

Rheological and Extrusion Behavior of Dispersed Multiphase Polymeric Systems

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Synopsis

An experimental study of temperature effect and composition effect on the rheological and extrusion properties of several dispersed multiphase polymer melts were investigated, using a cone-and-plate rheometer and a capillary rheometer. The polymeric systems studied included three homopolymers (two polystyrenes and one poly(methyl methacrylate) (PMMA)), a mechanically blended copolymer of polystyrene and PMMA, two graft copolymers (rubber-modified polystyrene and PMMA), and three particulate-filled polystyrenes (CaCO₃, milled glass fiber, and glass flake). It was found that the principal normal stress difference plotted against shear stress gives rise to a temperature independence for all dispersed multiphase polymeric systems. Composition independent correlations, however, do not exist for the principal normal stress difference. The extrudate swell plotted against shear stress becomes independent of temperature only for the homopolymers and graft copolymers. For the mechanically blended polymers and particulate-filled polymers, the temperature independent correlation does not exist. The reduction in viscosity of the glass fiber- and glass flake-filled polystyrenes is found due to the degradation of the base polymer during mixing.

INTRODUCTION

A rapidly growing interest in engineering thermoplastics has stimulated the polymer industry to develop dispersed multiphase polymeric systems. They comprise many polymeric materials being used in industry, including reinforced plastics, mechanically blended polymers and copolymers, and foamed thermoplastics. When considering the wide choice of base materials available, namely, polymers, solid reinforcing agents, and foaming agents, a vast number of combinations are possible for making dispersed multiphase polymeric materials. In all such cases, one tries to improve the mechanical or physical properties of the finished product, using an additional component as a modifying agent. On the other hand, the flow behavior of these materials also needs to be well understood in order to determine the proper processing conditions.

It has been amply demonstrated in the literature¹⁻⁴ that, in determining the rheological properties of dispersed multiphase polymeric systems, one must recognize the importance of the state of dispersion, regardless of whether the dispersed phase is solid particulates, liquid droplets, or gas bubbles. Therefore, the use of phenomenological theories that were developed for homopolymers (i.e., isotropic medium) in determining the rheological proper-

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ties of multiphase (i.e., anisotropic) polymeric systems is subject to serious objection.

For instance, during the determination of the rheological properties of polymer blends or copolymers forming two (or more) phases from the plunger-type capillary viscometer, the state of dispersion (i.e., the size and shape of the discrete phase dispersed in the continuous phase) in the reservoir section may not be the same as that in the capillary die.² Therefore, the use of entrance pressure drop, ΔP_{ent} , (or the Bagley end correction) is not justifiable in determining the rheological properties (e.g., wall shear stress, τ_w , recoverable shear strain, or the principal normal stress difference, $\tau_{11}-\tau_{22}$) of multiphase polymer blends.

Another example is that when a glass fiber-filled polymer is forced to flow through a reservoir and then into a capillary die, a large amount of energy is needed in the entrance region of the die in order to orient the glass fibers.⁵ Since glass fibers are rigid inelastic particulates, they cannot be considered the same as flexible long-chain macromolecules, therefore, the $\Delta P_{\text{ent}}/\tau_w$ ratio must not be constructed as a rough measure of relative elasticity when dealing with particulate-filled polymeric systems. It has been reported⁶⁻⁸ that when particulates are added to a polymer melt, the extrudate swell of the particulate-filled polymer decreases. This is consistent with the observation that $\tau_{11}-\tau_{22}$ of particulate-filled polymers is decreased as the amount of particulates is increased.^{1,9} However, the $\Delta P_{\text{ent}}/\tau_w$ ratio (or the Bagley end correction) is increased when particulates are added to a virgin polymer. Therefore, one must not attempt to correlate the $\Delta P_{\text{ent}}/\tau_w$ (or the Bagley end correction) with τ_w , $\tau_{11}-\tau_{22}$ or extrudate swell when dealing with the particulate-filled polymeric systems.

Generally, rotational-type rheometers, especially in the oscillatory mode, are more often used for measuring the rheological properties of multiphase polymeric systems than are capillary rheometers, because the former may have a lesser effect on the state of dispersion. Using rotational-type rheometers, many researchers^{1-4,10-16} have found that, when plotted against shear stress, the elastic responses ($\tau_{11}-\tau_{22}$ and storage modulus, G') of many multiphase polymeric systems under shearing motion gives rise to correlations which are independent of temperature. In other words, temperature-independent master curves of elastic responses may be obtained when shear stress, instead of shear rate, is used to correlate data. However, the materials being tested were mainly mechanically blended polymers and fine particulate-filled polymers. We question whether the conclusion from their experimental observations is valid for other multiphase polymeric systems, namely, graft copolymers and large particulate-filled polymers such as glass fiber- and glass flake-filled systems.

In this work, the rheological characteristics of four types of materials were studied using a Weissenberg Rheogoniometer: homopolymers, mechanically blended polymers, rubber-modified polymers produced by graft copolymerization, and particulate-filled polymers. The capillary rheometers, although being considered inappropriate for the rheological measurement of multiphase polymeric systems, are able to simulate the flow behavior in many important processing operations such as extrusion and injection molding. Therefore, experimental observations were also carried out by using an Instron capillary

rheometer to measure the extrusion behavior of the above-mentioned materials.

EXPERIMENTAL

Materials

The materials used in this study are listed in Table I. For homopolymers, two different grades of commercial, general-purpose polystyrenes, designated as PS-D and PS-H, were used; PS-D(styron-685D), which has a weight average molecular weight of 300,000 and a polydispersity of 1.9 was produced by Dow Chemical Company, while PS-H which has a weight average molecular weight of 250,000 and a polydispersity of 2.7 was produced by Huntsman Chemical Company. Also, an extrusion-grade poly(methyl methacrylate) (PMMA) produced by Plaskolite Company was used.

The mechanically blended polymer was a blend of PMMA and PS-D with a volume ratio of 20/80.

Two types of graft copolymers were studied. They include a series of five high-impact polystyrenes produced by Huntsman Chemical Company with

TABLE I
Materials Used in This Study

Sample code	Material
Homopolymer	
PS-D	Polystyrene, Dow styron-685D
PS-H	Polystyrene, Huntsman Chemical
PMMA	Poly(methyl methacrylate), Plaskolite PL-25
Mechanically blended polymer	
PMMA/PS = 20/80	Blend of 20 vol% PMMA and 80 vol% PS-D
Graft Copolymer	
HIPS-0.7	High-impact polystyrene with rubber loading
4	0.7 vol%, 4 vol%, 6 vol%, 8 vol%, 9 vol%
6	
8	
9	
HIPMMA	High-impact poly(methyl methacrylate) with rubber particle loading 25 vol%, Rohm & Haas DR
Particulate-filled polymer	
CaCO ₃ /PS = 10/90	Calcium carbonate-filled PS-D with calcium carbonate loading 10 vol%, 20 vol%, 30 vol%
20/80	
30/70	
GFB/PS = 10/90	Glass fiber-filled PS-D with glass fiber loading 10 vol%, 20 vol%, 30 vol%
20/80	
30/70	
GFK/PS = 10/90	Glass flake-filled PS-D with glass flake loading 10 vol%, 20 vol%, 30 vol%
20/80	
30/70	

different volume loadings of polybutadiene rubber. These copolymers were chosen to allow studies of compounds with a constant base polymer and structure but varying volume loading of rubber. Also employed was a rubber-modified poly(methyl methacrylate) (HIPMMA) produced by Rohm and Hass Company, which was produced by emulsion graft polymerization. Figure 1 illustrates the difference between the two types of graft copolymers. Both the dispersion size and the structure of these two copolymers are quite different. HIPMMA, synthesized by a multistage emulsion polymerization method¹⁷ has an elastomeric core surrounded by a rigid acrylic layer.

Three different types of particulate fillers were used to prepare a series of particulate-filled polystyrenes in which PS-D was the base polymer. These fillers were calcium carbonate (CaCO_3) (Calwhiite II, Georgia Marble company, particle size ranging from 1 to approximately 10 μm), 1/16 inch milled glass fiber (GFB), and glass flake (GFK). Both GFB and GFK were supplied by Owens Corning Fiberglas Company. The composition of each composite used in this study is listed in Table I.

Sample Preparation

The mechanically blended polymer and the particulate-filled polymers were prepared by using an electrically heated C. W. Brabender prep mixer with roller-type mixing blades. Operating temperature was set at 200°C. The mixing time was 20 minutes with a rotation speed of 20 rpm. The retrieved blend was ground into pellet-size pieces for rheological and extrusion measurements.

