

# Rheology of Unsaturated Polyester Resins. I. Effects of Filler and Low-Profile Additive on the Rheological Behavior of Unsaturated Polyester Resin

CHANG DAE HAN and KWOK-WAI LEM, *Department of Chemical Engineering, Polytechnic Institute of New York, Brooklyn, New York 11201*

## Synopsis

Measurements were taken of the *bulk* rheological properties of concentrated suspensions of particulates in unsaturated polyester resins, using a cone-and-plate rheometer. The particulates used were clay, calcium carbonate, and milled glass fiber. With clay and milled glass fibers, shear-thinning behavior of suspensions was observed at low shear rates or low shear stresses as the concentration of particulates was increased, whereas concentrated suspensions of calcium carbonate exhibited Newtonian behavior over the range of shear stresses or shear rates investigated. The cone-and-plate rheometer was also used for measurements of the bulk rheological properties of various mixtures of polyester resin and low-profile additives. For low-profile additives, solutions, in styrene, of poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) were used. It was found that the bulk viscosities of all mixtures of polyester resin and PVAc solution lie between those of the individual components, whereas the bulk viscosities of some mixtures of polyester resin and PMMA solution go through a minimum and a maximum, depending on the composition of the mixture. While all mixtures of polyester resin and PVAc solution exhibited negligible normal stress, some mixtures of polyester resin and PMMA solution exhibited noticeable normal stresses. It should be mentioned that polyester resin follows Newtonian behavior. It turned out that all mixtures of polyester resin and PVAc solution exhibited clear, homogeneous solutions, whereas mixtures of polyester resin and PMMA solution exhibited optical heterogeneity, i.e., turbidity. When polyethylene powders were used as low-profile additives, suspensions of polyester resin and polyethylene powders exhibited *negative* values of normal stress as the concentrations of suspension reached a critical value. When both filler and low-profile additive were put together in polyester resin, the rheological behavior became quite complex, indicating that some interactions exist between the filler and the low-profile additive.

## INTRODUCTION

In recent years, glass-fiber-reinforced polyester composites have received an increasing attention from the automotive industry. Such composites offer combinations of properties not found in other materials: high strength and dimensional stability with low weight, corrosion and chemical resistance, and excellent dielectric properties.<sup>1,2</sup> The advantages of composite for automotive bodies are that they can be as strong as conventional steel bodies and more resilient, so that they absorb shock to a degree rather than transmit it.

Polyester compounds suitable for hot press molding process, known as sheet molding compounds (SMC), bulk molding compounds (BMC), and thick molding compounds (TMC), have been developed in industry, providing processors (e.g., the automotive industry) with formulating and processing flexibility and the inherent strength needed to meet the requirements of specific applications.<sup>1,2</sup> These compounds are a composite of a polyester resin, low-profile thermoplastic

additive, catalyst, mold-release agent, pigment, inorganic filler, and glass fiber reinforcement. Both SMC and TMC are produced by a continuous process of saturating the glass fiber with the resin by means of impregnating rolls, and sandwiching the sheet so formed between two polyethylene-film carriers.

Depending upon the application and the manufacturing process selected, a number of other additives are employed to provide specific products or end-use properties. These include inert fillers, flame retardants, compounds to enhance surface finish and reduce shrinkage in the mold, release agents, and viscosity control materials. No-shrink systems of BMC, SMC, and TMC have been commercially available for a number of years. The goal of development work in this area has been molded parts with smooth surfaces, no warpage, and no sink marks.<sup>3,4</sup>

Filler type and amount have an effect on shrinkage and sink marks. Obviously more filler reduces both, but at the same time increases mixture viscosity, which is critical when working with molding compounds. A combination of coarse and fine particles produces the optimum results. Fillers, such as clay, calcium carbonate, and wollastonite, judiciously selected and in relatively high concentrations, can also impart flame retardancy and serve as a stress transfer medium, as well as reduce total compound cost. It should be pointed out that fillers strongly influence the flow characteristics of molding compounds.

The rheological properties of the molding compounds play a significant role in determining the processing conditions, which in turn affect the end-use properties of the composite materials. For example, the viscosity of bulk molding compounds is deliberately increased to about a million poises by adding a small amount of Group IIA metal oxide to make the material suitable for hot press molding without a great distortion of fiber orientation during fabrication.<sup>5,6</sup>

BMC and SMC are rheologically very complex, concentrated suspensions, especially with low-profile thermoplastic additives. A low-profile resin is defined as a resin that imparts low shrinkage characteristics to a molded part, permitting excellent reproduction of the mold surface and superior dimensional stability. Table I gives a typical composition of low-profile resin, consisting of fillers, viscosity thickener, reinforcing fibers, low-profile additive, organic peroxide, mold release agent, and unsaturated polyester prepolymer dissolved in styrene.<sup>7</sup>

Information on the rheological properties of the premix molding compounds would be helpful in establishing the "moldability" of the material. Too high a viscosity will result in a short-shot (incomplete filling of the mold cavity), upsetting the balance between the speeds of the flow process and curing process.

An investigation dealing with complex systems, such as the processing of fiber-reinforced thermoset resins, is extremely time-consuming because there are so many variables involved. These comprise the material variables (e.g., the molecular weight of the resin, catalyst, fiber size and fiber loading, additives, and coupling agents) and the processing variables (e.g., injection pressure, mold temperature, and cooling rate).

Due to the fact that several ingredients are involved in the preparation of polyester molding compounds (see Table I), it is virtually impossible for one to understand the role of each ingredient and the interactions, if any, among ingredients simply by determining the bulk rheological behavior of the mixture. With this in mind, we recently have embarked on a comprehensive research program to investigate the rheological behavior of unsaturated polyester resins

TABLE I  
Typical Composition of Low-Profile Polyester Molding Compound<sup>7</sup>

Component	Function	Wt %
Unsaturated polyester resin	Prepolymer	15.9 <sup>a</sup>
Thermoplastic in styrene	Low-profile additive	7.9 <sup>b</sup>
Styrene	Reactive solvent	2.6
Calcium carbonate	Filler	53.6
Magnesium oxide	Thickener	0.5-2.0 <sup>c</sup>
Glass fiber	Reinforcement	20.0
<i>t</i> -Butyl perbenzoate	Catalyst (initiator)	1.0 <sup>c</sup>
Zinc stearate	Mold release agent	3.0 <sup>c</sup>

<sup>a</sup> Unsaturated polyester resin containing approximately 30 wt % styrene.

<sup>b</sup> A 40 wt % solution of thermoplastic in styrene.

<sup>c</sup> Wt % based on resin.

containing particulate filler alone, low-profile additive alone, viscosity thickener alone, and combinations thereof.

In this paper we shall present the highlights of our findings on the effects of filler and low-profile additive on the bulk rheological behavior of unsaturated polyester resin.

