

Rheology of Unsaturated Polyester Resins. II. Thickening Behavior of Unsaturated Polyester and Vinyl Ester Resins

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Synopsis

The rheological properties of mixtures of unsaturated polyester resin and viscosity thickener were determined as thickening progressed. Two commercially available resins were used: (1) general purpose unsaturated polyester resin (Ashland Chemical, Aropol 7030), and (2) vinyl ester resin (Dow Chemical, XD-7608.05). As thickening agent, a magnesium oxide (MgO) paste dispersed in styrene monomer was used. No fillers, pigments, or other additives were used. During thickening, the following measurements were also made: (1) acid number by titration and (2) molecular weights by gel permeation chromatography (GPC). For the Ashland Chemical polyester resin, it was found that, over a period of 300 h, the titration method indicated that the number-average molecular weight (\bar{M}_n) increased by a factor of 2 and the weight-average molecular weight (\bar{M}_w) increased by a factor of 3. The GPC measurements, however, showed that \bar{M}_n increased very little whereas \bar{M}_w increased by a factor of about 2. Over the same period, the viscosity of the Ashland Chemical polyester resin increased from 0.9 N·s/m² (9 P) to 10⁴ N·s/m² (10⁵ P), and the viscosity of the Dow Chemical vinyl ester resin increased from 0.7 N·s/m² (7 P) to 2 × 10³ N·s/m² (2 × 10⁴ P). Such a large increase in viscosity cannot be explained by the existing molecular theory, in view of the fact that the molecular weights increased relatively little. We speculate that the exceedingly large increase in viscosity during thickening is attributable primarily to ionic associations between the carboxylic anions and the magnesium ions, rather than to the formation of chain branching suggested in the literature. It was found further that mixtures of polyester resins and viscosity thickener exhibit normal stress effects, increasing with thickening time and following the behavior of a second-order fluid when the first normal stress difference was plotted against shear rate. Interestingly enough, however, plots of first normal stress difference vs. shear stress yield a correlation which becomes independent of thickening time. An explanation is offered to the correlation obtained.

INTRODUCTION

In order to make fiber-reinforced polyester molding compounds (i.e., BMC, SMC, TMC) suitable for various matched molding operations, the viscosity of the materials is deliberately increased up to about 10⁶ P. It has been suggested in the literature¹ that the thickening is a result of chain extension brought about by the condensation reaction between the Group IIA metal oxides and the carboxylic acid groups present in the unsaturated polyester resins. Among Group IIA metal oxides and/or hydroxides used as thickeners, magnesium oxide is a popular choice because of its high reactivity and the low concentration required for thickening.

The viscosity of polyester molding compounds is determined by the level of chemical thickener in the mixture and the time/temperature history of the compound, and it will influence the molding characteristics. The higher the viscosity at the molding temperature, the more processing tonnage required. At

some point, complete fillout of the mold may become a problem, and rejects will result. On the other hand, too low a viscosity can cause the resin to flow ahead of the glass fibers and result in resin-rich areas with low mechanical properties.

Despite its technological importance, relatively little has been reported on the time-dependent rheological behavior of unsaturated polyester resins during thickening. The studies reported by Alvey,² Burns et al.,¹ and Walton³ were concerned only with the viscosity, but not with the elastic properties of the molding compounds during thickening. It is generally accepted that elastic properties are equally as important as viscous properties, in polymer fabrication processes.

We therefore very recently investigated both the viscous and elastic properties of unsaturated polyester resins, mixed with a viscosity thickener (magnesium oxide), using a cone-and-plate rheometer. Measurements were made over time, during thickening. In this paper we shall present the highlights of our findings.

EXPERIMENTAL

Two sets of experiments were performed: (a) the determination of the physical properties of the raw materials and (b) the thickening behavior of the unsaturated polyester resins. In our study, two resins were used: (1) general purpose unsaturated polyester resin (Ashland Chemicals, Aropol 7030) and (2) vinyl ester resin (Dow Chemical, XD-7608.05). There is a subtle difference between the molecular structures of the prepolymers used in the two resins, and it would be expected to have a profound effect on the rheological properties of the molding compounds during thickening or cure. As illustrated in Table I, the prepolymer in the general purpose unsaturated polyester resin contains structopendent-reactive groups for crosslinking and structoterminal-reactive groups for thickening, whereas the prepolymer in the vinyl ester resin contains structopendent-reactive groups for thickening and structoterminal-reactive groups for crosslinking.⁴

As viscosity thickener, a magnesium oxide (MgO) paste dispersed in styrene monomer, as supplied by U.S.S. Chemicals (Mod "Me"), was used. We have independently determined the amount of styrene monomer in the resins supplied to us and the amount of MgO in the viscosity thickener. Table II gives a summary of the physical properties of the materials used.

In studying the thickening behavior, we added 1 mol MgO to each mole of prepolymer. Both the resin and the viscosity thickener were weighed accurately in a disposable metal container, and the solution was mixed thoroughly at room temperature (22°C) with a double axial-flow impeller. The mixture was then transferred into a 500-mL wide-neck Wheaton glass jar, equipped with a glass stopper sealed with silicone grease to prevent the evaporation of styrene monomer. The sealed bottles were placed in an oven, maintained at 30°C ± 0.5°C, for the entire period of thickening which lasted about 3 weeks.

During thickening, we conducted the following measurements: (1) the determination of acid number by titration; (2) the determination of molecular weights by gel permeation chromatography (GPC); (3) the determination of viscoelastic properties, using a cone-and-plate rheometer.

