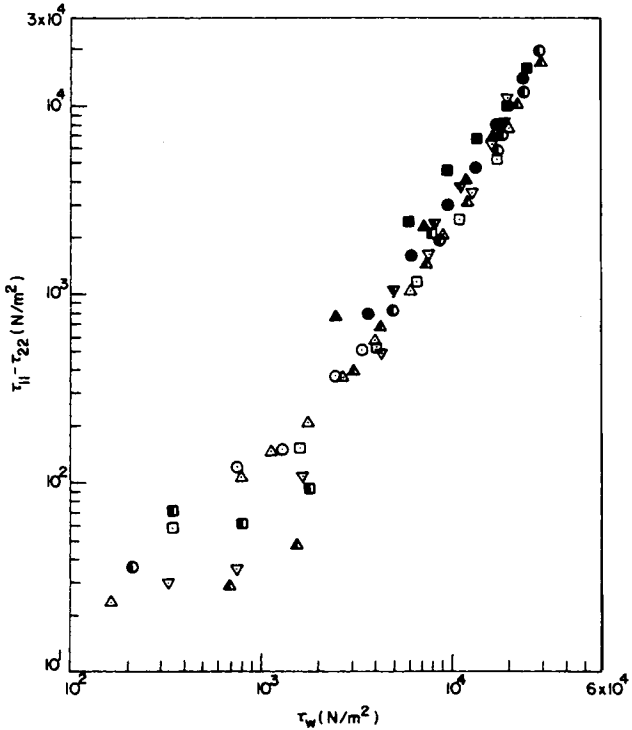

Fig. 18. First normal stress difference vs. shear stress for fluid 6 at various periods after thickening began. Symbols are the same as in Figure 14.
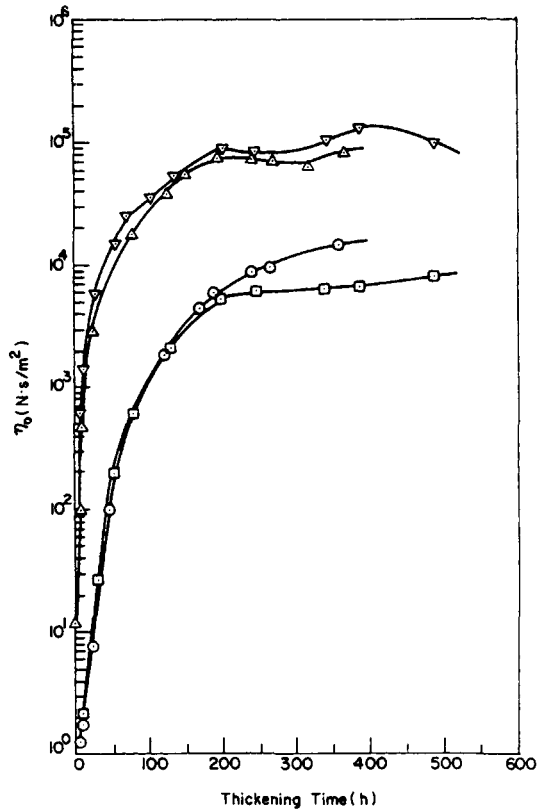
Fig. 19. Zero-shear viscosity vs. thickening time for: (⊙) polyester resin/MgO; (▲) fluid 1; (□) fluid 3; (▽) fluid 5.

thickening of unsaturated polyester resin in the presence of $CaCO_3$ particles alone, in the presence of PMMA solution alone, and in the presence of both $CaCO_3$ particles and PMMA solution. Figure 20 gives plots of zero-shear viscosity versus thickening time, in the thickening of unsaturated polyester resin in the presence of $CaCO_3$ particles, in the presence of PVAc solution, and in the presence of both $CaCO_3$ particles and PVAc solution. Comparison of Figure 19 and Figure 20 reveals that the two different types of low-profile additive used appear to have little influence on the thickening behavior of the respective filled systems. This observation is strictly from the rheological standpoint. There may be a discernible difference between the two low-profile additives in their performance in controlling the shrinkage of molded products. We shall investigate this problem in the future, by conducting controlled experiments, using injection molding, compression molding, or transfer molding processes with polyester premix molding compounds.
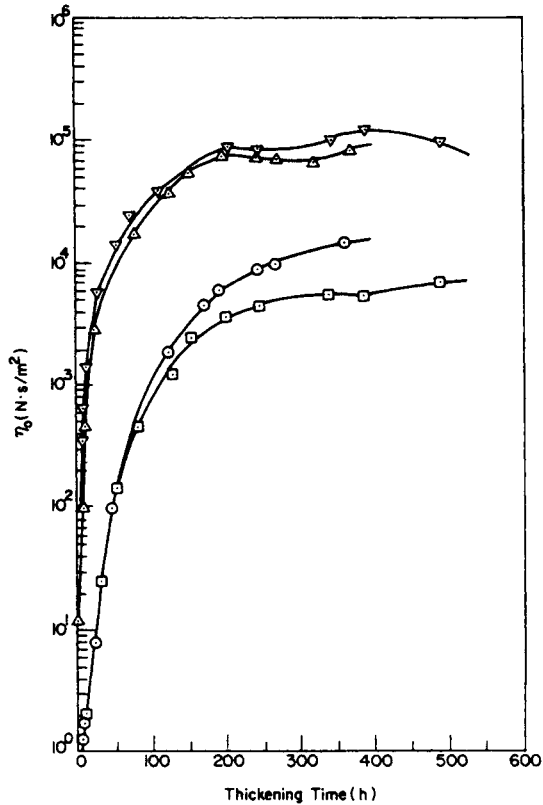
Fig. 20. Zero-shear viscosity vs. thickening time for: (⊙) polyester resin/MgO; (△) fluid 1; (□) fluid 4; (▽) fluid 6.

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