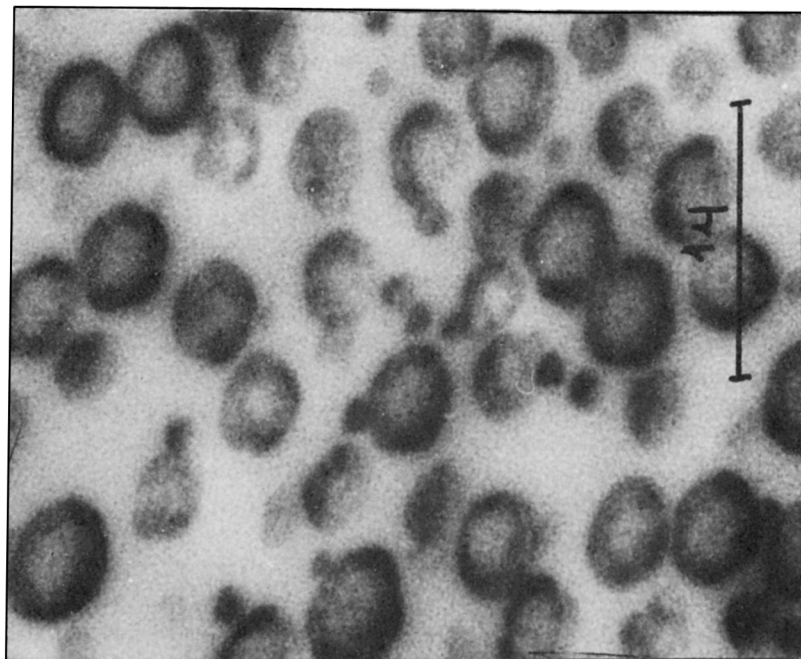
Rheological Measurement

A cone-and-plate rheometer with a cone diameter of 2.5 cm and a cone angle of 4°, Weissenberg Rheogoniometer (Model R-18), was used to measure steady shearing flow properties, namely viscosity, shear stress, and principal normal stress difference, at low shear rates. These quantities were determined using the expressions described in the literature.^{1,18}

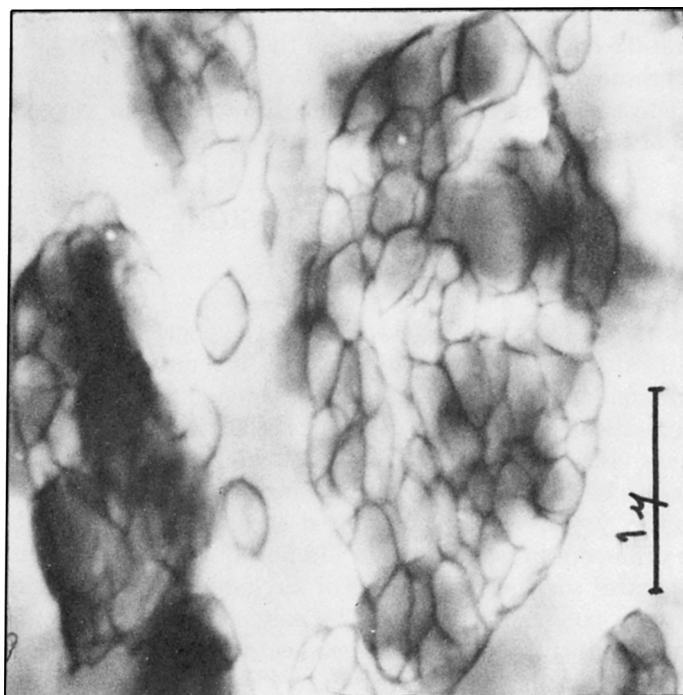
Extrusion Measurement

An Instron capillary rheometer (Type MCR) mounted on an Instron tensile testing machine (Model 1137) was used to measure the extrusion properties, namely apparent shear viscosity and extrudate swell. A die with a diameter of 1.27 mm, length/diameter ratio of 40, and an entrance angle of 90° was used. The wall shear stress was obtained without the end correction, while the shear rate at the die was determined by the Weissenberg relation.^{1,18} An optical microscope with a micrometer was used to determine the diameters of air-frozen extrudates.

Ideal extrudate swell measurements should be performed under the following conditions:¹⁹ (1) steady isothermal flow; (2) absence of gravitational force as well as interfacial tension; (3) the extrudate should be in a state of complete elastic recovery. There are several methods of measurement of extrudate swell.¹⁹⁻²² The simplest method is to quench the extrudate in air or liquid and then measure the extrudate diameter using a micrometer. The



HIPMMA



HIPS - 9

Fig. 1. Photomicrographs of HIPS-9 and HIPMMA.

second method is to anneal air- or liquid-quenched extrudate in an oil bath above the glass transition temperature (T_g) of the polymer. In the third, the polymer is extruded into a heated chamber and relaxed. The fourth method is to extrude polymer melt into an inert thermostated fluid of matched density and interfacial tension, and then measure the relaxed extrudate diameter using noncontacting-type devices such as photographic method or laser optical technique. In general, quenching introduces an additional thermal history, which in the case of crystallizable polymers may introduce additional stresses. Extrusion into a hot gas chamber increases the effect of gravitational sagging and interfacial tension. The last method seems to be most satisfactory, however, the experimental technique is more complicated than other methods.

In this study, several extrudate swell measurement methods were tried. For the materials used, it was found that the values of water-quenched extrudate swell were much less than those of other methods, but there was little difference between oil-annealed extrudate swell and air-quenched extrudate swell. It was also found that there is almost no difference between the oil annealing method and the isothermal extrusion into hot silicone oil when the effect of density change at different measuring temperatures was taken into account.²³ Since the thermostated oil bath was difficult to mount on the rheometer and the photographed extrudate swell sometimes tended to scatter a lot due to the refractive index change by natural convection of hot silicone oil, the air-quenched extrudate swells were used in this study. To obtain a specimen for measurement, the extrudate was carefully cut at about 2 cm long when the pressure drop reached the steady state. The extrudate diameter was measured about 0.5 cm near the lower end of the extrudate.

Three temperatures, 210, 220, 230°C, and various compositions were tried to study the effect of temperature and composition on shear viscosities, the principal normal stress difference, and extrudate swells.

RESULTS AND DISCUSSION

Shear Viscosity

Figure 2 shows plots of apparent shear viscosity versus shear rate for both PS-D and PS-H at three different temperatures. The data at low shear rates were obtained from the Weissenberg Rheogoniometer and the data at high shear rates were calculated from the capillary rheometer results. PS-D always has higher shear viscosity than PS-H due to its higher molecular weight. All viscosity data can be combined into a single master curve when plotting the reduced viscosity, $\dot{\gamma}\eta/T$, versus the reduced shear rate, η/η_0 , as shown in Figure 3. The difference in polydispersity did not affect the data reduction.

Figure 4 compares the shear viscosities of mechanically blended copolymer and its constituent polymers at 210°C. The polymer blend has lower viscosities than each constituent polymer at lower shear rates, but tends to show the same viscosities as the matrix polymer (e.g., PS-D), at higher shear rates. Many researchers^{1, 2, 24-27} have also reported the lower viscosity behavior of incompatible blend systems, very similar to the one shown in Figure 4. Han and co-workers^{1, 2, 24} explained this phenomenon on the basis of the deformability of the dispersed phase (i.e., droplets) when subjected to large shear rates.

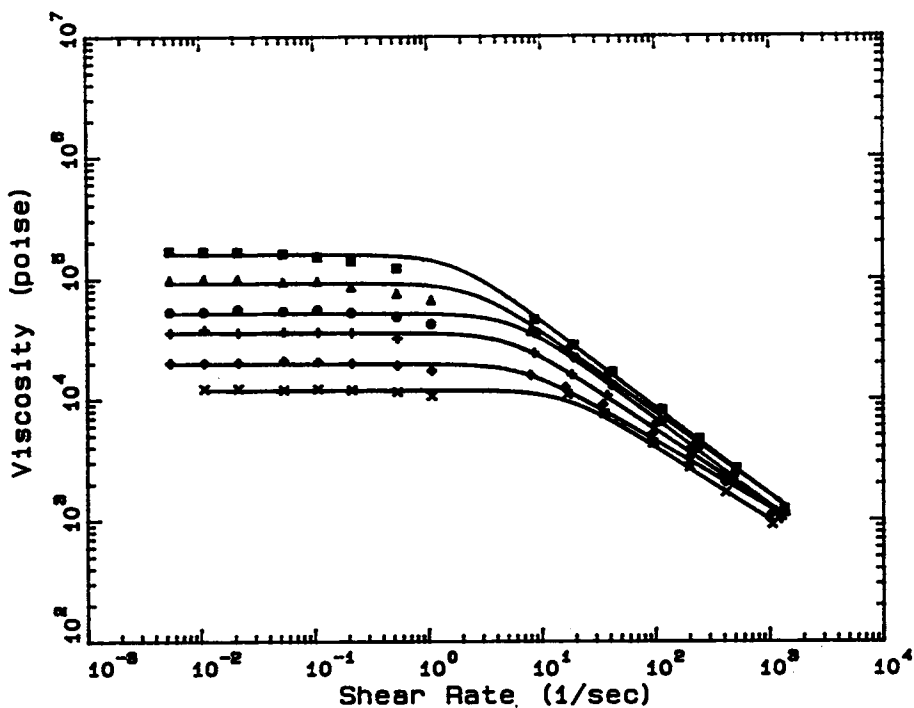


Fig. 2. Apparent shear viscosity vs. shear rate for both PS-D (\square -210°C , \triangle -220°C , \circ -230°C) and PS-H ($+$ -210°C , \diamond -220°C , \times -230°C).

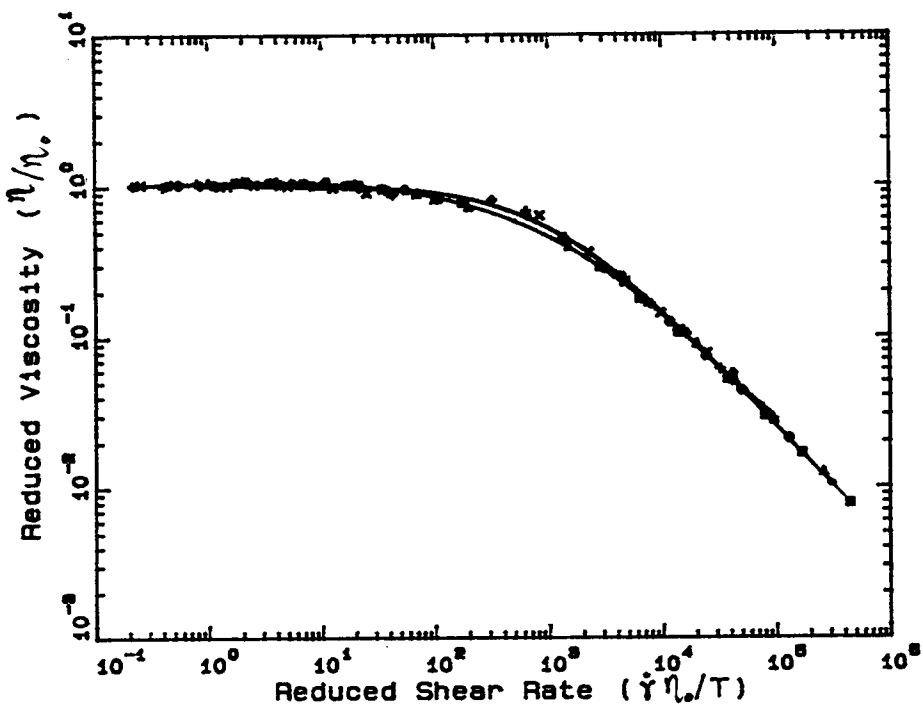


Fig. 3. Reduced viscosity vs. reduced shear rate for both PS-D and PS-H (symbols are the same as in Fig. 2).