## EXPERIMENTAL

### Apparatus and Experimental Procedure

For rheological measurements, a Model R-17 Weissenberg Rheogoniometer (Sangamo-Weston Controls Bognor Regis, Sussex, England) was employed. Figure 1 gives a schematic of the normal forces unit, consisting of the reservoir cone and plate suspended from a beam spring, and steadied by an air bearing. A magnification lever acts on a pivot to give a 10 times magnification of normal forces displacement. The transducer and set-zero mechanism are shown on the right-hand side in Figure 1. In this system, a stress normal to the rotational plane is measured by a sensitive transducer, which is attached to the instrument frame

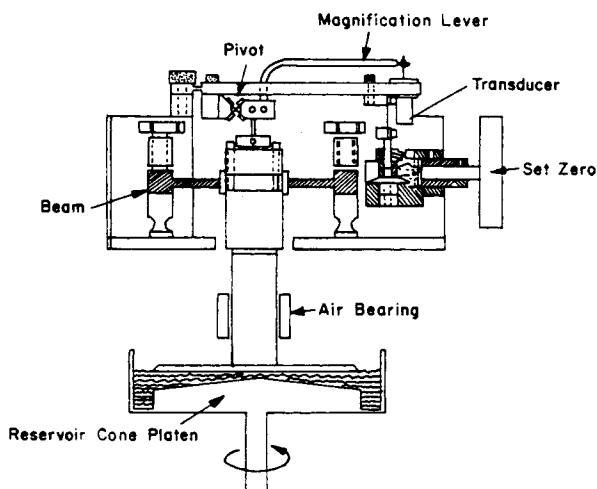


Fig. 1. Schematic view of the cone-and-plate rheometer employed.

and is connected to the beam. The experimental procedure employed is essentially the same as that described in a paper by Copley and King.<sup>8</sup>

### Materials

A general-purpose unsaturated polyester resin (Aropol 7030, Ashland Chemical Co.) was used for the study. Although the chemistry of the resin was not disclosed by the resin producer, we believe that it was prepared by the reaction of propylene glycol with a mixture of maleic anhydride and isophthalic acid.

Three different types of particulates were used: (a) calcium carbonate ( $\text{CaCO}_3$ ) (Camel-Wite and Camel-Fil, A Flintkote Co.); (b) clay, hydrous aluminum silicate (ASP 400P, Engelhard Minerals and Chemicals Corp.); (c) milled glass fibers (Ferro 650 Milled Fibers, Reichhold Corp.). Two particle sizes of  $\text{CaCO}_3$  were used, namely Camel-Wite, 3.0  $\mu\text{m}$  average diameter, and Camel-Fil, 6.5  $\mu\text{m}$  average diameter. Camel-Wite has a broader particle size distribution than Camel-Fil. The clay particles were in the form of thin flat and laminated plates, and their average size, as equivalent spheres, was 4.8  $\mu\text{m}$ . The Ferro milled fibers used are made from "E" glass (a low alkali, lime-alumina borosilicate glass), and have nominal dimensions of 0.00090-in. diameter and 0.0625-in. length.

In order to investigate the effect, if any, of surface treatment of the particulates on the rheological behavior of concentrated suspensions, the particulates were treated with the silane coupling agent  $\gamma$ -methacryloxy propyltrimethoxysilane (Union Carbide Corp., A174). In all cases, the amount of A174 used was 1.0 wt % of the particulates.

Three different types of low-profile additive were used: (a) a 40 wt % solution of polyvinyl acetate (PVAc) in styrene (Union Carbide, Chemical, LP-40A); (b) a 33 wt % solution of polymethyl methacrylate (PMMA) in styrene (Owens-Corning, P-701); (c) high-density polyethylene (HDPE) powders (Arco Polymer Inc., SDP-860). The HDPE powders have an average particle diameter of 40  $\mu\text{m}$  and are recommended by the manufacturer for use in the shrink control of polyester compounds.

## RESULTS

### Effects of Filler on the Rheological Behavior

Figure 2 gives plots of viscosity ( $\eta$ ) vs. shear stress ( $\tau_w$ ) for unsaturated polyester resin containing  $\text{CaCO}_3$  (Camel-Wite) particles, with and without surface treatment with the silane coupling agent A174. It is seen that, over the range of  $\tau_w$  investigated, the resin containing *untreated*  $\text{CaCO}_3$  particles is virtually Newtonian in behavior. However, the resin containing *treated*  $\text{CaCO}_3$  particles has viscosities higher than those of the resin containing *untreated*  $\text{CaCO}_3$  particles at low  $\tau_w$ , and lower viscosities at high  $\tau_w$ . In other words, the resin containing *treated*  $\text{CaCO}_3$  particles show shear-thinning behavior as  $\tau_w$  is increased. We speculate that, during the surface treatment, the particular coupling agent used might have formed agglomerates of  $\text{CaCO}_3$  particles, which then gave rise to higher viscosities at low shearing forces compared to the *untreated* system. However, as shearing forces were increased, the agglomerates of the surface-treated  $\text{CaCO}_3$  particles began to break down, yielding viscosities lower than that of the untreated system.

Figure 3 gives plots of  $\eta$  vs.  $\tau_w$  for untreated  $\text{CaCO}_3$  systems containing two

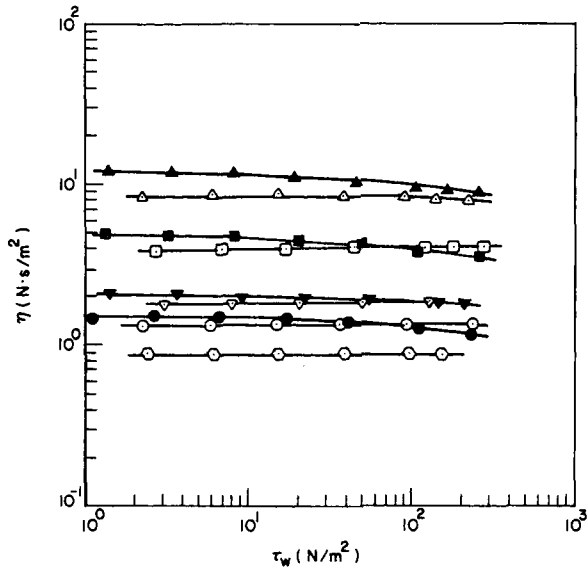


Fig. 2. Viscosity vs. shear stress for Ashland Chemical polyester resin with  $\text{CaCO}_3$  (Camel-Wite) particles (wt %): ( $\circ$ ) pure resin; ( $\bullet, \ominus$ ) 15; ( $\blacktriangledown, \nabla$ ) 25; ( $\blacksquare, \square$ ) 40; ( $\blacktriangle, \triangle$ ) 50. Open symbols denote untreated  $\text{CaCO}_3$  and closed symbols denote treated  $\text{CaCO}_3$ . ( $T = 30^\circ\text{C}$ .)

different  $\text{CaCO}_3$  particle sizes. It is seen that the system containing the small particle size material (Camel-Wite) gives rise to viscosities higher than those of the system containing the large particle size material (Camel-Fil). This behavior is expected because the smaller particles have more surface area available to interact with the resin than the same weight of larger particles. Similar observations have been reported in the literature dealing with highly filled molten thermoplastics.<sup>9,10</sup>

Figure 4 gives plots of  $\eta$  vs.  $\tau_w$  for unsaturated polyester resin containing clay particles, with and without surface treatment with the silane coupling agent A174.

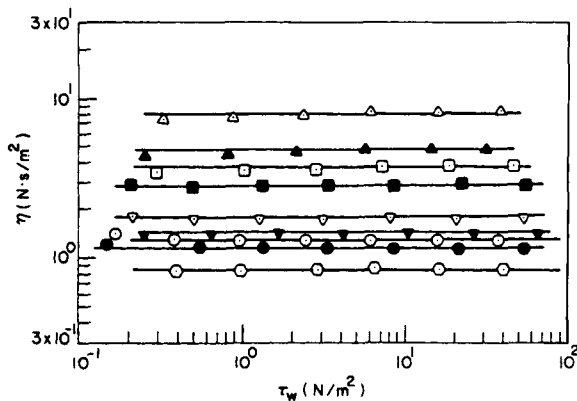


Fig. 3. Viscosity vs. shear stress for Ashland Chemical polyester resin with untreated  $\text{CaCO}_3$  particles (wt %): ( $\circ$ ) pure resin; ( $\bullet, \ominus$ ) 15; ( $\blacktriangledown, \nabla$ ) 25; ( $\blacksquare, \square$ ) 40; ( $\blacktriangle, \triangle$ ) 50. Open symbols denote Camel-Wite ( $d = 3.0 \mu\text{m}$ ) and closed symbols denote Camel-Fil ( $d = 6.5 \mu\text{m}$ ). ( $T = 30^\circ\text{C}$ .)