TABLE I
Speculative Prepolymer and Thickened Polymer Structure

Resin	Speculative prepolymer structure	Speculative structure thickened with MgO
Unsaturated polyester resin	$\text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}(\text{C}=\text{C})-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ <p style="text-align: center;">$n = 3-6$</p> <p>Structoterminal group for thickening</p> <p>Structoterminal group for crosslinking</p>	$\text{Mg}^{++} \text{O}^{\ominus}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}(\text{C}=\text{C})-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^{\ominus} \text{Mg}^{++} \text{O}^{\ominus}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}(\text{C}=\text{C})-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^{\ominus} \text{Mg}^{++}$ <p style="text-align: center;">$n = 3-6$</p>
Vinyl ester resin	$\text{C}=\text{C}-\text{C}(\text{C}=\text{C})-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ <p>Structoterminal group for thickening</p> <p>Structoterminal group for crosslinking</p>	$\text{Mg}^{++} \text{O}^{\ominus}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}(\text{C}=\text{C})-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^{\ominus} \text{Mg}^{++}$ <p style="text-align: center;">$n = 3-6$</p>

TABLE II
 Physical Properties of the Materials Used

Material	Manufacturer	Item	Specifications	
			Supplied by the manufacturer	Determined in our laboratory
Conventional unsaturated polyester resin	Ashland Chemical (Aropol 7030)	Styrene (wt %)	37-39	36.3
		Acid number (solids)	26-30	39.3
Vinyl ester resin	Dow Chemical (XD-7608.05)	Styrene (wt %)	33-34	35.9
		Acid number (solids)	—	58.0
Viscosity thickener	USS Chemical (Mod "Me")	MgO (wt %)	33-35	34.8

The method used for determining the acid number by titration was essentially the same as that described by Sorenson and Campbell.⁵ A sample was first withdrawn from the sealed bottle into a small glass test tube. Approximately, 1.0 g of the sample was weighed to the nearest milligram into a 125-mL Erlenmeyer flask. Several drops of 0.5 wt % phenolphthalein solution were added to a solvent mixture, consisting of toluene, isopropyl alcohol, and *N,N*-dimethyl formamide (DMF). The color of the mixture was brought to just about pink (i.e., a phenolphthalein end point, $\text{pH} \cong 9.0$) and 1 or 2 drops of 0.5N KOH. 30 mL of the solvent mixture was used to dissolve the resin sample and the light pink color disappeared as soon as the solvent came into contact with the resin. After the resin was dissolved, the mixture was titrated with 0.5N standard methanolic potassium hydroxide solution (0.497-0.503N, Fisher Scientific SO-P-222) to the pink phenolphthalein end point. Two runs were made for each sample, and the average value was taken as the final result. The acid number was calculated directly from the amount of titer.

For rheological measurements, two Weissenberg rheogoniometers were used, a Model R17, for the initial stage of thickening during which viscosities were still low (say, below 10^3 P), and a Model R16 when viscosities rose above that level. In this way, during the course of thickening we did not have to change the torsion bar in the cone-and-plate rheometer. Special features of the Model R17 were described in our earlier paper, Part I of this series.⁶

RESULTS

Acid Number and Molecular Parameters Determination during Thickening

Figure 1 gives plots of acid number versus thickening time for the Ashland polyester resin, and Figure 2 the same for the Dow vinyl ester resin. In our study, the acid number was determined by the following expression:

$$\text{acid number} = (28.05)(\text{mL of } 0.5\text{N KOH})/\text{g resin (solids)} \quad (1)$$

By assuming that each molecule contains two carboxylic acid groups and very few hydroxyl groups, one can calculate the number-average molecular weight \bar{M}_n of the resin during thickening, using the following expression:

$$\bar{M}_n = 1.12 \times 10^5 / \text{acid number} \quad (2)$$

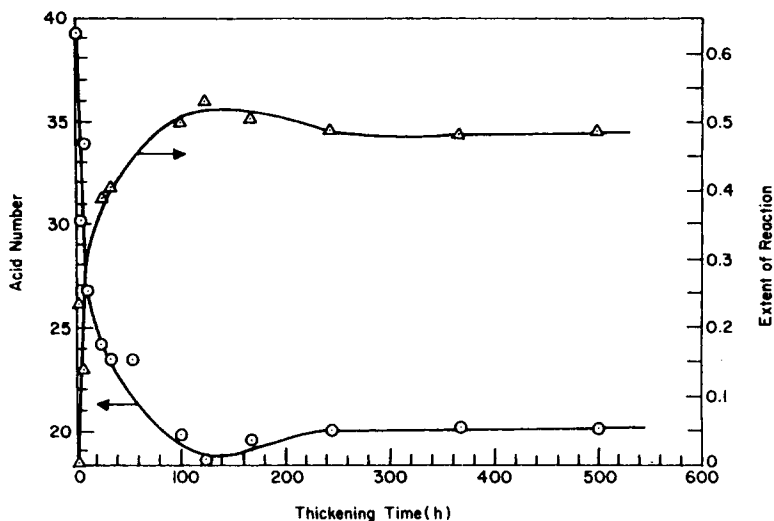


Fig. 1. Acid number (○) and extent of reaction (Δ) vs. thickening time for the Ashland Chemical polyester resin.

in which the acid number is defined by eq. (1). We have checked the accuracy of eq. (2) by titrating 0.0764 g succinic acid ($M_w = 118.09$) with 2.38 mL of 0.5N KOH. The experimentally determined \bar{M}_n by titration, with the aid of eqs. (1) and (2), is 128, whereas the true value of M_w of succinic acid is 118. Therefore, the error of the titration method is about 8.5%.

Figure 3 gives plots of \bar{M}_n versus thickening time for the Ashland polyester resin, and Figure 4 the same for the Dow vinyl ester resin.