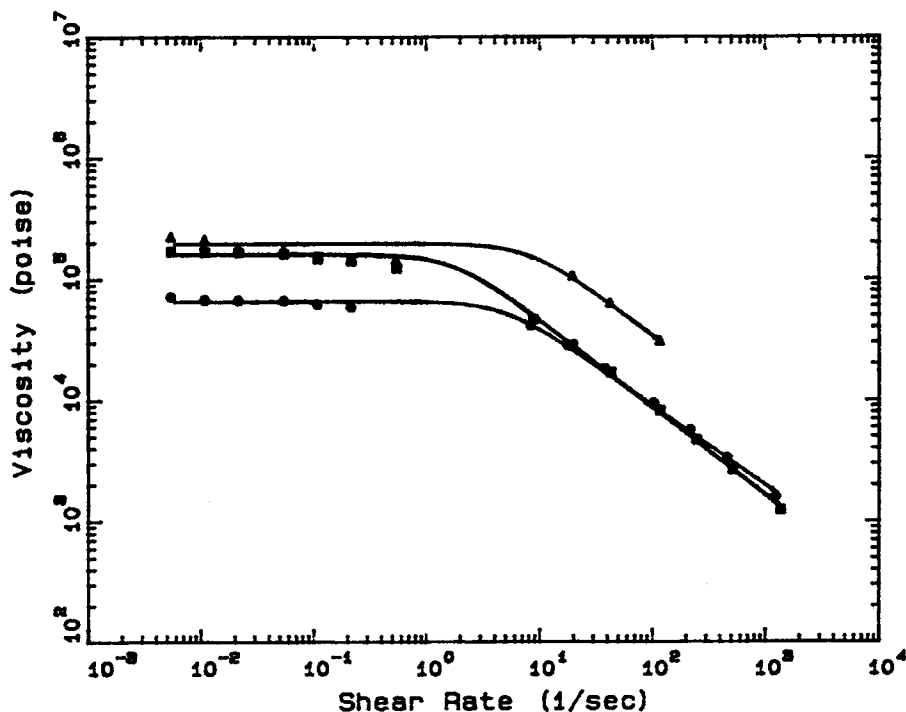


Fig. 4. Apparent shear viscosity vs. shear rate for PS-D (\square), PMMA (Δ) and PMMA/PS = 20/80 (\circ) at 210°C.

Others^{25,26} speculated that slippage between phases during the melt flow might cause a negative deviation of viscosity from simple additivity rules. Figure 5 gives plots of reduced viscosity versus reduced shear rate for both polymer blend and its constituent polymers at three different temperatures. Apparently, the polymer blend has a master curve very close to that of the matrix polymer.

For high-impact polystyrenes with different rubber loadings, all viscosity data fall into a single master curve, which is also very close to that of the matrix polystyrene. To avoid overcrowding, Figure 6 only shows data of PS-H, HIPS-4, and HIPS-9. The results of high-impact PMMA, however, are quite different from those of HIPS as Figure 7 indicates that rubber-modified PMMA tends to show a yield stress at low shear rates, which is not found in the rigid PMMA. Thus, viscosity data cannot be combined into a single master curve as in the case of HIPS. The existence of yield stress in HIPMMA may be attributed to its smaller particle size (0.5 μm vs. several μm) and higher rubber loading (25% vs. 9% by volume) compared to HIPS. Similar results were also reported in the study of mechanically blended, rubber-modified thermoplastics.^{28,29}

Yield stress was also found in fine particulate-filled polystyrenes by many researchers.²⁹⁻³² Figure 8 shows plots of apparent shear viscosity versus shear rate for PS-D at 210°C with different filler loadings. The CaCO_3 -filled polystyrene has higher viscosity than the base polystyrene and tends to show yield stress at a filler loading higher than 10% by volume.

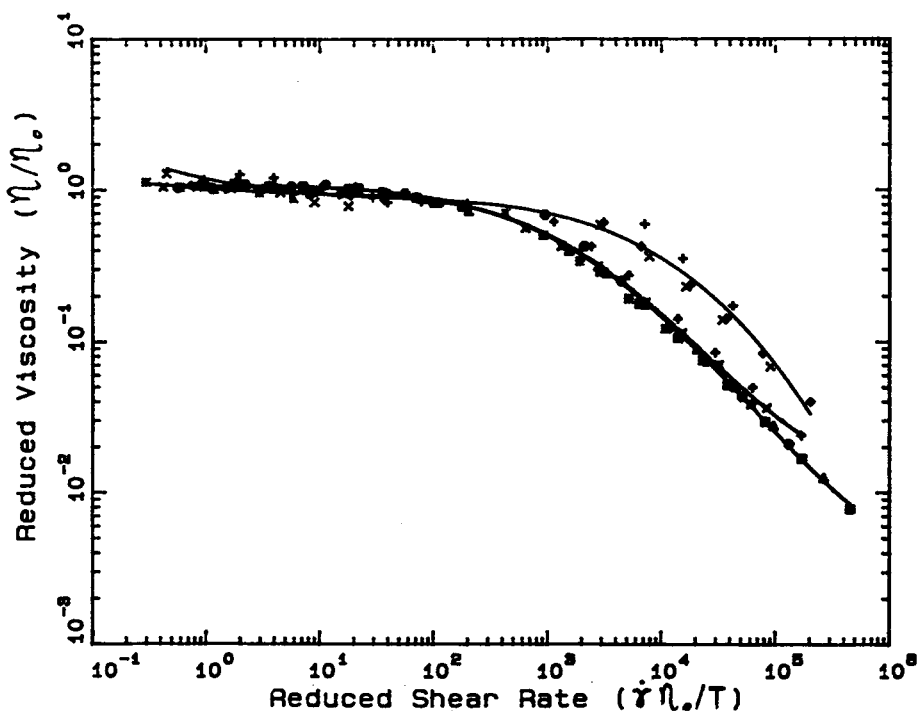


Fig. 5. Reduced viscosity vs. reduced shear rate for PS-D (\square -210°C , \triangle -220°C , \circ -230°C), PMMA ($+$ -210°C , \diamond -220°C , \times -230°C), and PMMA/PS = 20/80 (\blacktriangle -210°C , \otimes -220°C , $*$ -230°C).

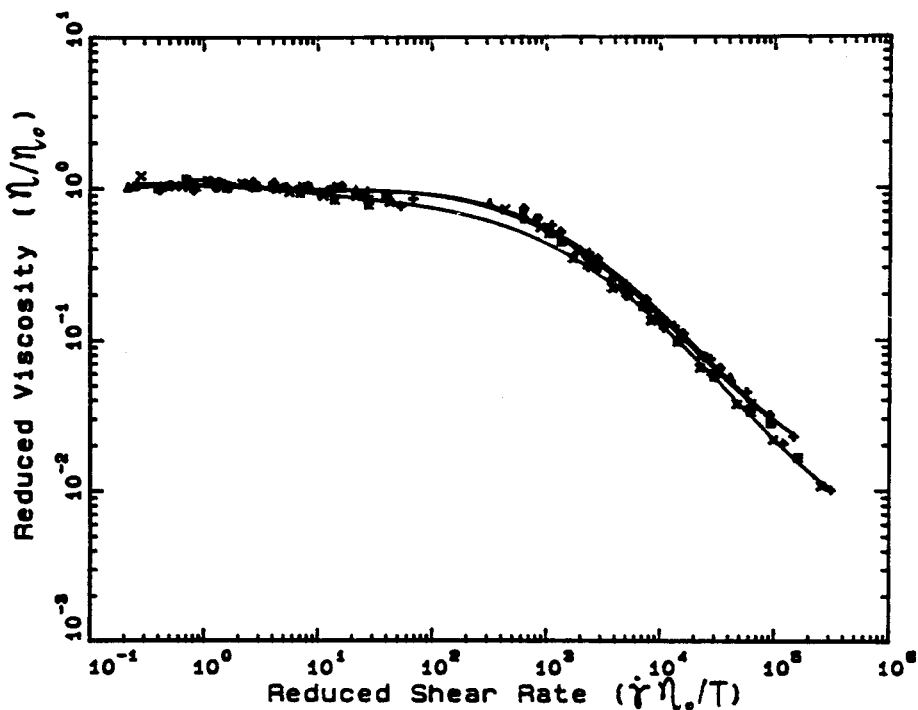


Fig. 6. Reduced viscosity vs. reduced shear rate for PS-H (\square -210°C , \triangle -220°C , \circ -230°C), HIPS-4 ($+$ -210°C , \diamond -220°C , \times -230°C), and HIPS-9 (\blacktriangle -210°C , \otimes -220°C , $*$ -230°C).