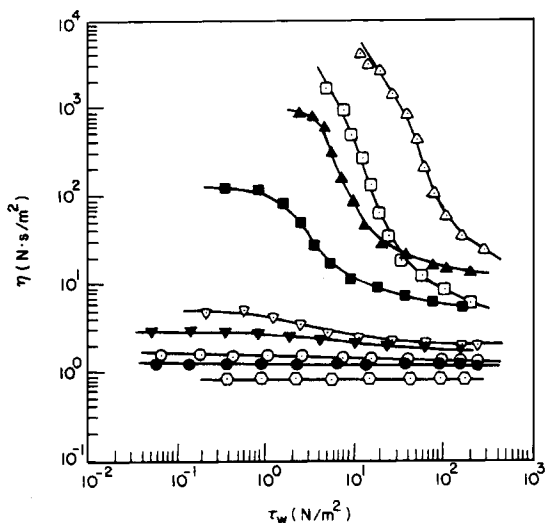


Fig. 4. Viscosity vs. shear stress for Ashland Chemical polyester resin with clay particles (wt %): ( $\odot$ ) pure resin; ( $\bullet, \circ$ ) 15; ( $\blacktriangledown, \triangledown$ ) 25; ( $\blacksquare, \square$ ) 40; ( $\blacktriangle, \triangle$ ) 45. Open symbols denote *untreated* clay and closed symbols denote *treated* clay. ( $T = 30^\circ\text{C}$ .)

Two observations are worth noting here: (1) The untreated system is more viscous than the treated system. Also, at low values of  $\tau_w$ , the highly concentrated *untreated* system exhibits yield behavior, whereas the *treated* system never exhibits yield behavior. (2) As the filler loading increases, both treated and untreated systems show strong shear-thinning behavior, but the shear-thinning behavior of the treated system begins to level off as the shear stress increases beyond a critical value. It is therefore concluded that the shear-thinning behavior observed is attributable to a "crowding" effect.<sup>9</sup> It is also

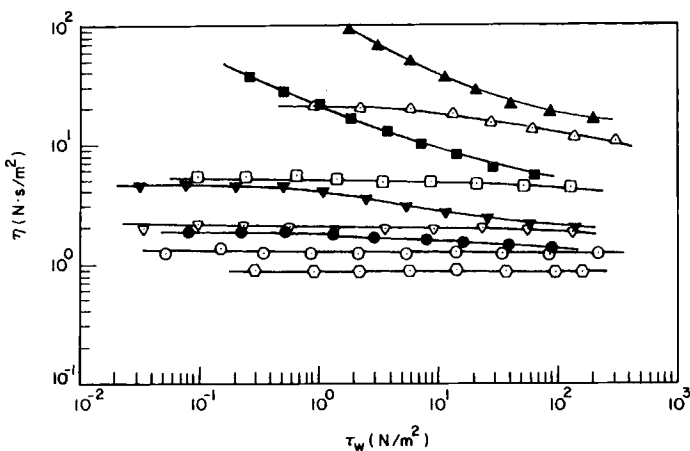


Fig. 5. Viscosity vs. shear stress for Ashland Chemical polyester resin with milled glass fibers (wt %): ( $\odot$ ) pure resin; ( $\bullet, \circ$ ) 15; ( $\blacktriangledown, \triangledown$ ) 25; ( $\blacksquare, \square$ ) 40; ( $\blacktriangle, \triangle$ ) 50. Open symbols denote *untreated* milled glass fibers and closed symbols denote *treated* milled glass fibers. ( $T = 30^\circ\text{C}$ .)

clear that the use of the coupling agent A174 helped reduce the viscosity of the clay-filled resin.

Figure 5 gives plots of  $\eta$  vs.  $\tau_w$  for unsaturated polyester resin containing milled glass fibers, with and without surface treatment with the silane coupling agent A174. It is seen that the untreated system gives rise to virtually Newtonian behavior, whereas at low values of  $\tau_w$  the treated system exhibits the shear-thinning behavior that is attributable to the "crowding" effect. Note that the treated system has higher viscosities than the untreated system, over the entire range of  $\tau_w$  investigated. We have observed, from an independent experiment, that milled glass fibers stick together when treated with the coupling agent A174, and this might have been the reason why the treated system had viscosities higher than the untreated system.

### Effects of Low-Profile Additive on the Rheological Behavior

Figure 6 gives plots of  $\eta$  vs.  $\tau_w$  for mixtures of unsaturated polyester resin and polyvinylacetate (PVAc) low-profile additive, and Figure 7 the same for mixtures of unsaturated polyester resin and polymethylmethacrylate (PMMA) low-profile additive. It is seen that the resin/PVAc mixture exhibits Newtonian behavior in all compositions tested, whereas some compositions of the resin/PMMA mixture exhibit shear-thinning behavior. In order to facilitate our discussion, we have prepared plots of bulk viscosity vs. concentration of low-profile additive, as given in Figures 8 and 9. The viscosity of the resin/PVAc mixture increases monotonically with the concentration of PVAc, whereas the viscosity of the resin/PMMA mixtures goes through a minimum and, also, a maximum as the concentration of PMMA increases. The viscosity behavior of resin/PMMA mixtures observed in Figure 9 very much resembles the one observed in emulsions of two immiscible liquids.<sup>9,11</sup> Indeed, we have observed that mixtures of unsaturated polyester resin and PMMA solution form two heterogeneous phases,

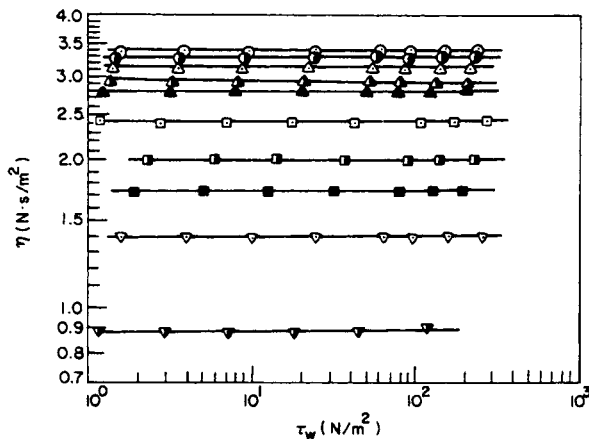


Fig. 6. Viscosity vs. shear stress for mixtures of Ashland Chemical polyester resin and various amounts of low-profile additive PVAc (wt %): ( $\nabla$ ) 0.0 (pure resin); ( $\nabla$ ) 10; ( $\blacksquare$ ) 20; ( $\square$ ) 30; ( $\square$ ) 40; ( $\blacktriangle$ ) 50; ( $\blacktriangle$ ) 60; ( $\blacktriangle$ ) 70; ( $\bullet$ ) 90; ( $\circ$ ) 100 (pure low-profile additive). ( $T = 30^\circ\text{C}$ .)