According to Burns et al.,¹ the following relationships may be used to determine the molecular parameters for the stoichiometric amounts of reactants (i.e., 1 mol MgO for each mole of prepolymer):

$$\bar{M}_n/M_0 = 1/(1 - P) \quad (3)$$

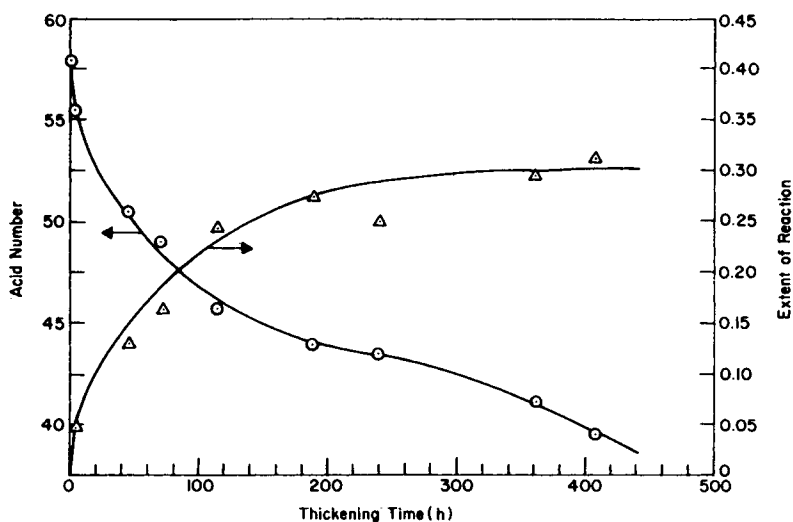


Fig. 2. Acid number (○) and extent of reaction (Δ) vs. thickening time for the Dow Chemical vinyl ester resin.

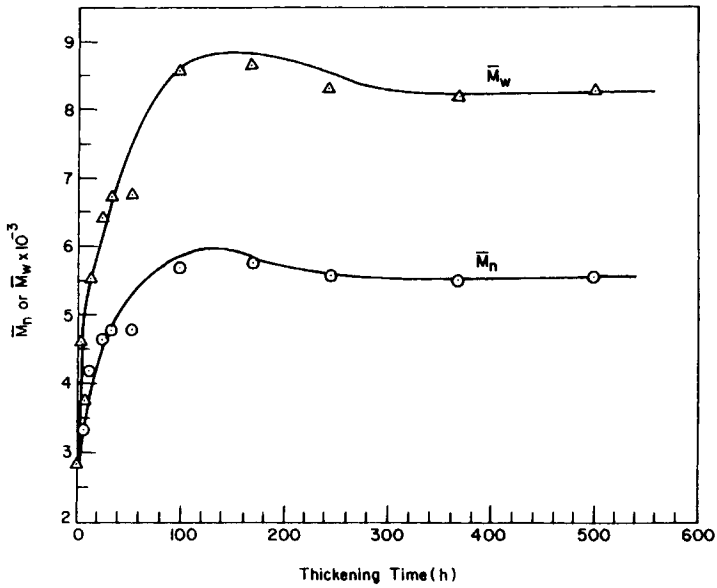


Fig. 3. Number-average (⊙) and weight-average (Δ) molecular weights vs. thickening time for the Ashland Chemical polyester resin.

$$\bar{M}_w/M_0 = (1 + P)/(1 - P) \quad (4)$$

in which P is the extent of reaction, \bar{M}_w is the weight-average molecular weight, and M_0 is the molecular weight of the prepolymer before thickening begins. Equation (3) permits us to determine the extent of reaction P ,

$$P = 1 - (M_0/\bar{M}_n) \quad (5)$$

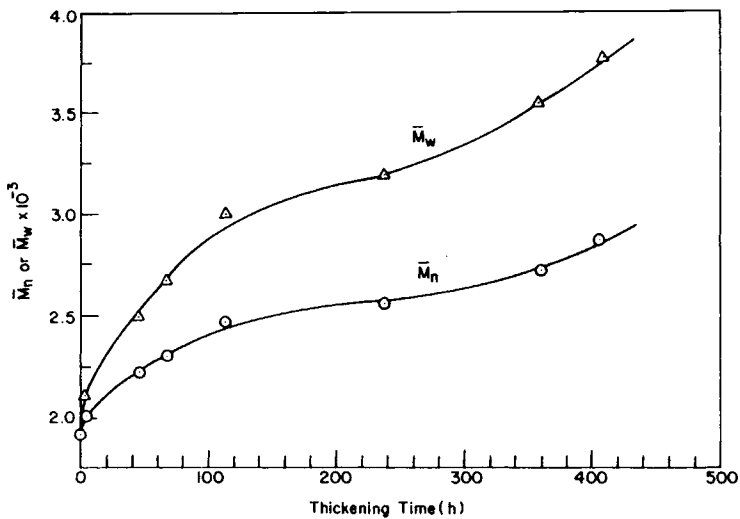


Fig. 4. Number-average (⊙) and weight-average (Δ) molecular weights vs. thickening time for the Dow Chemical vinyl ester resin.

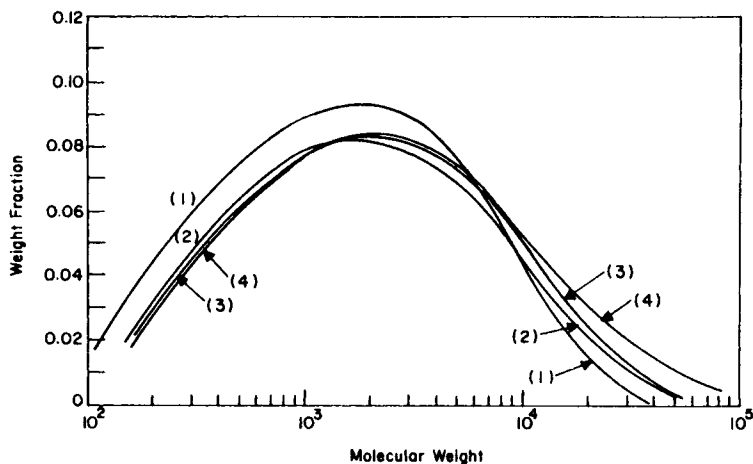


Fig. 5. Molecular weight distribution curves determined by GPC of the Ashland Chemical resin during the thickening period: (1) before thickening began; (2) 20 h after thickening began; (3) 200 h after thickening began; (4) 480 h after thickening began.

and the substitution of eq. (3) into eq. (4) gives

$$\bar{M}_w = (1 + P)\bar{M}_n \quad (6)$$

The extent of reaction P determined from the titration method during thickening, with the aid of eq. (5), is given in Figures 1 and 2. The weight-average molecular weight \bar{M}_w during thickening, calculated with the aid of eq. (6), is given in Figures 3 and 4. Figure 3 shows that, over the entire thickening period (ca. 20 days), \bar{M}_n for the Ashland polyester resin increased from 2,850 to 5,580, and \bar{M}_w increased from 2,850 to 8,310. Figure 4 shows that \bar{M}_n for the Dow vinyl ester resin is increased from 1,920 to 2,860, and \bar{M}_w increased from 1,920 to 3,790.