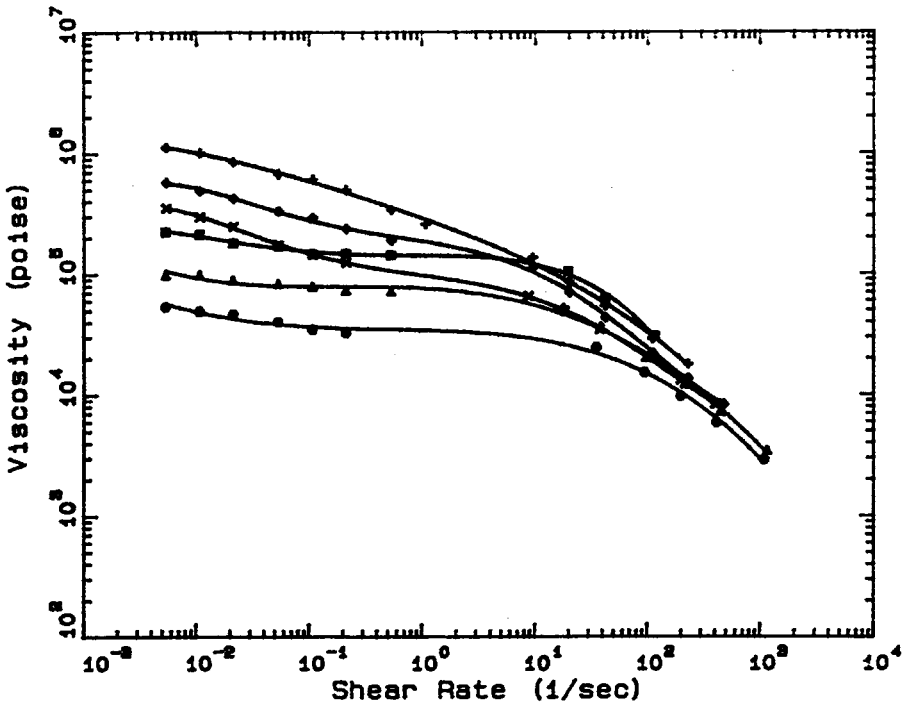


Fig. 7. Apparent shear viscosity vs. shear rate for PMMA (\square — -210°C , \triangle — -220°C , \odot — -230°C) and HIPMMA ($+$ — -210°C , \diamond — -220° , \times — -230°C).

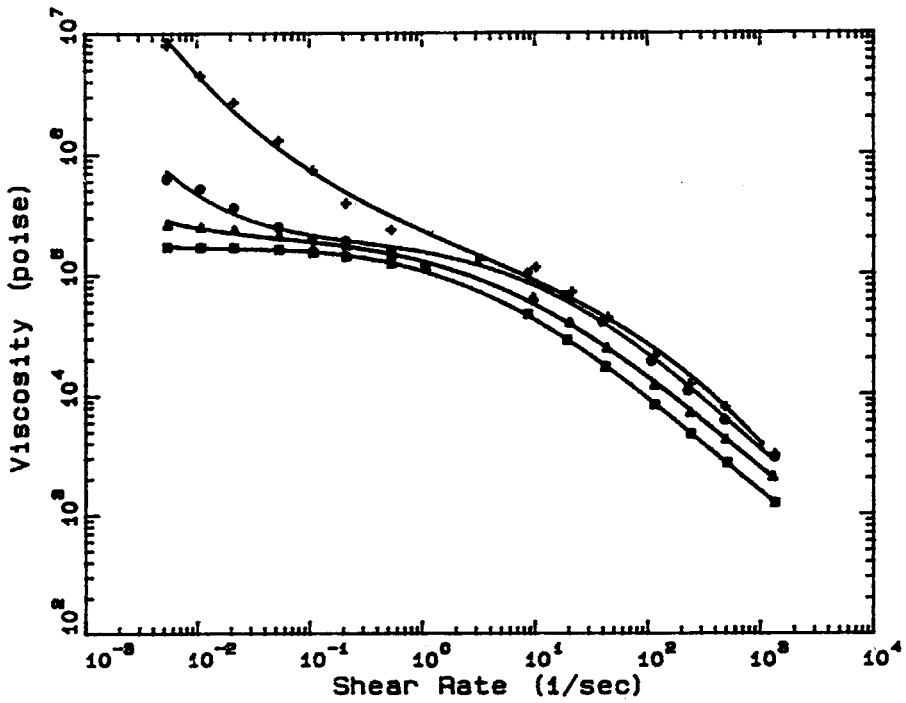


Fig. 8. Apparent shear viscosity vs. shear rate for CaCO_3 -filled PS at 210°C (\square — 0% , \triangle — 10% , \odot — 20% , $+$ — 30%).

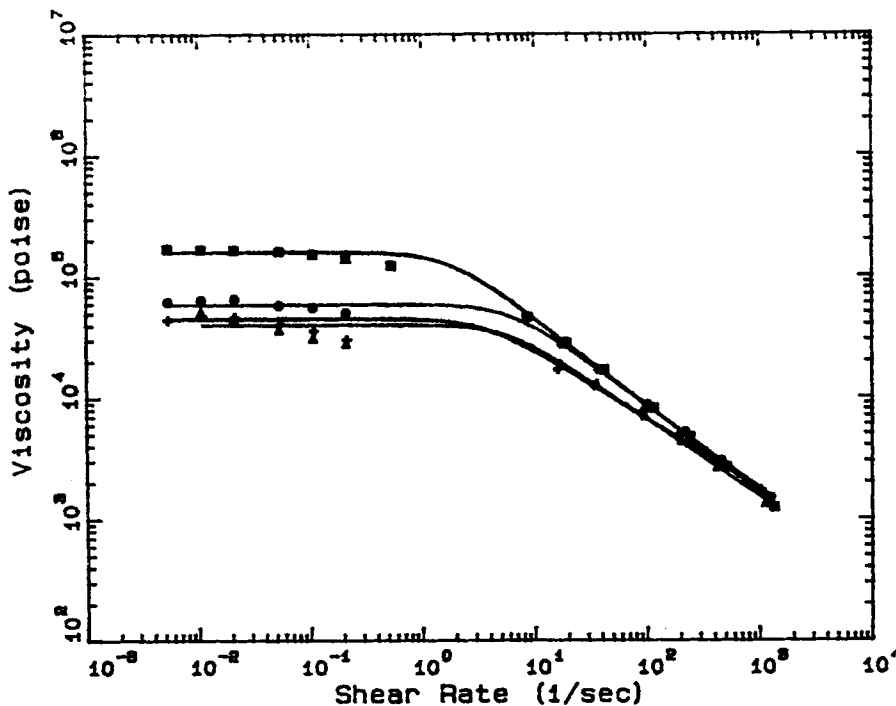


Fig. 9. Apparent shear viscosity vs. shear rate for GFB-filled PS at 210°C (\square —0%, Δ —10%, \circ —20%, $+$ —30%).

Contrary to the CaCO_3/PS blend system, the GFB/PS and GFK/PS blend systems show an unusual result. As revealed in Figures 9 and 10, the milled glass fiber- or glass flake-filled polystyrene melt possesses lower shear viscosities compared to the base polystyrene at low shear rates. Similar results were also reported by Charrier and Rieger,³³ and Mutel and Kamal.³⁴ A variety of factors might contribute to reducing viscosity. One factor might be the degradation of the resin during mixing and testing. In order to test the degradation of the base polymer during mixing, the Weissenberg Rheogoniometer was employed to compare the viscosities of pure polystyrene, polystyrene dissolved by tetrahydrofuran (THF) and then dried, and polystyrenes extracted from the GFB/PS and GFK/PS blends with tetrahydrofuran. Figure 11 shows the result that there is almost no difference in viscosity between polystyrene and solvent-treated polystyrene, but viscosities of the polystyrenes extracted from the blends are much lower than those of the pure polystyrene. This implies that, in this study, the degradation of the base polymer during mixing is the main factor which results in reducing viscosity. If we use the extracted polystyrene as the base polymer, both GFB/PS and GFK/PS blends show an increase of viscosity, as in the case of CaCO_3/PS blend.

Despite the degradation of the base polymer, the CaCO_3/PS blend, mixed under the same conditions as the GFB/PS and GFK/PS blends, possesses a higher viscosity compared to the rigid polystyrene as shown in Figure 8. Therefore, there seem to be two competing mechanisms influencing the

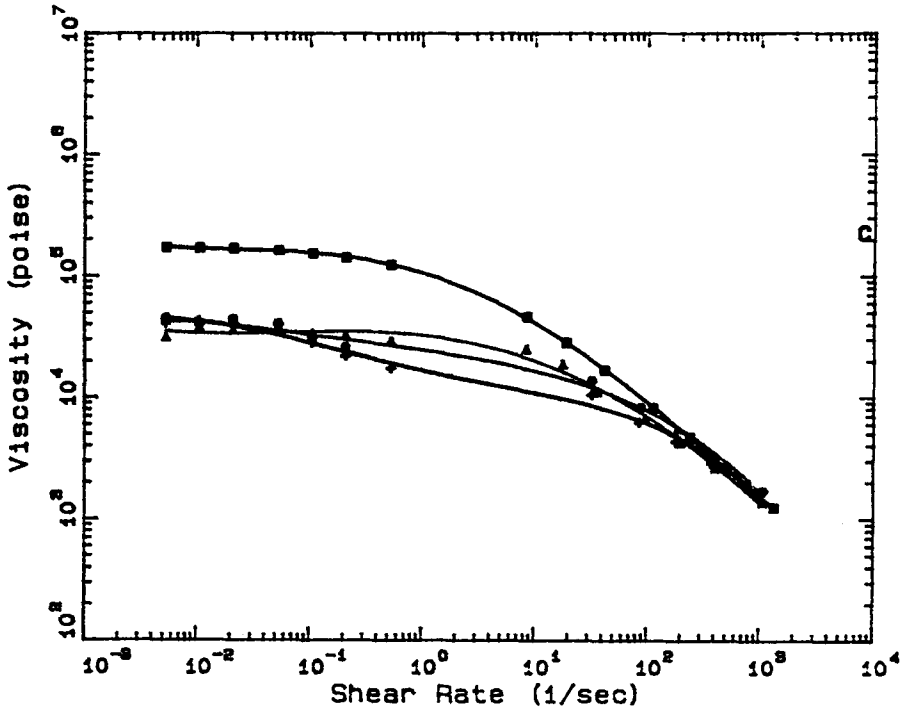


Fig. 10. Apparent shear viscosity vs. shear rate for GFK-filled PS at 210°C (\square —0%, Δ —10%, \odot —20%, $+$ —30%).

