

Wall Effects on Flow of Polymer/Particulate/(Carboxylic acid) in Dies and Rheometers

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ABSTRACT: The addition of carboxylic acids to polyolefins results in an apparent slippage flow along rheometer and die walls. In this article, we seek to extend this investigation to polymer/particulate compounds. An experimental study on the influence of carboxylic acid additive in polyethylene/filler and polystyrene/filler compounds in rheometers is described. Capillary and cone-plate experiments are reported. A series of particle fillers of varying character, including carbon black, calcium carbonate, zinc oxide, and talc are compared. The aliphatic fatty acid, octadecanoic

acid, was used as an additive. Significant viscosity reductions were observed. The greatest effects were found in polyethylene/(carbon black) and polystyrene/(calcium carbonate) compounds. All of the polyethylene compounds exhibited slip flow, but the polystyrene compounds did not. Apparently much of the octadecanoic acid was interacting with the polar particle fillers and not with the die wall. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 651–658, 2004

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INTRODUCTION

It has been found by many investigations that amphiphatic (polar, nonpolar) additives compounded into polyolefin thermoplastics migrate to the surfaces.^{1–6} Our own investigations^{7,8} have found that various low molecular weight additives, including fatty carboxylic acids and amides as well as zinc stearate, induce slippage in polyethylene and polypropylene but not in polystyrene and polyamide-12.

Generally industrial compounds possess complex compositions that include many ingredients. Among these ingredients are particles, which enhance the mechanical behavior of polyolefin compounds. Questions arise about the interactions of the ternary system polymer-reinforcing particle-polar additives. This should be especially applicable to systems involving nonpolar thermoplastics with polar mineral fillers and fatty carboxylic acids, which have the possible occurrence of slip.

In the present article, we compare polyethylene and polystyrene compounds with various particulates, ranging from essentially nonpolar carbon black to polar calcium carbonate, zinc oxide, and talc.

EXPERIMENTAL

Materials

In this study, we focused on a series of ternary compounds involving the polymer filler fatty carboxylic

acid. The polymers included in this study are polyethylene (PE) and atactic polystyrene (PS). The fatty carboxylic acid is octadecanoic acid (C₁₈H₃₆O₂). The particle fillers are carbon black (CB), calcium carbonate (CaCO₃), zinc oxide (ZnO), and talc.

PE is an aliphatic polymer, and PS is an aromatic polymer. These polymers were examined in a differential scanning calorimeter. Figure 1 shows the DSC traces, indicating a crystalline melting point of 111°C for PE and a glass transition temperature of 100°C for PS. These thermoplastic polymers are molten and processable in the temperature range of about 180–220°C.

The characteristics of the materials involved in this study are summarized in Table I.

Compounding process

The mineral fillers (0.10 volume fraction) and aliphatic fatty carboxylic acid (0.01 weight fraction) were mixed into each of the individual thermoplastics in a Werner and Pfleiderer ZSK-30 modular co-rotating twin-screw extruder at 200°C and 150 rpm. Thermoplastics and mineral fillers were fed into the first hopper. Carboxylic acid was fed into the second hopper to prevent any slippage during compounding.

Rheological measurements

The shear viscosities of the neat thermoplastics and their binary compounds with particles were determined at low shear rates in a Rheometrics Mechanical Spectrometer (RMS 800) and at higher shear rates in

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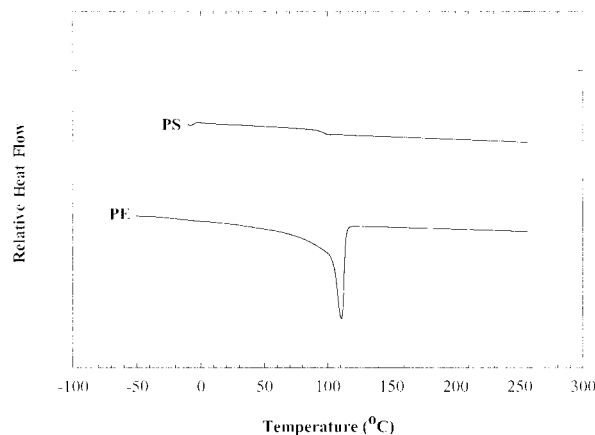


Figure 1 DSC traces for the polymers included in this study at a heat rate of 10°C/min.

an Instron Capillary Rheometer (Instron 3211). A temperature of 200°C was used.