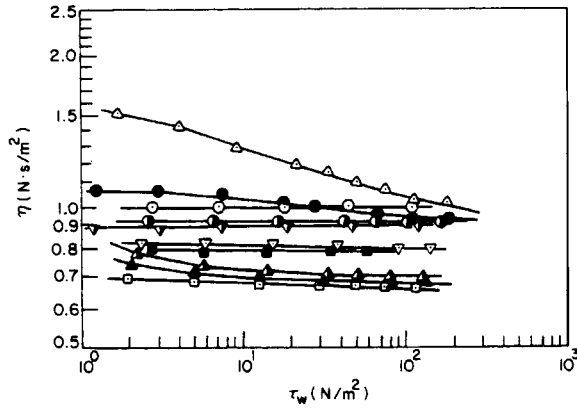


Fig. 7. Viscosity vs. shear stress for mixtures of Ashland Chemical polyester resin and various amounts of low-profile additive PMMA (wt %): ( $\nabla$ ) 0.0 (pure resin); ( $\nabla$ ) 10; ( $\blacksquare$ ) 20; ( $\square$ ) 40; ( $\blacktriangle$ ) 50; ( $\triangle$ ) 60; ( $\Delta$ ) 70; ( $\bullet$ ) 80; ( $\odot$ ) 90; ( $\circ$ ) 100 (pure low-profile additive). ( $T = 30^\circ\text{C}$ .)

giving rise to turbidity, whereas mixtures of unsaturated polyester resin and PVAc solution form optically homogeneous solutions.

Figure 10 gives plots of the first normal stress difference ( $\tau_{11} - \tau_{22}$ ) vs. shear rate ( $\dot{\gamma}$ ) for mixtures of unsaturated polyester resin and PVAc low-profile additive, and Figure 11 the same for mixtures of unsaturated polyester resin and PMMA low-profile additive. It is seen in Figure 10 that, when a viscoelastic PVAc solution is added to a Newtonian polyester resin, the value of  $\tau_{11} - \tau_{22}$  of the mixture increases regularly with the amount of PVAc solution added. In view of the fact that polyester resin and PVAc low-profile additive form homo-

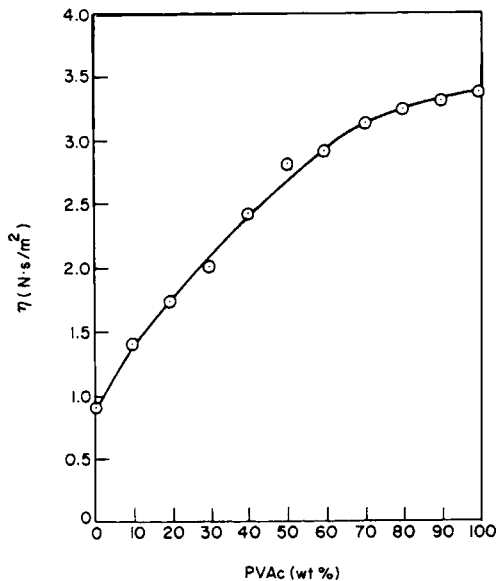


Fig. 8. Viscosity vs. concentration of PVAc in mixtures of Ashland Chemical polyester resin and low-profile additive PVAc ( $T = 30^\circ\text{C}$ ).



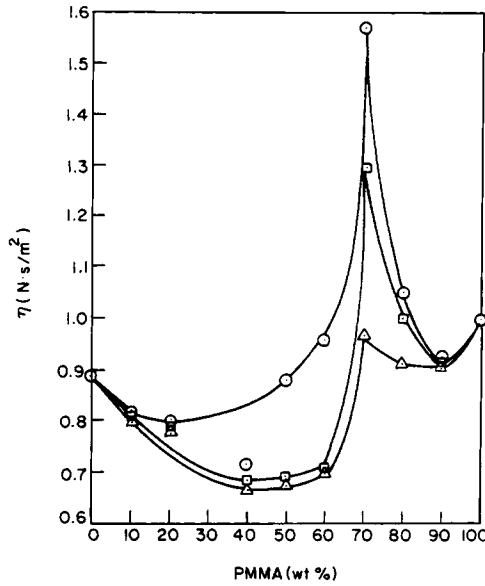


Fig. 9. Viscosity vs. concentration of PMMA in mixtures of Ashland Chemical polyester resin and low-profile additive PMMA ( $T = 30^{\circ}\text{C}$ ), at various shear stresses ( $\text{N}/\text{m}^2$ ): ( $\circ$ ) 1.0; ( $\square$ ) 10; ( $\Delta$ ) 200.

geneous solutions, as discussed above in conjunction with their viscous behavior (see Fig. 8), the observed normal stress behavior of the mixtures is not surprising, if not expected. On the other hand, as may be seen in Figure 11, when a viscoelastic PMMA solution is added to a Newtonian polyester resin, the values of

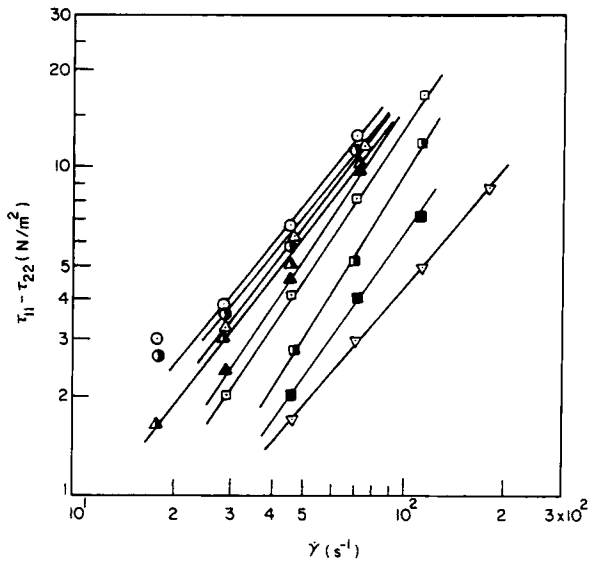


Fig. 10. Normal stress difference vs. shear rate for mixtures of Ashland Chemical polyester resin and various amounts of low-profile additive PVAc ( $30^{\circ}\text{C}$ ). Symbols are the same as in Figure 6.

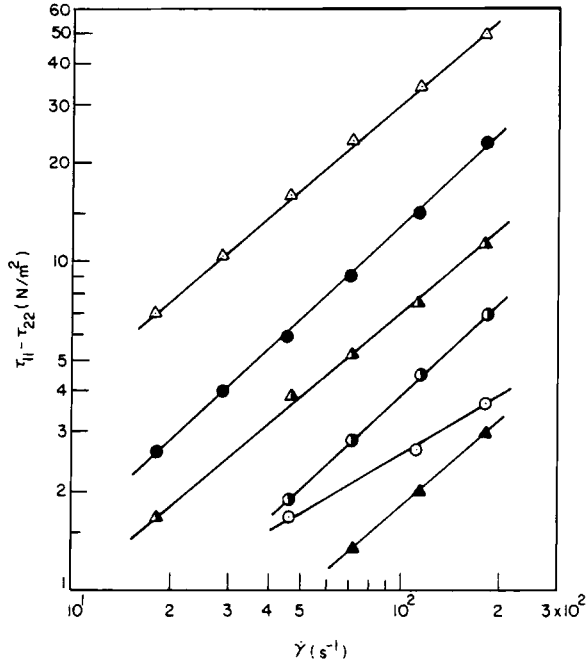


Fig. 11. Normal stress difference vs. shear rate for mixtures of Ashland Chemical polyester resin and various amounts of low-profile additive PMMA (30°C). Symbols are the same as in Figure 7.