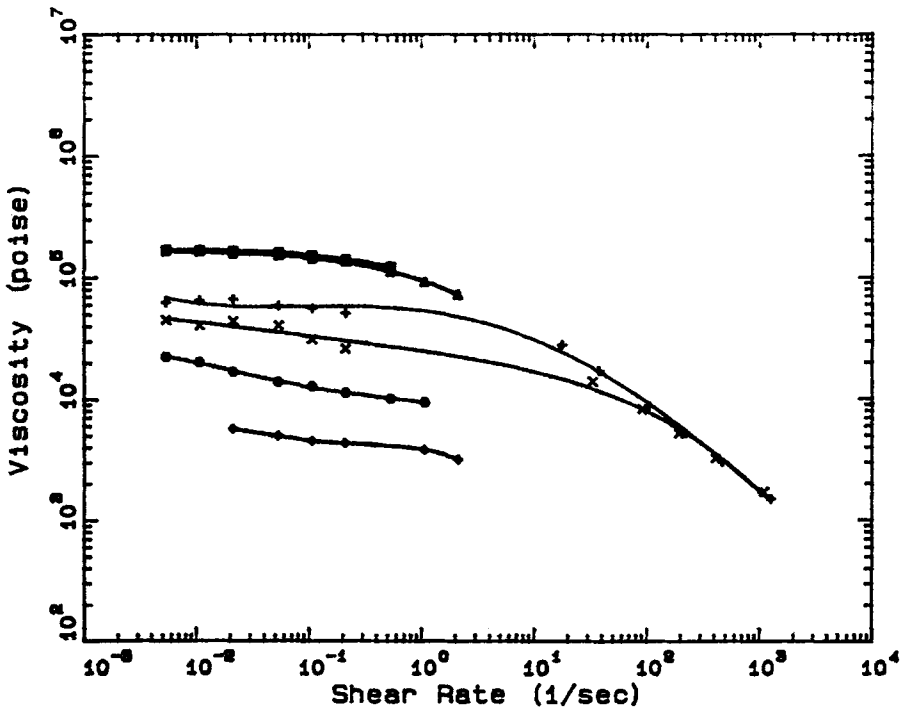


Fig. 11. Apparent shear viscosity vs. shear rate for samples before and after solvent treatment (before: \square —PS-D, $+$ —GFB/PS = 20/80, \times —GFK/PS = 20/80; after: Δ —PS-D, \odot —PS-D from GFB/PS = 20/80, \diamond —PS-D from GFK/PS = 20/80).

rheological behavior of particulate-filled polymer melts. One is the rupture and partial destruction of the polymer chains by the shearing action between the particulates and by particulates motion. This decreases the viscous dissipation caused by polymer chain entanglements. The other is the increased viscous dissipation due to the hydrodynamic interaction between particulates. The data of our experiments reveal that the former mechanism, as a result of mixing in a high intensity mixer, is dominant in milled glass fiber- and glass flake-filled polystyrenes and the latter one is dominant in CaCO_3 -filled polymers.

Principal Normal Stress Difference

Experimental results showed that the data of $\tau_{11}-\tau_{22}$ versus shear stress tended to scatter at low shear stresses. Some researchers³⁵⁻³⁸ have reported that transient yield stresses exist in the normal stress measurements due to the loading of the sample in the instrument. As a result, a proper zero point for measurement is sometimes difficult to determine, which may induce errors in the measurement of normal stresses, especially at low shear rates. In this study, the loaded samples were allowed to rest for at least 15 minutes before each measurement, yet the data scattering was still found at lower shear rates. Those data were not included in the following figures.

Figure 12 shows plots of principal normal stress difference versus shear stress measured by using the Weissenberg Rheogoniometer for PS-D and

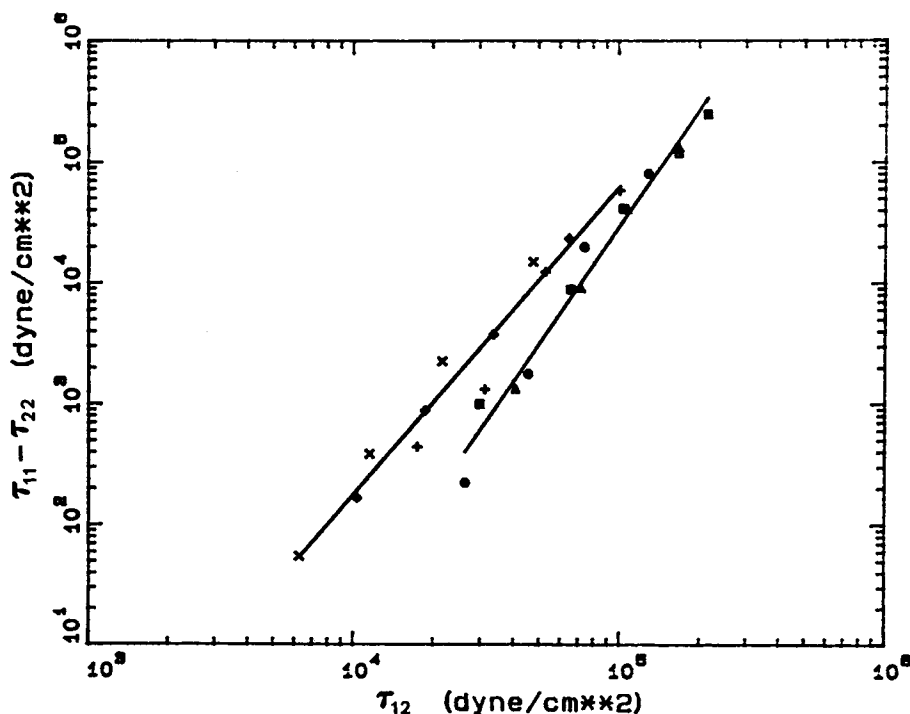


Fig. 12. $\tau_{11}-\tau_{22}$ shear stress for both PS-D (\square -210°C , Δ -220°C , \odot -230°C) and PS-H ($+$ -210°C , \diamond -220°C , \times -230°C).

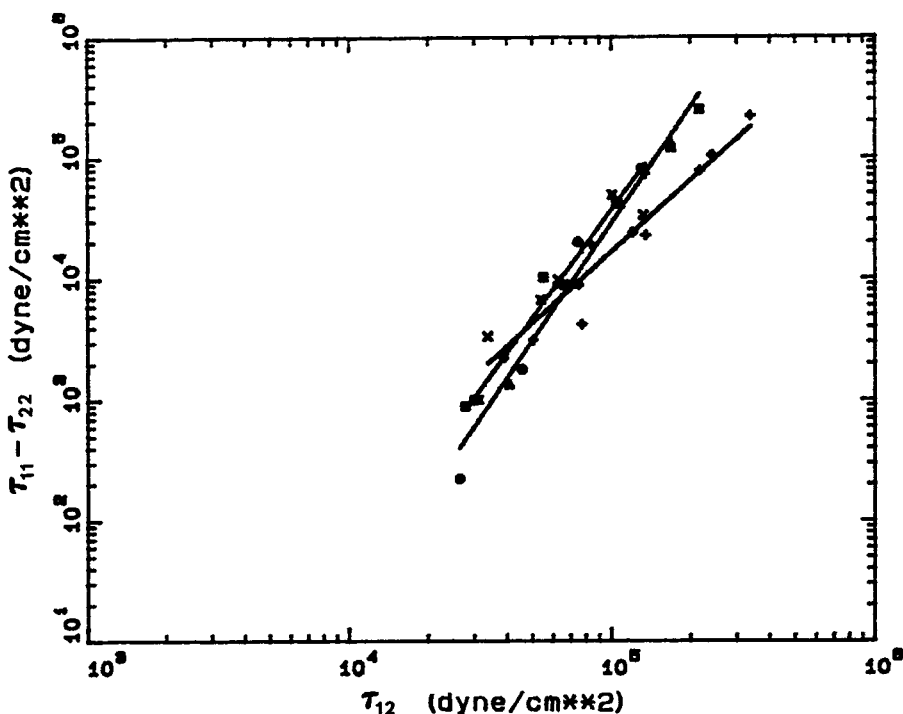


Fig. 13. $\tau_{11}-\tau_{22}$ vs. shear stress for PS-D (\square -210°C , Δ -220°C , \circ -230°C), PMMA ($+$ -210°C , \diamond -220°C , \times -230°C) and PMMA/PS = 20/80 (\blacktriangle -210°C , \oplus -220°C , $*$ -230°C).

PS-H at three different temperatures (210, 220, 230°C). It is observed that such plots give rise to a temperature-independent correlation for each pure polymer melt. PS-H has higher $\tau_{11}-\tau_{22}$ than PS-D, which may be due to the fact that PS-H has a broader molecular weight distribution. Figure 13 compares the principal normal stress difference versus shear stress for both mechanically blended copolymer PMMA/PS and its constituent polymers. Again, $\tau_{11}-\tau_{22}$ is found independent of temperature when plotted against the shear stress for all three materials. The blend shows a normal stress difference close to that of the polymer forming the continuous phase as in the case of shear viscosity.

Figure 14 gives plots of $\tau_{11}-\tau_{22}$ versus shear stress for HIPS with various rubber loadings. $\tau_{11}-\tau_{22}$ is also independent of temperature when plotted against the shear stress, but it apparently depends on the content of rubber loading. As shown in the figure, HIPS gives lower $\tau_{11}-\tau_{22}$ than pure polystyrene at any given shear stress. This means that adding the rubber into polystyrene tends to increase the shear stress (i.e., energy dissipated) more than the principal normal stress difference (i.e., energy stored), which is typical for small particle-filled polymers.³⁹ The same observation was also found in rubber modified PMMA as shown in Figure 15.