The capillary measurements were made at higher shear rates. The shear stress at the capillary die wall (σ_{12})_w is related to the total pressure (p_T) by^{9,10}

$$p_T = 4(\sigma_{12})_w(L/D) + \Delta p_{\text{ends}} \quad (1)$$

where Δp_{ends} is the sum of pressure losses at the die entrance and die exit, L is the length of the capillary die, and D is the diameter of the capillary die. The die wall shear rate ($\dot{\gamma}_w$), in the absence of wall slippage is^{11,12}

$$\dot{\gamma}_w = \frac{32Q}{\pi D^3} \left(\frac{3n' + 1}{4n'} \right) \quad (2)$$

$$\text{with } n' = \frac{d \log \sigma_w}{d \log (4Q/\pi R^3)}$$

where Q is the extrusion rate, D is the diameter of the capillary die, and σ_w is the shear stress at the capillary die wall.

In many of the experiments, we present the total pressure (p_T) or the shear stress at the capillary die wall (σ_{12})_w measurements as a function of time. This follows the approach of Lee and White^{13,14} and our earlier articles.^{7,8}

For flow in a cone-plate rheometer, the shear stress (σ_{12}) is related to the torque through¹⁵

$$\sigma_{12} = \frac{3M}{2\pi R^3} \quad (3)$$

TABLE I
Materials Included in Study

Thermoplastic Polymers						
Name	Structural unit	T_g (°C)	T_m (°C)	Supplier and grade		
Polyethylene		—	111	Dow Chemical	Dow LDPE 6401	
Atactic polystyrene		100	—	Dow Chemical	Styron 666D	
Fatty Carboxylic Acid						
Name	Structure	M_w (g/mol)	T_m (°C)	T_b (°C)	Supplier	
Octadecanoic acid	CH ₃ (CH ₂) ₁₆ COOH	284.48	67–69	361	Aldrich	
Particle Fillers						
Particle Type	Source	BET surface area (m ² /g)	Particle diameter (μm)			
Carbon black (CB)	Engineered Carbons, Inc.	136.2	0.02			
Calcium carbonate (CaCO ₃)	Specialty Minerals Inc.	19	0.07			
Zinc oxide (ZnO)	Zinc Co. of America	9	0.12			
Talc	Luzenac	13.6	1.50			

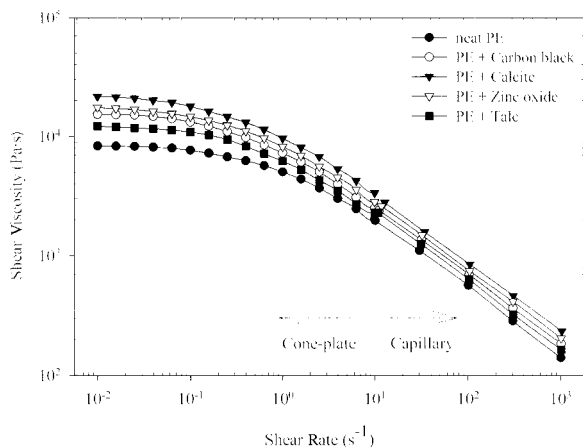


Figure 2 Shear viscosity of polyethylene and its 0.10 vol % compounds with carbon black, calcium carbonate and zinc oxide at 200°C.

where M is the torque and R is the instrument radius. If there is no slip, the shear rate, $\dot{\gamma}$, is essentially

$$\dot{\gamma} = \frac{\Omega}{\alpha} \quad (4)$$

where Ω is the rotation rate and α is the angle between the cone and the plate.

Slippage measurements

When additive induced shear pressure reductions occurred, the magnitude of the die wall slippage was determined. It is possible to determine die wall slippage for capillary measurements using dies of varying diameters. This is obtained from Mooney's expression.¹²

$$v_s = \left. \frac{\partial(Q/\pi R^3)}{\partial(1/R)} \right|_{(\sigma_{12})_w} \quad (5)$$

where v_s is the slip velocity, Q is the extrusion rate, and R is the radius of the capillary die.

Eq. (5) represents the basis of Mooney's method for determining die wall slippage. A series of capillary dies of diameter 1.52, 1.94 and 2.28 mm and L/D ratios of 10, 15, and 30 were used to determine the wall slip.