$\tau_{11} - \tau_{22}$  of some of the mixtures are much greater than that of the PMMA solution itself, which is quite unexpected, considering the behavior of the resin/PVAc system. However, the plots given in Figures 10 and 11 do not show how

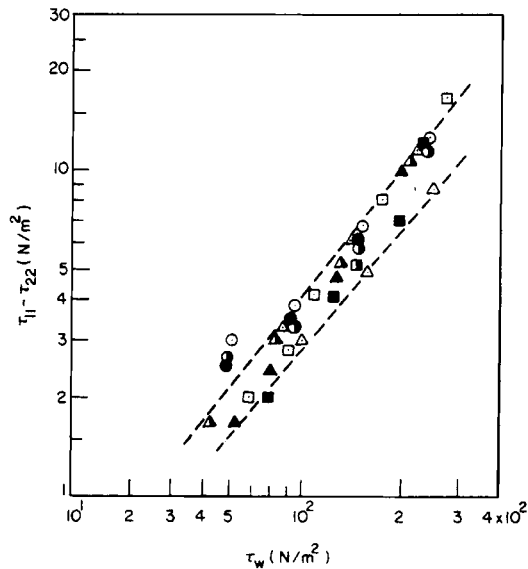


Fig. 12. Normal stress difference vs. shear stress for mixtures of Ashland Chemical polyester resin and various amounts of low-profile additive PVAc (30°C). Symbols are the same as in Figure 6.

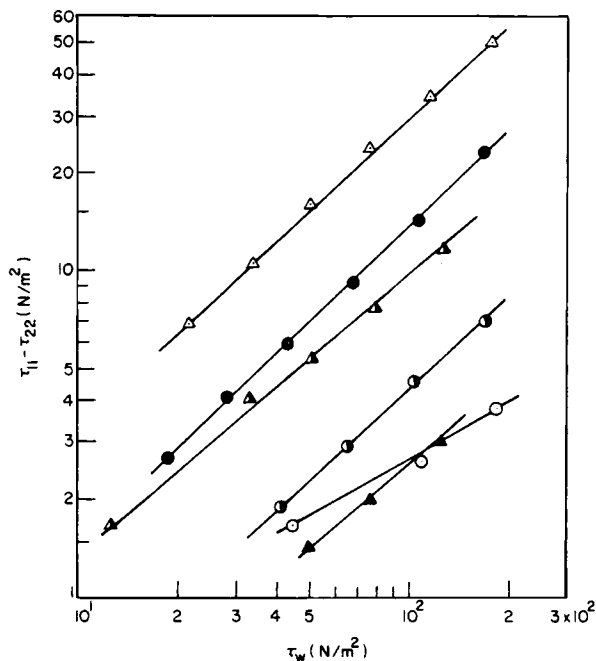


Fig. 13. Normal stress difference vs. shear stress for mixtures of Ashland Chemical polyester resin and various amounts of low-profile additive PMMA (30°C). Symbols are the same as in Figure 7.

significant are the normal stress effects of mixtures of polyester resin and low-profile additive. What is meaningful is to determine the ratio of normal stress difference to shear stress, in order to judge whether or not the normal stress effects experimentally observed are significant.

Figure 12 gives plots of  $\tau_{11} - \tau_{22}$  vs.  $\tau_w$  for the resin/PVAc mixtures, and Figure 13 for the resin/PMMA mixtures. It is seen in Figure 12 that there is no clear trend in the trend of  $\tau_{11} - \tau_{22}$  with the composition of the mixture. Also, the magnitude of  $\tau_{11} - \tau_{22}$  is 3–5% of the magnitude of  $\tau_w$ , quite independent of composition over the entire range of  $\tau_w$  investigated. It can therefore be concluded that, to all intents and purposes, normal stress effects in the polyester resin/PVAc system are negligible. On the other hand, for the polyester resin/PMMA system, as may be seen in Figure 13, the magnitude of  $\tau_{11} - \tau_{22}$  varies from 3% to 30% of the magnitude of  $\tau_w$ , clearly dependent upon the composition of the mixture. In order to facilitate our discussion, crossplots of Figure 13 (i.e., plots of  $\tau_{11} - \tau_{22}$  vs. composition of the resin/PMMA mixture) are displayed in Figure 14. It is seen that  $\tau_{11} - \tau_{22}$  goes through a maximum, as is often observed in mixtures of two immiscible liquids.<sup>9,11</sup> In other words, in the resin/PMMA system, mixtures of certain compositions give rise to noticeable normal stress effects. We have already mentioned that mixtures of the resin/PMMA system form two phases.

Figure 15 gives plots of  $\eta$  vs.  $\tau_w$  for mixtures of unsaturated polyester resin and high-density polyethylene (HDPE) powders, SDP-860. In view of the fact that HDPE powders cannot be dissolved in polyester resin, the mixtures may be considered as concentrated suspensions. The behavior that may be observed

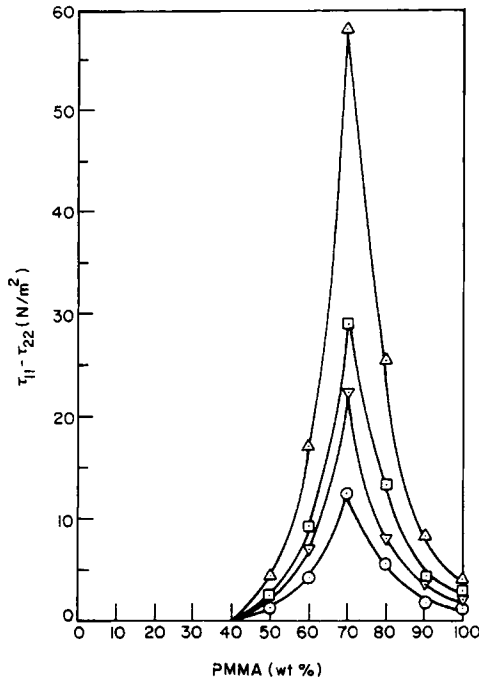


Fig. 14. Normal stress difference vs. concentration of PMMA in mixtures of Ashland Chemical polyester resin and various amounts of low-profile additive PMMA (30°C), at various shear stresses ( $\text{N}/\text{m}^2$ ): ( $\circ$ ) 40; ( $\nabla$ ) 70; ( $\square$ ) 100; ( $\Delta$ ) 200.

in Figure 15 is typical of concentrated suspension (see, for instance, Fig. 4), namely, at low shear stresses yield behavior is observed, and shear-thinning behavior occurs due to the breakdown of "crowding."

Figure 16 gives plots of  $\tau_{11} - \tau_{22}$  versus  $\tau_w$  for resin/SDP-860 suspensions.

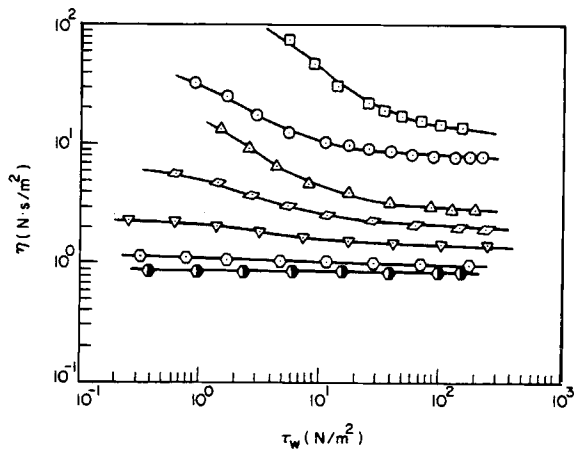


Fig. 15. Viscosity vs. shear stress for mixture of Ashland Chemical polyester resin and low-profile additive polyethylene SDP-860 powders (wt %): ( $\bullet$ ) 0.0 (pure resin); ( $\diamond$ ) 5; ( $\nabla$ ) 10; ( $\triangle$ ) 15; ( $\Delta$ ) 20; ( $\circ$ ) 25; ( $\square$ ) 30. ( $T = 30^\circ\text{C}.$ )