Figure 5 gives molecular weight distribution (MWD) curves and Table III gives the molecular weights of the Ashland polyester resin as determined by using a GPC. It is seen in Table III that, over the entire thickening period, \bar{M}_n increased from 2,073 to 2,578, and \bar{M}_w increased from 4,997 to 8,122. The GPC method thus indicates that only a relatively small change in molecular weight of the resin occurs during thickening. It is seen in Figure 5 that, as thickening progresses, the MWD curves are shifted toward the right, indicating that larger molecules are formed.

TABLE III
Summary of the Molecular Weight Measurements of the Ashland Polyester Resin by GPC

Period of thickening (h)	\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_w/\bar{M}_n
0	2,073	4,997	10,113	2.39
20	2,187	6,655	16,679	3.04
200	2,568	7,245	17,114	2.82
480	2,578	8,122	24,267	3.27

Rheological Behavior during Thickening

Figure 6 gives plots of viscosity η vs. shear rate $\dot{\gamma}$ at various periods during thickening for Ashland polyester resin, and Figure 7 the same for the Dow vinyl ester resin. It is seen that the mixture of unsaturated polyester and thickening agent initially follows Newtonian behavior and then begins to exhibit shear-thinning behavior as the viscosity increases beyond 100 N·s/m² (1,000 P). It is of great interest to note that, at about 70 h after thickening began, the viscosity of the solution was of the same order of magnitude as that often observed in the processing of many thermoplastic molten polymers.

Figure 8 describes the increase in zero-shear viscosity η_0 of the Ashland Chemical unsaturated polyester resin and Dow Chemical vinyl ester resin as the thickening progressed. It is seen that the Dow vinyl ester resin reached an equilibrium of viscosity much sooner than the Ashland unsaturated polyester resin did and that, in both resins, the viscosity tended to go through a maximum as the thickening progressed. Note that the viscosities of the control samples (i.e., without a thickening agent) remained constant over the period of 500 h.

Figure 9 gives plots of first normal stress difference $\tau_{11}-\tau_{22}$ vs. shear rate $\dot{\gamma}$ at various periods during thickening for the Ashland polyester resin, and Figure 10 the same for the Dow vinyl ester resin. At about 40 h after thickening began, the solution started to exhibit normal stresses. It is of great interest to note in Figures 9 and 10 that the solution followed second-order fluid behavior very

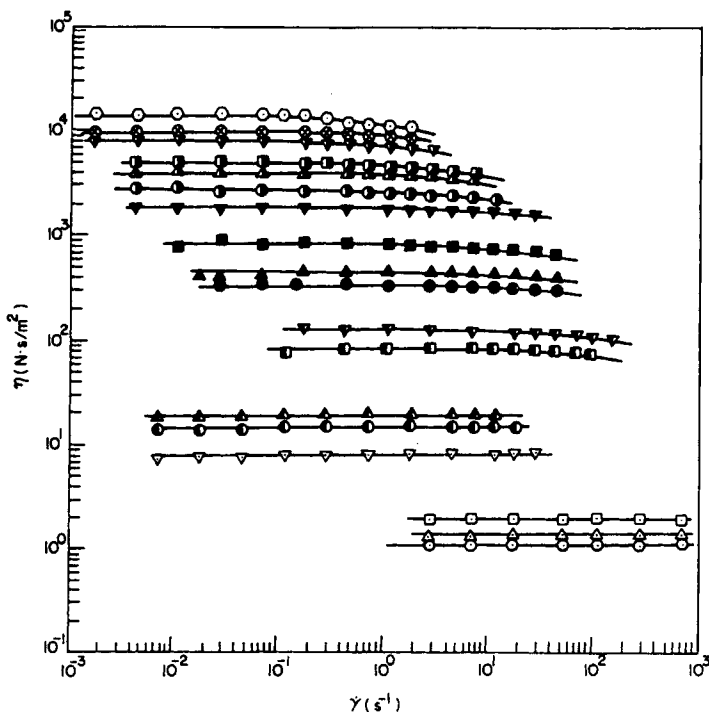


Fig. 6. Viscosity vs. shear rate for the Ashland polyester resin at various periods after thickening began (h): (○) 1.3; (△) 5.3; (◻) 11.1; (▽) 25.9; (●) 31.4; (▲) 34.6; (◼) 38.8; (▼) 55.3; (●) 73.1; (▲) 82.5; (■) 103; (▼) 124.3; (●) 151.5; (▲) 198.7; (◻) 272.7; (▽) 338.1; (○) 436.1; (⊗) 509.1.

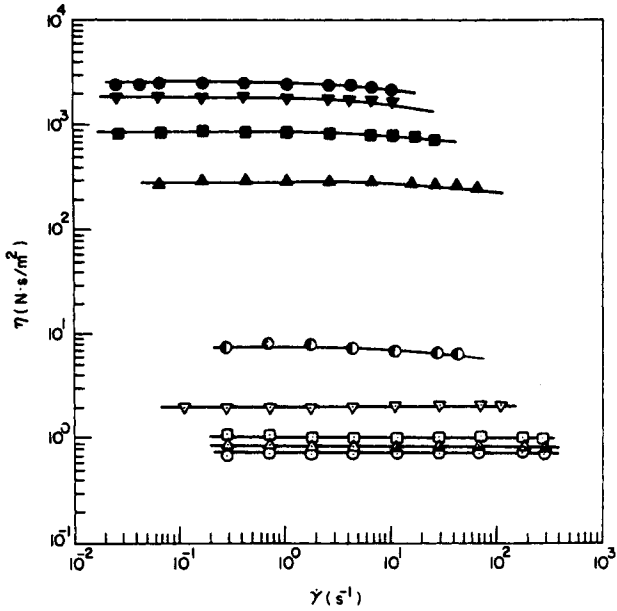


Fig. 7. Viscosity vs. shear rate for the Dow vinyl ester resin at various periods after thickening began (h): (○) 0.8; (▲) 2.6; (□) 6.6; (▽) 20.7; (●) 29.4; (▲) 49.5; (■) 70.6; (▼) 119.7; (●) 142.0.