For the solid particulate-filled polystyrenes, $\tau_{11}-\tau_{22}$ was, again, found to be independent of temperature when plotted against the shear stress, but was dependent on the type of particles. Figure 16 shows the comparison of three

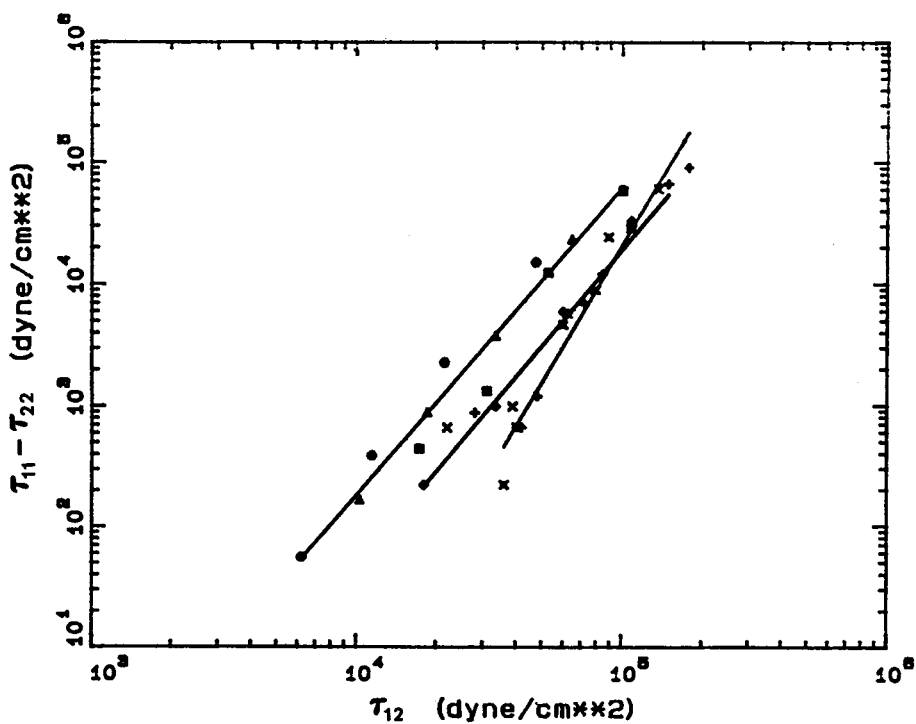


Fig. 14. $\tau_{11} - \tau_{22}$ vs. shear stress for PS-H (\square -210°C, Δ -220°C, \circ -230°C), HIPS-4 ($+$ -210°C, \diamond -220°C, \times -230°C), and HIPS-9 (\blacktriangle -210°C, \diamond -220°C, $*$ -230°C).

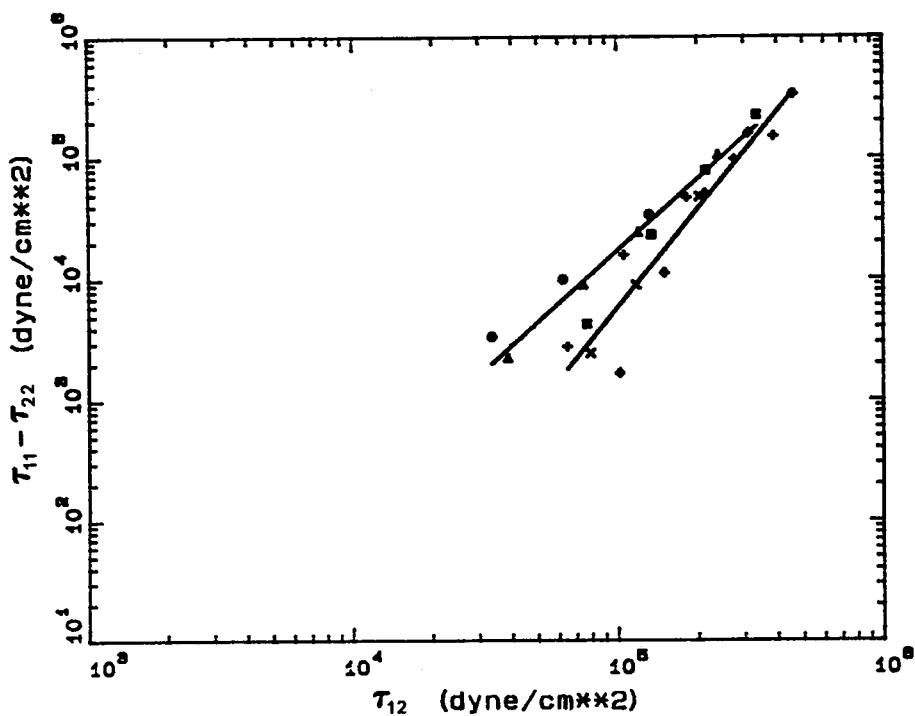


Fig. 15. $\tau_{11} - \tau_{22}$ vs. shear stress for PMMA (\square -210°C, Δ -220°C, \circ -230°C) and HIPMMA ($+$ -210°C, \diamond -220°C, \times -230°C).

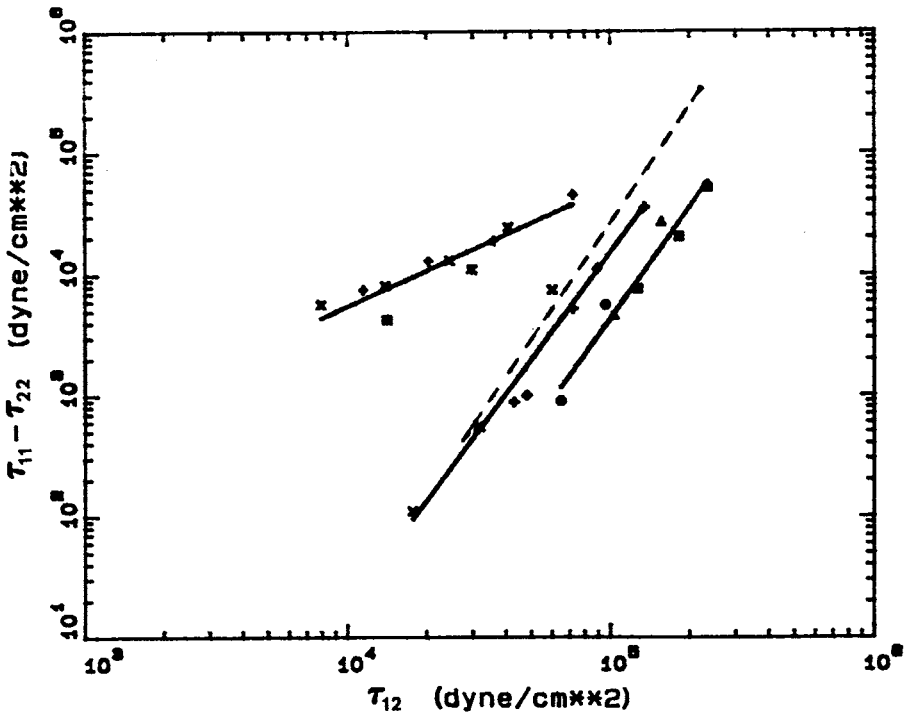


Fig. 16. $\tau_{11}-\tau_{22}$ vs. shear stress for particulate-filled PS ($\text{CaCO}_3/\text{PS} = 20/80$: \square —210°C, \blacktriangle —220°C, \circ —230°C; GFB/PS = 20/80: $+$ —210°C, \diamond —220°C, \times —230°C; GFK/PS = 20/80: \blacktriangle —210°C, \diamond —220°C, $*$ —230°C; --- PS).

different solid fillers in polystyrene at a volume loading of 20%. The dash line represents $\tau_{11}-\tau_{22}$ for the pure polystyrene. The results show that the addition of CaCO_3 reduces the principal normal stress difference at any given shear stress, while the addition of glass flake increases $\tau_{11}-\tau_{22}$. Adding milled glass fiber to polymer apparently has much less effect on the change of $\tau_{11}-\tau_{22}$ versus shear stress than adding the other two fillers. Similar results have been observed by White.⁴⁰ He found that glass beads seem to leave the $\tau_{11}-\tau_{22}$ vs. shear stress relationship unchanged, while large rigid fibers increase $\tau_{11}-\tau_{22}$ at fixed shear stress and small particles reduce $\tau_{11}-\tau_{22}$. The solid particle filled polystyrenes also exhibit a composition dependent correlation, i.e., the principal normal stress difference is dependent on the composition when plotted against the shear stress. Figure 17 shows such a plot for CaCO_3 -filled polystyrene at 210°C. The data, however, scatter more than those of graft copolymers. It is believed that variation of particle orientation and distribution in each sample causes the scattering of measured normal stress difference.

Extrudate Swell

The extrudate swell is defined as the value of sample diameter divided by the value of die diameter. Figure 18 shows plots of extrudate swell versus shear stress for PS-D and PS-H at three different temperatures (210, 220, 230°C). It is observed that such plots give rise to a temperature-independent

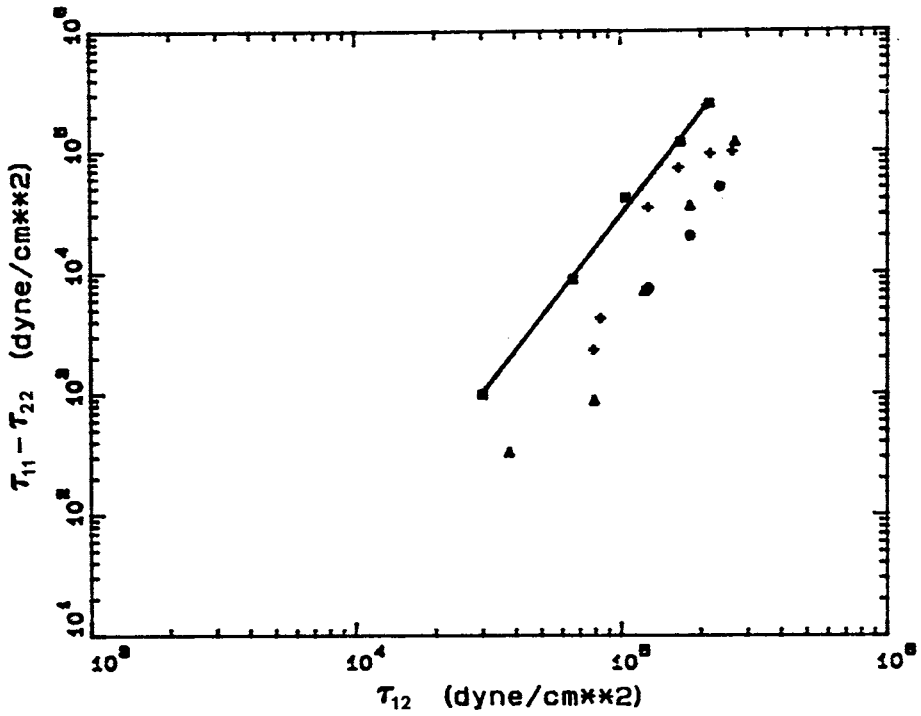


Fig. 17. $\tau_{11} - \tau_{22}$ vs. shear stress for CaCO₃-filled PS at 210°C (□—0%, Δ—10%, ○—20%, +—30%).