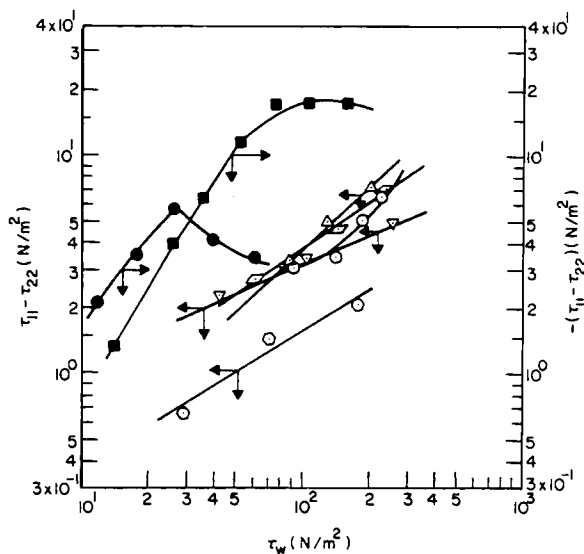


Fig. 16. Normal stress difference vs. shear stress for mixture of Ashland Chemical polyester resin and low-profile additive polyethylene powders (wt %): ( $\circ$ ) 5; ( $\nabla$ ) 10; ( $\diamond$ ) 15; ( $\Delta$ ) 20; ( $\bullet$ ,  $\odot$ ) 25; ( $\blacksquare$ ) 30. Open symbols denote *positive* values of  $\tau_{11} - \tau_{22}$ , and closed symbols denote *negative* values of  $\tau_{11} - \tau_{22}$ . ( $T = 30^\circ\text{C}$ .)

Note that while the polyester resin itself is a Newtonian liquid, suspensions containing the irregularly shaped HDPE powders exhibit normal stress effects. It is seen in Figure 16 that the suspensions containing up to 20 wt % SDP-860 show *positive* values of  $\tau_{11} - \tau_{22}$  and that those containing 25 wt % and above show *negative* values of  $\tau_{11} - \tau_{22}$ . In view of the fact that the same rheometer was employed throughout the entire study reported here, dealing with other types of suspension as well as emulsions, and that the magnitude of  $\tau_{11} - \tau_{22}$  obtained with the resin/HDPE suspensions is about the same as that obtained with mixtures of two liquids (compare Fig. 16 with Fig. 13), we do believe that the *negative* values of  $\tau_{11} - \tau_{22}$  observed with some suspensions are real, not an artifact. A detailed discussion of the *negative* values of  $\tau_{11} - \tau_{22}$  given by the polyester resin/HDPE system is presented elsewhere.<sup>12</sup>

### Effects of the Combined Addition of Filler and Low-Profile Additive on the Rheological Behavior

Having investigated the effects of filler and low-profile additive, separately, on the rheological behavior of unsaturated resin, we then proceeded to investigate the effects of the two ingredients, when added together. Although we could conceive of many different combinations of filler and low-profile additive, because of the exploratory nature of this research and the limited time available, we selected a relatively small number of different combinations on the basis of our previous experience.

Figures 17–19 show the effects of the combined addition of  $\text{CaCO}_3$  and PMMA solution on the rheological behavior of unsaturated polyester resin. Note in these

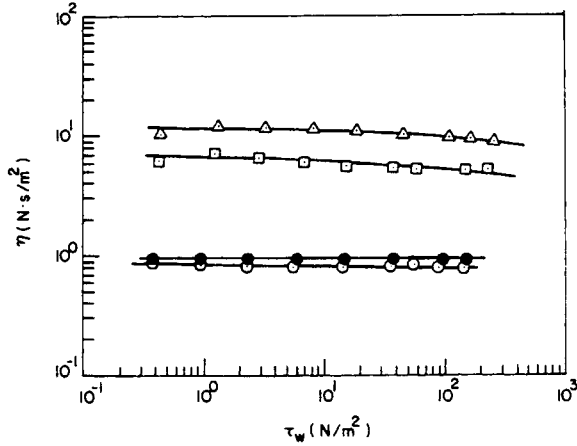


Fig. 17. Viscosity vs. shear stress for Ashland Chemical polyester resin ( $T = 30^{\circ}\text{C}$ ) with various additives: (●) pure resin; (○) 20 wt % low-profile additive (PMMA); (Δ) 50 wt % filler ( $\text{CaCO}_3$ ); (◻) 20 wt % PMMA and 50 wt %  $\text{CaCO}_3$ .

figures that the amount of  $\text{CaCO}_3$  is fixed at 50 wt % and only the amount of PMMA solution is varied. In order to facilitate our discussion, we have also shown in these figures the viscosity variations when  $\text{CaCO}_3$  alone and PMMA solution alone was added to the polyester resin.

Figure 17 shows that when 20 wt % PMMA solution was added to the suspension, the net effect was to reduce its viscosity by about 35%. Note that an addition of 20 wt % PMMA solution alone reduced the viscosity of the polyester resin by about 10%.

Figure 18 shows that when 40 wt % PMMA solution was added to the suspension, the net effect was more complicated. Shear-thinning behavior was observed, and no viscosity reduction was obtained at low shear stresses. How-

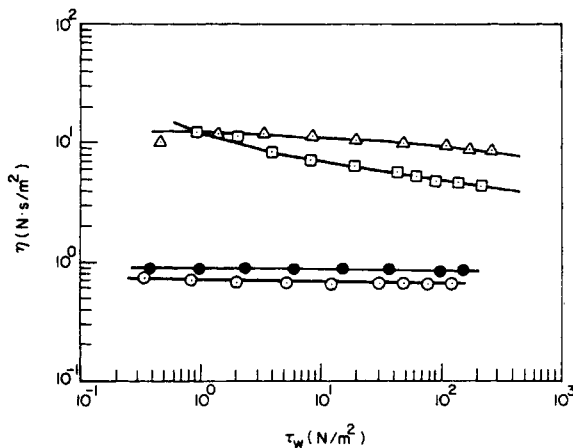


Fig. 18. Viscosity vs. shear stress for Ashland Chemical polyester resin ( $T = 30^{\circ}\text{C}$ ) with various additives: (●) pure resin; (○) 40 wt % low-profile additive (PMMA); (Δ) 50 wt % filler ( $\text{CaCO}_3$ ); (◻) 40 wt % PMMA and 50 wt %  $\text{CaCO}_3$ .

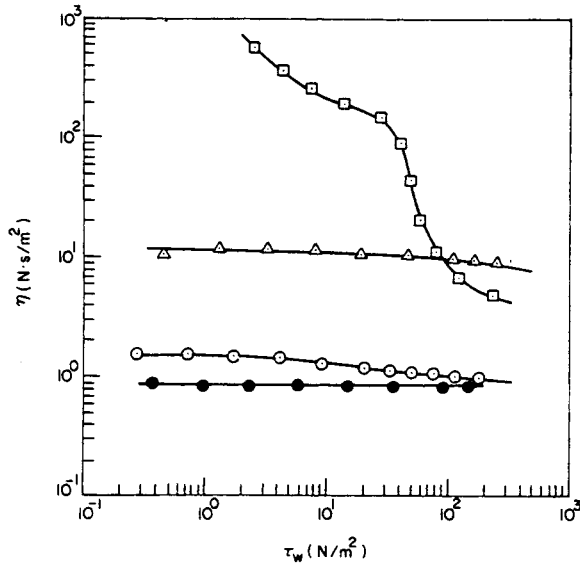


Fig. 19. Viscosity vs. shear stress for Ashland Chemical polyester resin ( $T = 30^\circ\text{C}$ ) with various additives: (●) pure resin; (○) 70 wt % low-profile additive (PMMA); (△) 50 wt % filler ( $\text{CaCO}_3$ ); (□) 70 wt % PMMA and 50 wt %  $\text{CaCO}_3$ .

ever, as shear stress was increased, the viscosity of the suspension was reduced by about 45%. Note that an addition of 40 wt % PMMA solution alone reduced the viscosity of the polyester resin by about 20%.