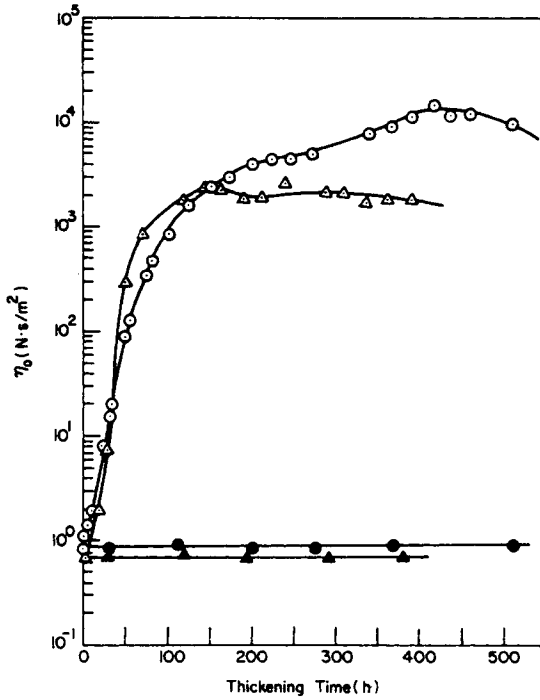


Fig. 8. Zero-shear viscosity vs. thickening time for (a) Ashland Chemical unsaturated polyester resin (○, ●) and (b) Dow Chemical vinyl ester resin (Δ, ▲). Closed symbols represent control samples.

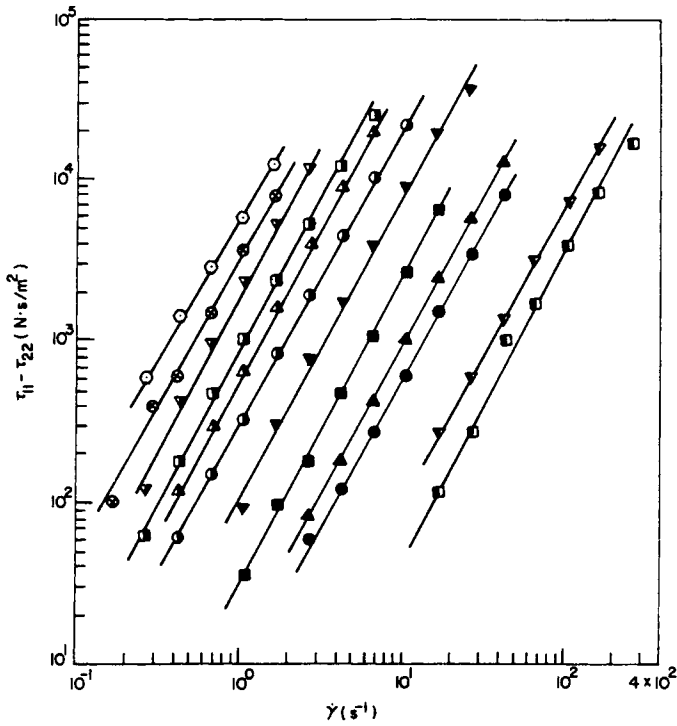


Fig. 9. First normal stress difference vs. shear rate for the Ashland polyester resin at various periods after thickening began. Symbols are the same as in Figure 6.

closely, over the entire period of thickening. Since the solution became more viscous as the thickening progressed, the maximum level of shear rate that permitted us to run the rheometer was decreased.

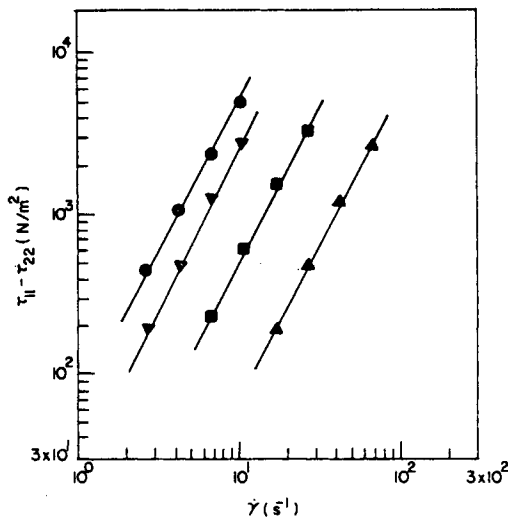


Fig. 10. First normal stress difference vs. shear rate for the Dow vinyl ester resin at various periods after thickening began. Symbols are the same as in Figure 7.

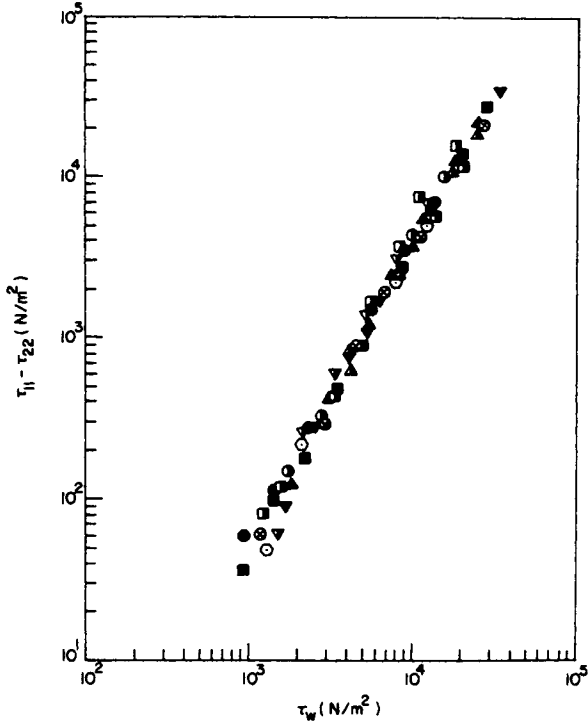


Fig. 11. First normal stress difference vs. shear stress for the Ashland polyester resin at various periods after thickening began. Symbols are the same as in Figure 6.