Long time extrusion experiments

Long time extrusion experiments were conducted on the various compounds and corresponding neat thermoplastics following the methods of Lee and White.^{13,14} The applied total pressure, p_T , from eq. (1), was determined as a function of time. The pressure loss through a capillary die of diameter 1.02 mm and length-diameter ratio of 30.2 was measured. The pres-

sure loss at the ends is negligible for such a long capillary die, and no corrections were made. The extrusion pressure was followed as a function of time. An extrusion rate of 0.032 cm³/s, equivalent to an apparent shear rate ($32Q/\pi D^3$) of 292 s⁻¹ was chosen as the standard condition. It was chosen because this extrusion rate accentuates the extrusion pressure reduction in a reasonable time. Essentially two full barrels of the compound were sequentially extruded.

RESULTS AND DISCUSSION

Shear viscosity of (polymer/particle) binary compounds

The shear viscosities of binary (polymer/particle) compounds of PE are shown in Figure 2. The data from the capillary and cone-plate compounds are consistent. All of the 10 vol % compounds investigated exhibited a constant viscosity (η_0) at low shear rates. At higher shear rates, the viscosity decreased. The level of viscosity increase varied from particle to particle. The greatest viscosity increase occurred with calcium carbonate, and the least with talc.

The shear viscosities of the binary compounds of PS are shown in Figure 3. These are similar to those for PE. The small particles enhanced the shear viscosity, with the smallest increases occurring for talc and the largest for calcium carbonate.

Long time extrusion experiments

PE/particle/(carboxylic acid) compounds

The total pressure (p_T) or the shear stress at the capillary die wall (σ_{12}) of PE/(particle filler)/(carboxylic acid) compounds are shown as a function of time in Figure 4(a-d). The discontinuity in the shear stress

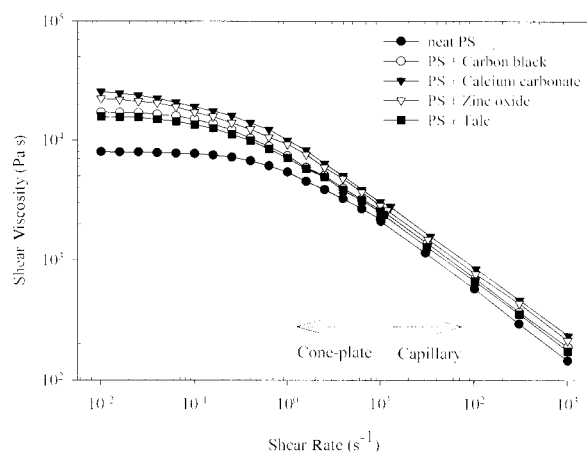


Figure 3 Shear viscosity of polystyrene and its 0.10 vol % compounds with carbon black, calcium carbonate and zinc oxide at 200°C.