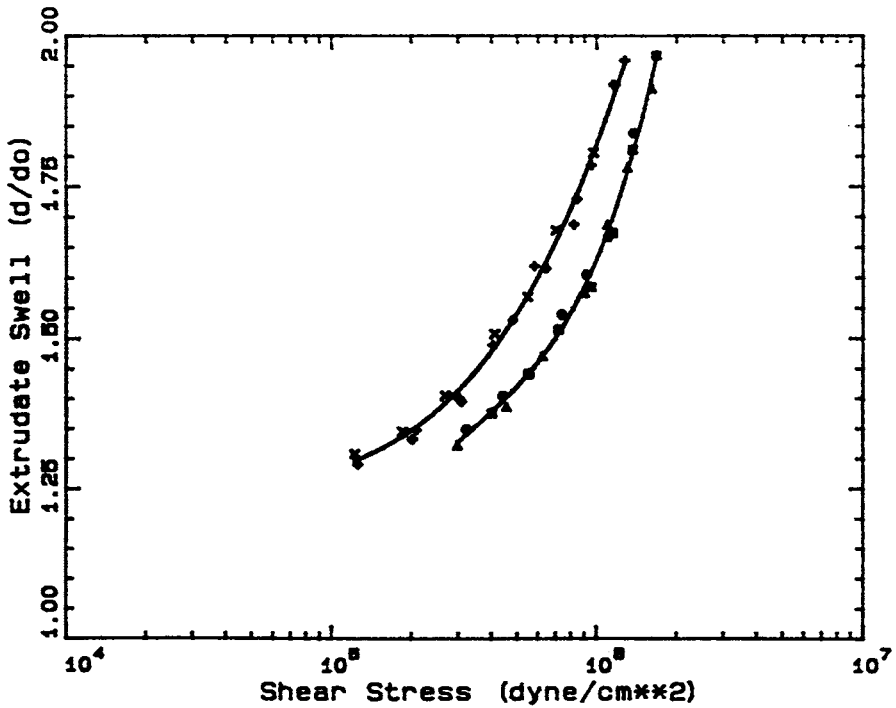


Fig. 18. Extrudate swell vs. shear stress for PS-D (□—210°C, Δ—220°C, ○—230°C) and PS-H (+—210°C, ◇—220°C, ×—230°C).

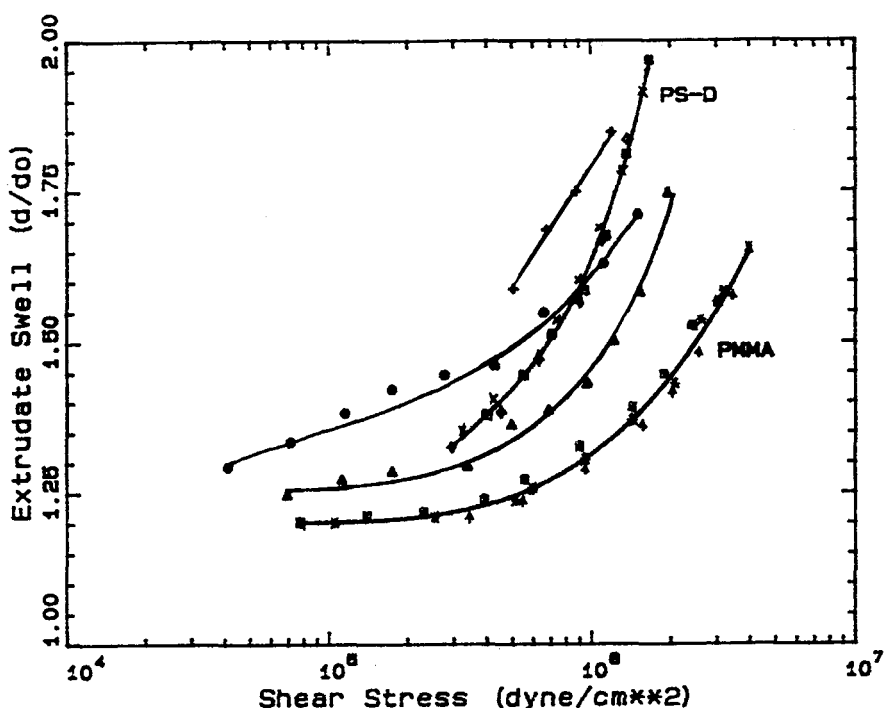


Fig. 19. Extrudate swell vs. shear stress for PS-D (\square -210°C , \diamond -220°C , \times -230°C), PMMA (\blacktriangle -210°C , $*$ -220°C , \square -230°C), and PMMA/PS = 20/80 (Δ -210°C , \circ -220°C , $+$ -230°C).

correlation for each pure polymer melt, very similar to the temperature independence of the principal normal stress difference. As expected, PS-H has higher extrudate swell than PS-D due to the broader molecular weight distribution, which is the same as that in the principal normal stress difference.

Figure 19 shows plots of extrudate swell versus shear stress for the PMMA/PS blend and its constituent polymers. For the homopolymers, PS and PMMA, the extrudate swell is independent of temperature, but for the polymer blend, a strong temperature-dependent correlation exists. The extrudate swell increases as temperature increases at any given shear stress. Figures 20 and 21 show plots of extrudate swell versus shear stress for HIPS and HIPMMA at three different temperatures. As shown in those figures, HIPS-4, HIPS-9, and HIPMMA exhibit independence of extrudate swell on temperature, which is different from the mechanically blended polymers. A possible explanation is that the droplets of the mechanically blended polymers may easily deform and rupture in a given flow field, while for HIPS and HIPMMA, the graft reaction between the rubber phase and the plastic phase tends to link the two phases together, furthermore, the rubber phase is partially crosslinked during the graft reaction. These features may make the droplets more difficult to deform and rupture than the noncross-linked and nongrafted droplets. For the steady shearing flow in a cone-and-plate rheometer, the flow field is uniform. One may speculate that the state of dispersion is the same at different temperatures. Therefore, both mechanically blended

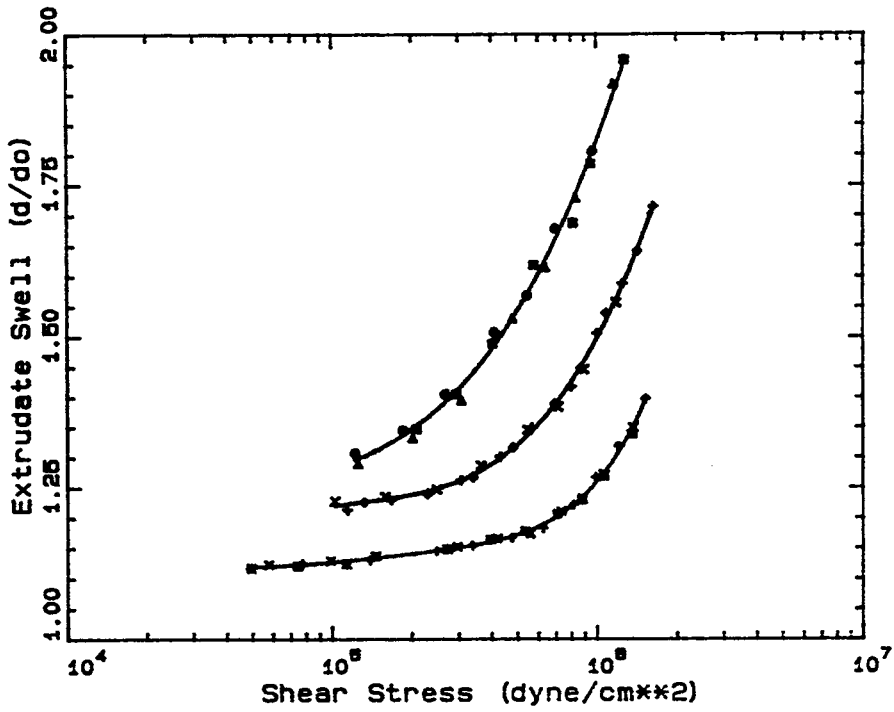


Fig. 20. Extrudate swell vs. shear stress for PS-H (\square —210°C, Δ —220°C, \circ —230°C), HIPS-4 ($+$ —210°C, \diamond —220°C, \times —230°C), and HIPS-9 (\blacklozenge —210°C, \otimes —220°C, $*$ —230°C).