Figure 11 gives plots of $\tau_{11}-\tau_{22}$ vs. shear stress τ_w for the Ashland unsaturated polyester resin during thickening, and Figure 12 the same for the Dow vinyl ester resin. It is seen in Figures 11 and 12 that the plots show a correlation which is independent of the duration of thickening (i.e., the level of thickening). A close examination of the figures reveals that the thickened Ashland polyester resin

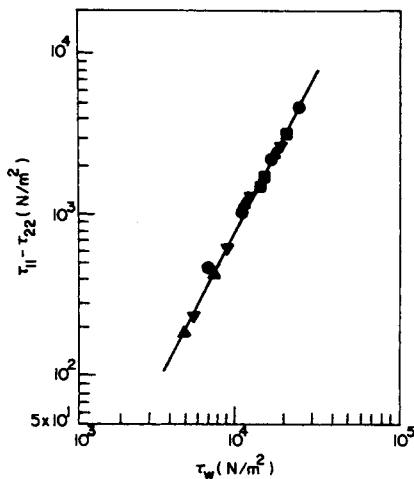


Fig. 12. First normal stress difference vs. shear stress for the Dow vinyl ester resin at various periods after thickening began. Symbols are the same as in Figure 7.

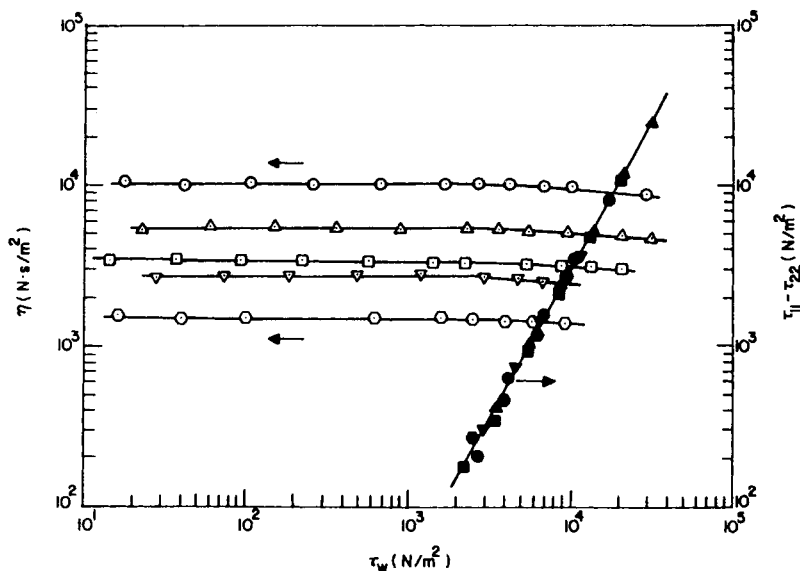


Fig. 13. Viscosity and first normal stress difference vs. shear stress for the thickened Ashland polyester resin at various temperatures ($^{\circ}\text{C}$): (\circ , \bullet) 30; (Δ , \blacktriangle) 35; (\square , \blacksquare) 40; (∇ , \blacktriangledown) 45; (\circ , \bullet) 50.

exhibits larger normal stress effects than the thickened Dow vinyl ester resin. This discernible difference, which corresponds to a difference in the three-dimensional network structure consisting of ionic aggregates, arises primarily from the difference in the molecular structure of the prepolymers used (see Table I), mentioned previously.

Figure 13 gives plots of viscosity η and first normal stress difference $\tau_{11}-\tau_{22}$

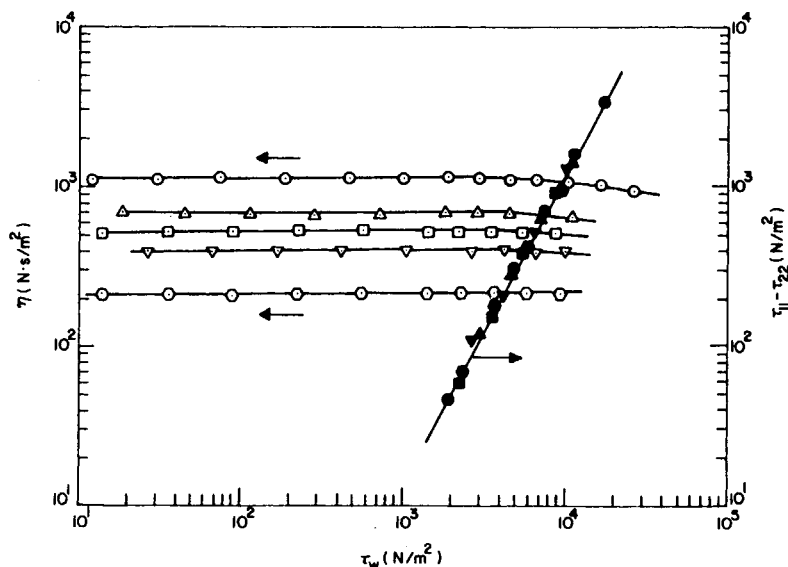


Fig. 14. Viscosity and first normal stress difference vs. shear stress for the thickened Dow vinyl ester resin at various temperatures ($^{\circ}\text{C}$). Symbols are the same as in Figure 13.