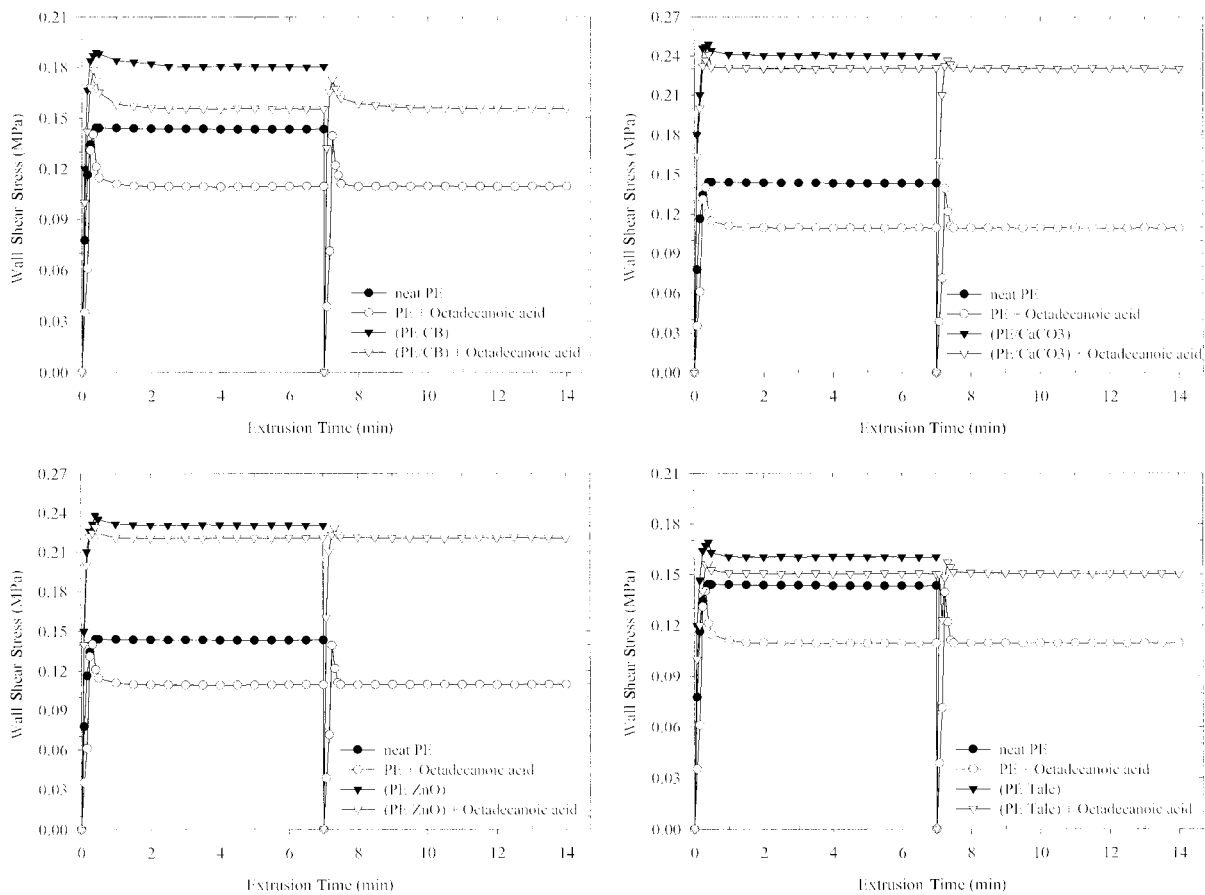


Figure 4 Wall shear stress as a function of time for polyethylene compounds: (a) polyethylene, polyethylene/(carbon black) (10 vol %), polyethylene/(carbon black) (10 vol %)/(carboxylic acid) (1 wt %); (b) polyethylene, polyethylene/(calcium carbonate) (10 vol %), polyethylene/(calcium carbonate) (10 vol %)/(carboxylic acid) (1 wt %); (c) polyethylene, polyethylene/(zinc oxide) (10 vol %), polyethylene/(zinc oxide) (10 vol %)/(carboxylic acid) (1 wt %); (d) polyethylene, polyethylene/talc (10 vol %), polyethylene/(carboxylic acid) (1 wt %); and polyethylene/talc (10 vol %)/(carboxylic acid) (1 wt %). Diameter of capillary = 1.04 mm, L/D ratio = 30.2, temperature = 200°C.

(σ_{12}) is associated with refilling the rheometer barrel. Figure 4(a) compares shear stress values for PE, PE/CB compounds and their compounds with octadecanoic acid. The value of the shear stress (σ_{12}) increases with CB content (0.10 vol %). The reduction for PE due to the octadecanoic acid was 23%, and for the PE/CB it was 15%.

A similar plot for the calcium carbonate compound is given in Figure 4(b). There are significant differences among the behaviors of the various compounds. The behavior of the PE/ CaCO_3 compound is quite different from that of the others. The addition of octadecanoic acid leads to almost no reduction in the pressure and shear stress.

The behavior of the (carboxylic acid)/(zinc oxide)/PE compound is shown in Figure 4(c). The level of reduction of the pressure/shear stress of the compound when the carboxylic acid is added to the compound is much smaller than the reduction in the CB compound. It is similar to the CaCO_3 /PE compound.

The behavior of the (carboxylic acid)/talc/PE compound is shown in Figure 4(d). Again the level of the shear stress is reduced when the carboxylic acid is introduced. The level of reduction is small and similar to that of the CaCO_3 and ZnO compounds.

PS/particle/(carboxylic acid) compounds

The shear stress (σ_{12}) behavior of the PS compounds is shown in Figure 5(a–d). The results are quite different from those for the PE compounds. The carboxylic acid has little or no effect on PS or PS/CB compounds, as shown in Figure 5(a).

The situation is quite different for the PS/(calcium carbonate) compounds. Here, the carboxylic acid produces a significant viscosity reduction for the compound, as shown in Figure 5(b). The level of reduction is 10%, compared to about 4.5% for the neat PS/(carboxylic acid) compound. There are also some re-