Figure 19 shows the viscosities of the suspension when 70 wt % PMMA solution

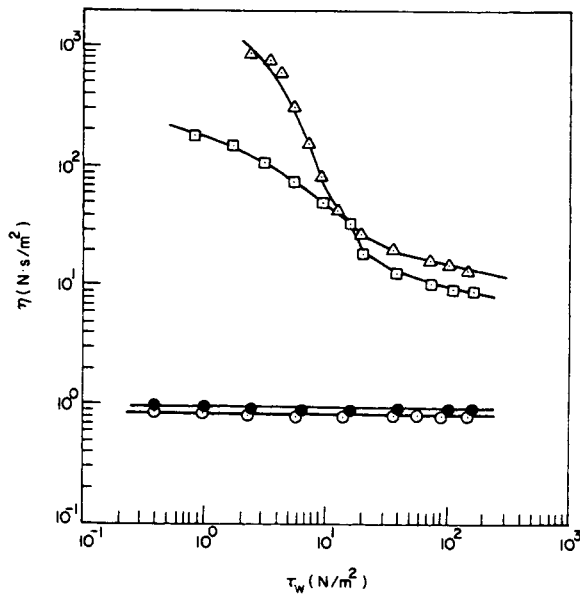


Fig. 20. Viscosity vs. shear stress for Ashland Chemical polyester resin ( $T = 30^\circ\text{C}$ ) with various additives: (●) pure resin; (○) 20 wt % low-profile additive (PMMA); (△) 45 wt % filler (clay); (□) 20 wt % PMMA and 45 wt % clay.

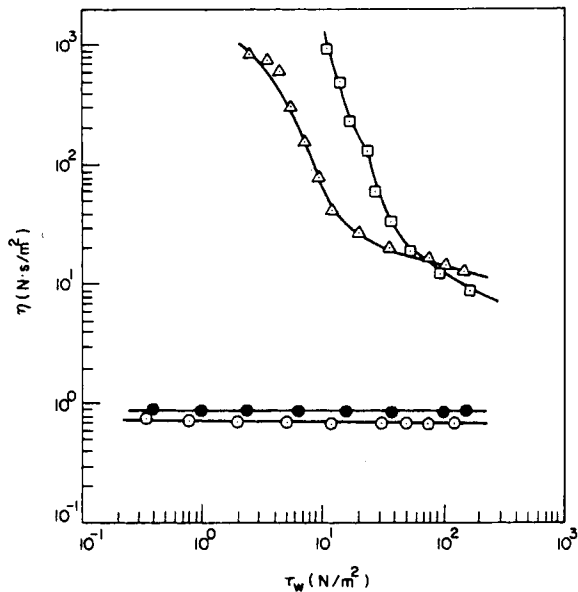


Fig. 21. Viscosity vs. shear stress for Asland Chemical polyester resin ( $T = 30^{\circ}\text{C}$ ) with various additives: (●) pure resin; (○) 40 wt % low-profile additive (PMMA); (Δ) 45 wt % filler (clay); (□) 40 wt % PMMA and 45 wt % clay.

was added. Note that an addition of 70 wt % PMMA solution alone increased the viscosity of the polyester resin by about 80% at low shear stress ( $10\text{ N/m}^2$ ) and by about 8% at high shear stress ( $200\text{ N/m}^2$ ) (see Fig. 9). However, when the same amount of this low-profile additive was added to the suspension containing 50 wt %  $\text{CaCO}_3$ , the mixture formed three phases, i.e., two immiscible liquids and solid particles. The mixture was very viscous at low shear stresses, but, as shear stress was increased, the viscosity initially decreased slowly and then, at a critical value of shear stress, very rapidly. In other words, a critical value of shear stress appears to exist at which a change in structure may occur under a shearing motion. Considering the seemingly very complex nature of the three-phase system, the very unusual shape of viscosity curve shown in Figure 19 does not surprise us. At this juncture, we speculate that, at low shear stresses, some of the  $\text{CaCO}_3$  particles might have been encapsulated inside the droplets of PMMA solution and strong interactions (or interference) might have existed between the domains of the PMMA solution droplets and the  $\text{CaCO}_3$  particles. The rapidly decreasing viscosity at and above a critical value of shear stress, shown in Figure 19, may be attributable to the breakdown of "crowding" between the PMMA solution droplets and the  $\text{CaCO}_3$  particles.

Figures 20–22 show the effects of the combined addition of clay and PMMA solution on the rheological behavior of unsaturated polyester resin. Note in these figures that the amount of clay added is constant at 45 wt % and only the amount of PMMA solution is varied. In order to facilitate our discussion, we have also shown in these figures the viscosity variations when clay alone, and PMMA solution alone, was added to the polyester resin.

It should be remembered that concentrated suspensions containing clay particles behave quite differently from those containing  $\text{CaCO}_3$  particles (com-



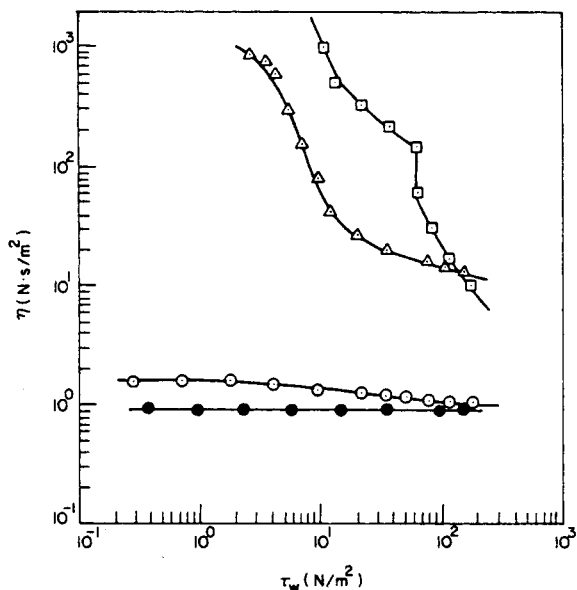


Fig. 22. Viscosity vs. shear stress for Ashland Chemical polyester resin ( $T = 30^{\circ}\text{C}$ ) with various additives: (●) pure resin; (○) 70 wt % low-profile additive (PMMA); (Δ) 45 wt % filler (clay); (◻) 70 wt % PMMA and 45 wt % filler (clay);

pare Fig. 2 with Fig. 4). It is seen in Figures 20–22 that an addition of PMMA solution to the suspensions of clay particles has little effect, in general, on the shear-dependent behavior of the viscosities of the suspensions.

More specifically, Figure 20 shows that the addition of 20 wt % PMMA solution decreased the viscosity of the suspension, in a manner very similar to the  $\text{CaCO}_3$  case (see Fig. 17). When greater amounts (40 wt % and 70 wt %) of PMMA solution were added, as may be seen in Figures 21 and 22, the viscosities of the suspensions were increased considerably at low shear stresses, but, as shear stress was increased, they decreased rapidly, eventually giving rise to values lower than the viscosities of the suspensions. It is of interest to note in Figures 21 and 22 that the shape of the  $\eta$  vs.  $\tau_w$  curves for the resin/clay/PMMA system very much resembles the one for the resin/ $\text{CaCO}_3$ /PMMA system containing 70 wt % PMMA solution (see Fig. 19).