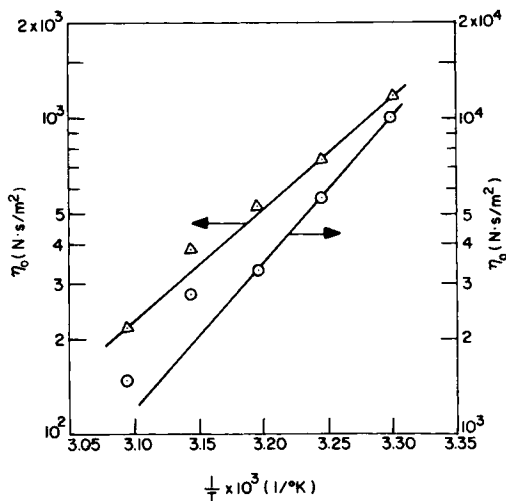


Fig. 15. Zero-shear viscosity vs. reciprocal of temperature for the thickened samples: (○) Ashland polyester resin; (△) Dow vinyl ester resin.

vs. shear stress τ_w at various temperatures for the Ashland polyester resin, and Figure 14 for the Dow vinyl ester resin. The materials used in Figures 13 and 14 are the ones already thickened (i.e., about 2 weeks after the thickening experiment began). It is seen that as the temperature is increased, the viscosity is decreased; however, plots of $\tau_{11} - \tau_{22}$ vs. τ_w show a correlation which is independent of temperature. Earlier, Han and co-workers⁷⁻¹¹ and White and co-workers^{12,13} reported similar results when plotting $\tau_{11} - \tau_{22}$ against τ_w for thermoplastic molten polymers.

Figure 15 gives plots of zero-shear viscosity vs. the reciprocal of temperature for both the Ashland polyester and Dow vinyl ester resins. Applying the Arrhenius relationship, $\eta_0(T) = k \exp(E/RT)$, we have determined the activation energy of viscous flow as follows: (a) for the Ashland polyester resin, $E = 21.54$ kcal/g-mol; (b) for the Dow vinyl ester resin, $E = 17.4$ kcal/g-mol.

DISCUSSION

Thickening Mechanism

In the past, the thickening reaction has been discussed by several investigators.^{1-3,14-17} Two different theories have been proposed: (1) one postulating a two-stage reaction^{2,14,15} and (2) another postulating the formation of chain extension and chain entanglement.^{1,17} In the two-stage reaction theory, it is postulated that, first, a higher molecular weight salt is formed by the reaction between magnesium oxide and carboxylic acid groups on a polyester chain, and then a complex is formed between the salt and carboxyl groups of the ester linkages. The formation of a metal complex (Mg in this case) during the thickening reaction may occur at the reactive sites on the carbon atoms adjacent to the carboxyl groups. In this theory, the second stage of reaction is considered to be responsible for a large increase in viscosity (i.e., thickening behavior).

In the chain extension/chain entanglement theory, it is postulated that the dicarboxylic acid groups on a polyester chain react with magnesium oxide (MgO), yielding very high molecular weight species (via condensation polymerization) and thus giving rise to a large increase in viscosity. Burns et al.¹ reported that a small proportion (0.5–1%) of the polyester resin employed contained high-molecular-weight species, with weights in the range 10^5 – 10^6 , as determined by GPC, and then postulated that this high-molecular-weight material in the system might have been primarily responsible for the viscosity thickening observed. In explaining the very large observed increase in viscosity, Burns et al.¹ invoked the zero-shear viscosity (η_0)-molecular-weight (M_w) relationship represented by $\eta_0 = K(M_w)^n$, where n was found to lie somewhere between 3 and 4. On the basis of this observation, they speculated further that the large increase in viscosity may arise from chain entanglement in polyester resin.

Using oscillatory shearing flow measurement, Gruskiewicz and Collister¹⁷ interpreted the thickening behavior of an unsaturated polyester with magnesium oxide in terms of molecular viscoelasticity theories. They concluded that the formation of a high-molecular-weight fraction (i.e., the presence of a high-molecular-weight tail in the MWD curve) during the thickening reaction may be primarily responsible for the large increase in viscosity observed and that the Burns theory of chain extension/chain entanglement is consistent with molecular viscoelasticity theories.

In our study, however, we have *not* observed the presence of a high-molecular-weight tail in the MWD curves, as may be seen in Figure 5. As the thickening progresses, the MWD curves move toward the high-molecular-weight side. However, as may be seen in Table III, the observed increase in the molecular weights \bar{M}_n and \bar{M}_w cannot possibly explain the exceedingly large increase in viscosity, as given in Figures 6–8. In other words, we observe that the power-law index n in the viscosity-molecular weight relationship, $\eta_0 = K(M_w)^n$, is about 6.5, which is much too large to be attributable to the formation of chain entanglement at a critical molecular weight that is commonly observed with polymer melts.

It should be remembered that the measurements of molecular weights by GPC used a polar solvent (DMF) to dissolve the already thickened samples. We speculate that the use of DMF might have dramatically reduced, if not destroyed completely, any ionic associations between the magnesium cations and the carboxylic anions in the mixtures of unsaturated polyester resin and MgO paste.

It is worth pointing out that the addition of an appropriate polar solvent to metal carboxylate and metal sulfonate ionomers dramatically reduce the degree of ionic association and hence the solution viscosities.¹⁸ In other words, the viscosities measured during the course of thickening are the responses of the state (i.e., ionic association) of the mixtures of unsaturated polyester resin and MgO paste, not the responses of the dissolved resin. Therefore, we are of the opinion that there is little relationship between the bulk viscosities of unsaturated polyester resin/MgO paste mixtures and the molecular weights of the dissolved resin, as determined both by GPC and by titration.

In their study of the rheological behavior of sulfonate and carboxylate ionomers, Lundberg and Makowski¹⁸ reported that, at a comparable level of functionality, the melt viscosity of sodium sulfonate ionomers was higher by a factor of 1000 than that of sodium carboxylate ionomers. They attributed this dif-

ference to a stronger ionic association for the sodium sulfonate ionomers compared with the carboxylates over the range of functionalities studied. They noted further that the backbone molecular weight changes, as determined by GPC, in sodium sulfonate ionomer during the sulfonation of polystyrene, were negligible.