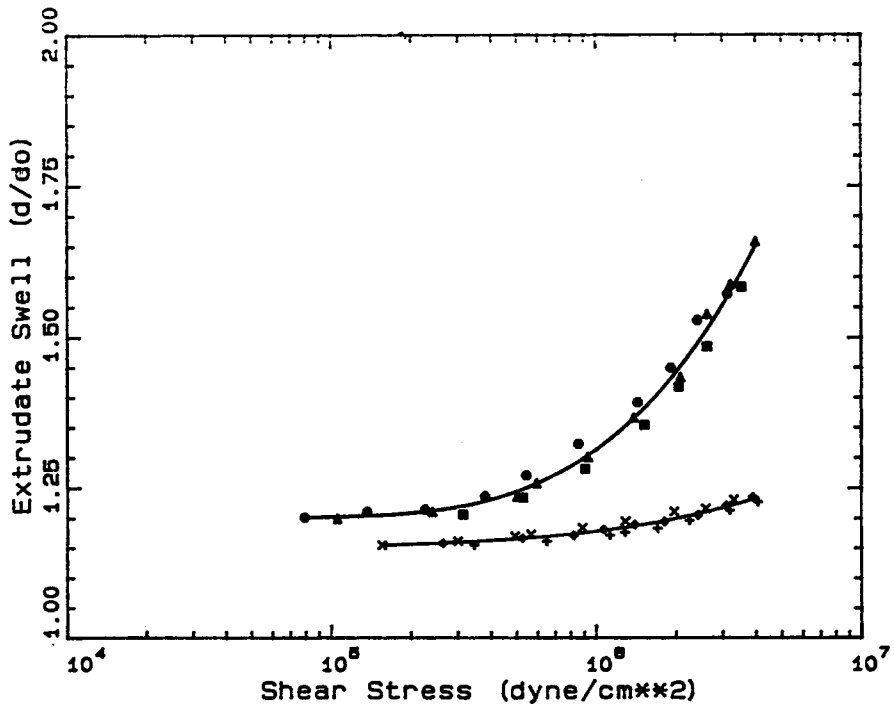


Fig. 21. Extrudate swell vs. shear stress for PMMA (\square —210°C, Δ —220°C, \circ —230°C) and HIPMMA ($+$ —210°C, \diamond —220°C, \times —230°C).

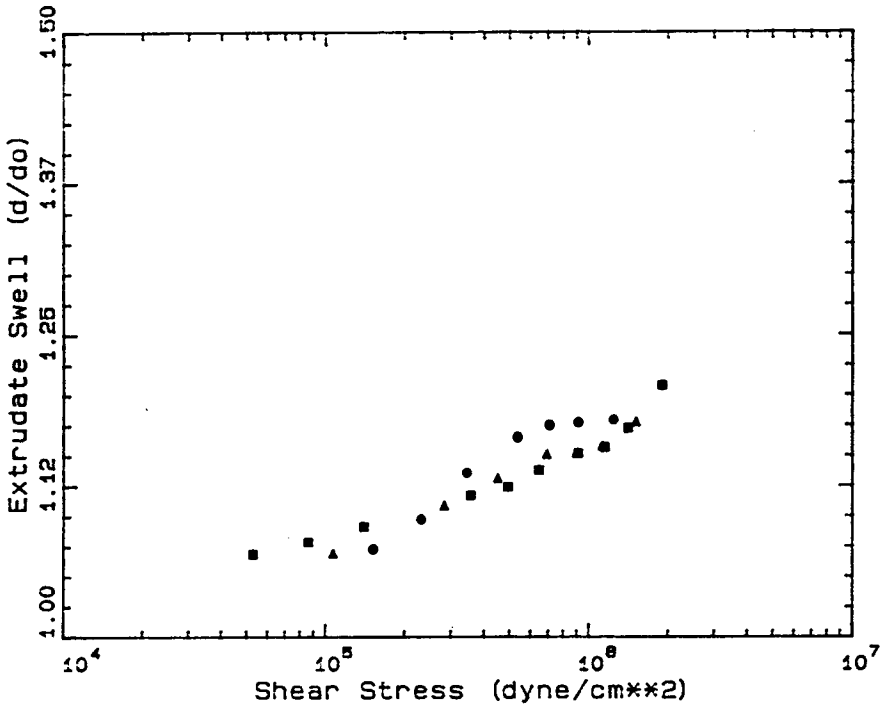


Fig. 22. Extrudate swell vs. shear stress for GFB/PS = 20/80 (□ —210°C, △ —220°C, ○ —230°C).

copolymer and graft copolymer show independence of temperature when plotted $\tau_{11}-\tau_{22}$ versus shear stress. On the other hand, the shearing flow field is nonuniform in a capillary die even in the fully developed region. The flow field in the entrance region between the barrel and the die is even more complicated. It is not surprising to speculate that the state of dispersion of mechanically blended polymers may vary at different temperatures. Therefore, extrudate swell is temperature dependent since it cannot be considered as the pure elastic response in the multiphase polymeric systems.^{2,4,29} For graft copolymers, the temperature independence of extrudate swell when plotted against shear stress seems to imply that the state of dispersion does not vary at different temperatures in the capillary flow, which may be due to the chemical bonding between the two phases and the crosslinking in the rubber droplets.

For particulate-filled polystyrene systems, extrudate swell tends to vary at different temperatures when plotted against shear stress. But the value of extrudate swell is often too small to be accurately determined. Figure 22 shows such a plot for glass flake-filled polystyrene. In our study, only the diameters of air-frozen extrudates were measured. White and co-workers^{30,39} have investigated the influence of annealing on extrudate swell. They found that the presence of solid particulates greatly reduced the additional recovery usually occurring with annealing. There was essentially no difference of extrudate swell between annealed and unannealed particulate-filled polymers.

Extrudate swell is strongly dependent on the composition for particulate-filled systems. Figure 23 shows such an example for glass flake-filled poly-

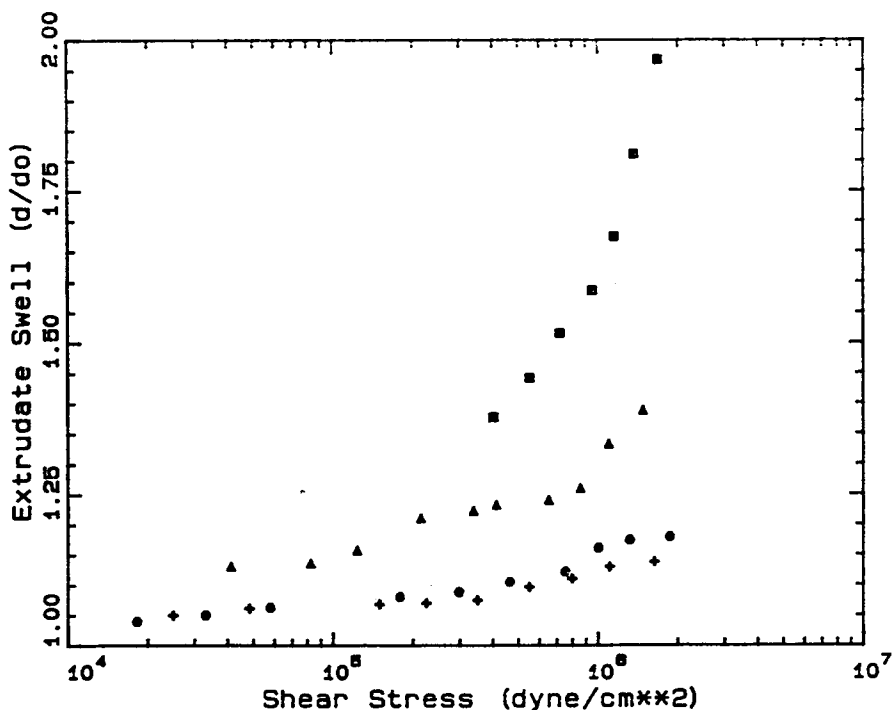


Fig. 23. Extrudate swell vs. shear stress for GFK/PS at 210°C (\square —0%, Δ —10%, \circ —20%, +—30%).

styrene at 210°C. Extrudate swell decreases sharply with an increase of solid loading.

Extrudate swell has long been known to have its origins in unconstrained elastic recovery following Poiseuille flow.⁴¹⁻⁴³ The reduction in extrudate swell due to the addition of particulate solids is a general one, as similar effects have been observed in other systems, such as clay,⁴⁴ carbon black,^{7,39,44} titanium dioxide,⁴⁵ and glass fibers.³⁰ The mechanism of this is not well understood. It may be, in part, attributable to the lower proportion of polymer in particulate-filled extrudates, but this is an insufficient mechanism in itself. One of the more reasonable hypotheses³⁹ for systems containing high levels of particulates is that small particulates are able to interact or aggregate in such a way as to produce a gel-like structure or apparent gel-like structure which must be disrupted by high stress levels before flow can begin. The gel can reform when stresses are removed. This explains the reduction in extrudate swell in the highly particulate-filled systems. Another hypothesis³⁹ for the systems containing glass fibers is that the oriented fibers or other solid particles have little tendency on their own to disorient on exiting from the die. They are too bulky to be influenced by Brownian motion. Their failure to disorient prevents any significant swell.

CONCLUSION

When plotted against shear stress, the principal normal stress difference $\tau_{11} - \tau_{22}$, determined in steady shearing flow, gives rise to correlations which are

independent of temperature. This is demonstrated to be valid not only for the homopolymers but also for the dispersed multiphase polymer melts. Since both the principal normal stress difference (i.e., the energy stored) and the shear stress (i.e., the energy dissipated) are increased as temperature is decreased (or they are decreased as temperature is increased), it can be concluded from our experimental observations that, temperature seems to have little effect on the ratio of the principal normal stress difference to the shear stress for multiphase polymeric systems.

However, the extrudate swell plotted against shear stress becomes independent of temperature only for the homopolymers and graft copolymers in steady shearing flow. For the mechanically blended multiphase polymer melts, and the particulate-filled systems studied in this work, the temperature independence of extrudate swell does not exist.

For all multiphase polymeric systems studied, both principal normal stress difference and extrudate swell show composition dependence when plotted against shear stress, but the results are quite different. Adding a dispersed phase to a homopolymer always decreases the extrudate swell at any given shear stress. This is not true for the principal normal stress difference which depends on the type of particulate added. Also, the composition dependence of the principal normal stress difference is not as strong as that of extrudate swell. Since the flow in a capillary rheometer is more representative of the flow in most polymer processing operations, such as extrusion and injection molding, than that in a cone-and-plate rheometer, a complete measurement of flow properties of multiphase polymeric systems should include both types of rheometers.

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