## DISCUSSION

### Rheological Behavior of Concentrated Suspensions

The rheological behavior of concentrated suspensions has long been studied by many investigators, as summarized in a recent monograph by Han.<sup>9</sup> As a whole, the rheological behavior of concentrated suspensions presented above is very similar to that reported in the literature.<sup>9</sup> However, the present report on the effects of surface treatment of particulates on the viscosities of concentrated suspensions is rather new. We have observed different effects on the rheological properties of concentrated suspensions of the surface treatment of particulate fillers with a coupling agent. Depending on the type of particulate,

the viscosities of suspensions may be increased or decreased by such treatment. Earlier, Han and co-workers<sup>13,14</sup> reported the effects of coupling agents on the rheological behavior of highly filled molten thermoplastic resins.

The role of coupling agents in suspension rheology may be understood better only when one has information on the details of the interface or interactions, if any, between the coupling agent and particulates, and between the coupling agent and matrix resin. From the point of view of the processing of reinforced polyester composites, a better understanding of the role of coupling agents in controlling the curing process is of practical importance. Having investigated the effects of coupling agents on the rheology of unsaturated polyester resin without cure, we plan, in the near future, to conduct curing experiments with unsaturated polyester resin, in the presence of coupling agents and various types of particulates as filler.

The reason why we have used shear stress  $\tau_w$ , instead of shear rate, in presenting the viscosity data in Figures 2-5 is worth mentioning. In dealing with the flow of two-phase systems consisting of liquid and solid phases, the shear rate (i.e., velocity gradient) across the shearing plane may *not* be continuous at the interface between the phases, but shear stress may be. Therefore, the shear stress is more appropriate than the shear rate in presenting the rheological data of two- or multiphase systems.<sup>9,10</sup> Indeed, White and co-workers<sup>15,16</sup> and Han and co-workers<sup>14</sup> have correlated the rheological properties of highly filled molten polymers, using shear stress.

### Rheological Behavior of Concentrated Emulsions

The rheological behavior of concentrated emulsions has also been discussed in the literature, as summarized in a recent monograph by Han.<sup>9</sup> As a matter of fact, the rheological behavior of concentrated emulsions is far more complex than that of concentrated suspensions, because, in shearing flow, the discrete phase (i.e., droplets) in an emulsion may undergo deformation, whereas the discrete phase (i.e., solid particles) in a suspension does not deform. The deformability of the droplets in an emulsion makes an analysis of experimental data quite difficult, in general.

As demonstrated with the polyester resin/PVAc system, when mixtures of two liquids give homogeneous solutions, they do not show any anomalous rheological behavior (see Figs. 6 and 8). However, as in the polyester resin/PMMA system, when mixtures of two liquids form two phases (i.e., an emulsion), they often exhibit very complex rheological behavior (see Figs. 7 and 9). The complexity depends on the state of dispersion of the discrete phase, as demonstrated in a paper by Han and King.<sup>11</sup> The same degree of complexity of rheological behavior has also been observed with two-phase molten polymers.<sup>9,10,17-20</sup> Therefore, analysis of the rheological behavior of two-phase liquid systems is not feasible without information on the state of dispersion, such as the size and shape of the droplets. It should be pointed out that, in a given emulsion system, the state of dispersion depends on the type of flow field, the intensity of flow, and also the composition.<sup>9</sup>

In correlating the *bulk* (or *effective*) rheological properties of concentrated emulsions, the use of shear stress is more appropriate than the use of shear rate, because the shear rate (i.e., velocity gradient) at the interface may *not* be con-

tinuous, whereas shear stress may be. This is precisely the reason why we presented our data using shear stress (see Figs. 7 and 13).

### Rheological Behavior of Three-Phase Mixtures

As may be seen in Table I, a typical polyester molding compound consists of resin, filler, low-profile additive, viscosity thickener, glass fiber, curing agent, and other ingredients (e.g., pigments, mold release agent). One can easily imagine how complex the state of dispersion must be. As a way of understanding the *bulk* rheological behavior of polyester molding compounds, we have tried increasing the number of ingredients in a stepwise fashion. Thus, as a first step, we added two ingredients, filler and low-profile additive, to a polyester resin. The particular low-profile additive used, PMMA solution, being immiscible with the resin, we ended up with three-phase mixtures, i.e., liquid-liquid-solid, which then gave rise to very complex rheological behavior (see Figs. 18-22).

When two different discrete phases, in our case deformable droplets and solid particles, are present in a suspending medium, the interactions between the discrete phases seem to be an important factor, controlling the observed *bulk* rheological behavior. The state of dispersion of the individual phases depends on the mixing conditions, the composition of ingredients, the rheological properties of the individual phases (namely, the droplet phase and the suspending medium), the particle size and shape of the solid particles, and the intensity of the flow field to which the mixture is subjected.

The purpose of the present paper, the first of the series, is to show the degree of complexity in the rheological behavior of mixtures of polyester resin, filler, and low-profile additive. In future publications, we shall discuss, in greater detail, the effects of the chemistry of the resins, the particle size and shape of the fillers, and the chemistry of the low-profile additives on the *bulk* rheological behavior of polyester premix molding compounds.

### References

1. J. G. Mohr, S. S. Oleesky, G. D. Shook, and L. S. Meyer, *SPI Handbook of Technology and Engineering of Reinforced Plastics/Composites*, 2nd ed., Van Nostrand Reinhold, New York, 1973.
2. G. Lubin, Ed., *Handbook of Fiberglass and Advanced Plastics Composites*, Van Nostrand Reinhold, New York, 1969.
3. H. J. Boyd, the 31st Annual Technical Conference of SPI, Reinforced Plastics/Composites Institute, Section 2-C, 1976.
4. F. M. Wright, the 27th Annual Technical Conference of SPI, Reinforced Plastics/Composites Institute, Section 12-A, 1972.
5. F. B. Alvey, *J. Polym. Sci., A-1*, **9**, 2233 (1971).
6. R. Burns, K. S. Gandhi, A. G. Hankin, and B. M. Lynsky, *Plastics Polym.*, **43**, 228 (1975).
7. K. E. Atkins, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, Vol. 2, Chap. 23.
8. A. L. Copley and R. G. King, *Biorheol.*, **12**, 5 (1975).
9. C. D. Han, *Multiphase Flow in Polymer Processing*, Academic, New York, 1981, Chap. 3.
10. C. D. Han, *Rheology in Polymer Processing*, Academic, New York, 1976, Chap. 7.
11. C. D. Han and R. G. King, *J. Rheol.*, **24**, 213 (1980).
12. K. W. Lem and C. D. Han, presented at the 53rd Annual Meeting of the Society of Rheology, Louisville, Kentucky, October 1981.
13. C. D. Han, C. Sandford, and H. J. Yoo, *Polym. Eng. Sci.*, **18**, 849 (1978).

14. C. D. Han, T. Van den Weghe, P. Shete, and J. R. Haw, *Polym. Eng. Sci.*, **21**, 196 (1981).
15. H. Tanaka and J. L. White, *Polym. Eng. Sci.*, **20**, 949 (1980).
16. L. Czarnecki and J. L. White, *J. Appl. Polym. Sci.*, **25**, 1217 (1980).
17. C. D. Han and T. C. Yu, *Polym. Eng. Sci.*, **12**, 81 (1972).
18. C. D. Han and Y. W. Kim, *Trans. Soc. Rheol.*, **19**, 245 (1975).
19. C. D. Han, Y. W. Kim, and S. J. Chen, *J. Appl. Polym. Sci.*, **19**, 2831 (1975).
20. Y. W. Kim and C. D. Han, *J. Appl. Polym. Sci.*, **20**, 2905 (1976).

Received August 17, 1982

Accepted September 24, 1982