In other words, during the course of a thickening reaction, magnesium ions in mixtures of unsaturated polyester resin and MgO paste are not *permanently* associated with any particular carboxylic acid groups. In view of the fact that there are at least two carboxyl groups along each polymer molecule, a three-dimensional network structure consisting of ionic aggregates may be formed. The size of ionic aggregates is expected to increase as thickening progresses. When subjected to shearing deformation, the three-dimensional network structure may give rise to large values of viscosity. The fact that polar solvents (e.g., DMF) nullified the thickening effect supports the view that thickening behavior is attributable to physical (temporary) association, *not* chemical (permanent) reaction. In this sense, our study tends to support the thickening mechanism of a two-stage reaction due to Szmercsanyi.^{14,15}

Rheological Behavior

Earlier investigators^{1,2} have employed a Brookfield viscometer, which is *not* capable of determining the normal stress effects of test fluids. However, the use of the cone-and-plate type of rheometer employed in our study generates information on both the viscosity and the normal stress effects of test fluids. As shown in Figures 6, 7, 9, and 10, mixtures of unsaturated polyester resin (or vinyl ester resin) and MgO paste very closely follow the behavior of second-order fluids, over the range of shear rates investigated. This observation is of practical importance to modeling the flow problems involved with processing such mixtures (e.g., SMC, BMC). To the best of our knowledge, rheological information of the significance reported in this paper, in Figures 6, 7, 9, and 10, has never been published elsewhere.

Of particular interest are the plots of $\tau_{11}-\tau_{22}$ vs. τ_w given in Figures 11 and 12, in that the duration of thickening does not affect the correlation obtained. Considering the fact that thickening progresses with time, one would not expect to obtain such a correlation if indeed permanent, chemical reactions take place, yielding macromolecules of greatly different molecular sizes and/or greatly different degrees of chain branching.¹⁹ In view of the fact that plots of $\tau_{11}-\tau_{22}$ vs. τ_w give a correlation which becomes independent of how long the polyester resin underwent thickening, we speculate that, during the course of thickening, there might have been very little change in the basic structure of the mixtures of unsaturated polyester resin (or vinyl ester resin) and MgO paste. This speculation supports the view we presented above that thickening behavior involves ionic association (the formation of ionic aggregates), rather than chain extension/chain branching. It is worth mentioning that, earlier, Han^{8,10,11} suggested the use of plots of $\tau_{11}-\tau_{22}$ vs. τ_w in distinguishing the elastic property of one polymer from others when they have different degrees of chain extension (i.e., different molecular weight distributions) and/or different degrees of chain branching (i.e., different degrees of long chain branching, for example, in low-density polyethylenes).

It is a well-accepted fact today that the elastic property is far more sensitive to a change in molecular structure (or chain extension/chain branching) than the viscous property. In this sense, the normal stress measurements reported above provide additional, important information on the thickening mechanism.

CONCLUDING REMARKS

Based on the results presented above, it is concluded that the very large values of viscosity of polyester resin observed during thickening is attributable to the formation of strong ionic associations between the magnesium ion (Mg^{++}) and the carboxylic anion (COO^-) in the resin. This conclusion is based on (1) the measurement of the molecular weights of mixtures of unsaturated polyester resin and MgO paste and (2) the correlation between the first normal stress difference ($\tau_{11}-\tau_{22}$) and the shear stress (τ_w).

Although it would be a formidable task, it would be useful to determine the structure (or the state of molecular conformation) of a mixture of unsaturated polyester resin (or vinyl ester resin) and MgO paste during thickening, without dissolving the mixture in a polar solvent. Such a task should prove very valuable for proving or disproving the thickening mechanism proposed in this study.

References

1. R. Burns, K. S. Gandhi, A. G. Hankin, and B. M. Lynsky, *Plastics Polym.*, **43**, 228 (1975).
2. F. B. Alvey, *J. Polym. Sci., A-1*, **9**, 2233 (1971).
3. J. P. Walton, in *Unsaturated Polyester Technology*, P. F. Bruins, Ed., Gordon and Breach, New York, 1976, p. 109.
4. S. H. Rider and E. E. Hardy, in *Polymerization and Polycondensation Processes*, N. A. J. Platzer, Ed., Adv. Chem. Ser. No. 34, Am. Chem. Soc., Washington, D.C., 1962, p. 173.
5. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961, p. 133.
6. C. D. Han and K. W. Lem, *J. Appl. Polym. Sci.*, **28**, 743 (1983).
7. C. D. Han and Y. W. Kim, *Trans. Soc. Rheol.*, **19**, 245 (1975).
8. C. D. Han and C. A. Villamizar, *J. Appl. Polym. Sci.*, **22**, 1677 (1978).
9. C. D. Han and D. A. Rao, *J. Appl. Polym. Sci.*, **23**, 225 (1979).
10. C. D. Han, *Rheology in Polymer Processing*, Academic, New York, 1976.
11. C. D. Han, *Multiphase Flow in Polymer Processing*, Academic, New York, 1981.
12. K. Oda, J. L. White, and E. S. Clark, *Polym. Eng. Sci.*, **18**, 25 (1978).
13. W. Minoshima, J. L. White, and J. E. Spruiell, *Polym. Eng. Sci.*, **20**, 1166 (1980).
14. V. I. Szmercsanyi, *Kunststoffe Bel.*, **58**, 907 (1968).
15. V. I. Szmercsanyi, *Kunststoffe Bel.*, **60**, 1066 (1970).
16. D. Ludwig and J. Collister, *Proc. Annu. Conf.-Reinf. Plast./Compos. Inst., Soc. Plast. Ind.*, **34**, 24-C (1979).
17. M. Gruskiewicz and J. Collister, *Proc. Annu. Conf.-Reinf. Plast./Compos. Inst., Soc. Plast. Ind.*, **35**, 7-E (1980).
18. R. D. Lundberg and H. S. Makowski, in *Ions in Polymers*, A. Eisenberg, Ed., Adv. Chem. Ser. No. 187, Am. Chem. Soc., Washington, D.C., 1980, p. 21.
19. K. W. Lem and C. D. Han, *J. Appl. Polym. Sci.*, **27**, 1367 (1982).

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