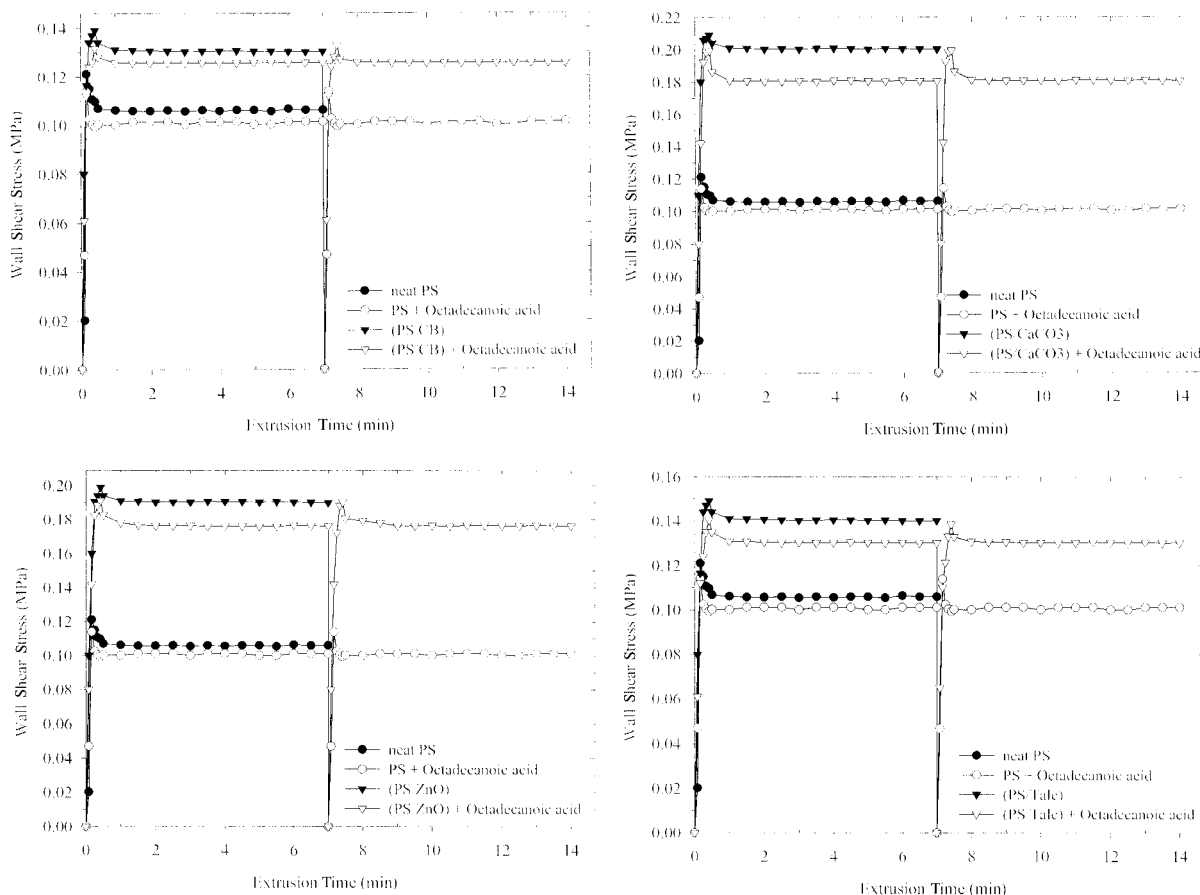


Figure 5 Wall shear stress as a function of time for polystyrene compounds: (a) polystyrene, polystyrene/(carbon black) (10 vol %), polystyrene/(carboxylic acid) (1 wt %) and polystyrene/(carbon black) (10 vol %)/(carboxylic acid) (1 wt %); (b) polystyrene, polystyrene/(calcium carbonate) (10 vol %), polystyrene/(carboxylic acid) (1 wt %) and polystyrene/(calcium carbonate) (10 vol %)/(carboxylic acid) (1 wt %); (c) polystyrene, polystyrene/(zinc oxide) (10 vol %), polystyrene/(carboxylic acid) (1 wt %) and polystyrene/(zinc oxide) (10 vol %)/(carboxylic acid) (1 wt %); (d) polystyrene, polystyrene/talc (10 vol %), polystyrene/(carboxylic acid) (1 wt %); and polystyrene/talc (10 vol %)/(carboxylic acid) (1 wt %). Diameter of capillary = 1.04 mm, L/D ratio = 30.2, temperature = 200°C.

ductions for the zinc oxide and talc compounds [Fig. 5(c,d)].

The behavior of the PS compounds differs from that of the PE compounds. The carboxylic acids produce no reduction in the shear stress (σ_{12}) for PS. This difference also applies to the CB compound, but the calcium carbonate and, to a lesser extent, zinc oxide and talc, exhibit significant viscosity reductions.

Cone-plate rheometer studies

PE/particle/(carboxylic acid) compounds

Values of torque (M) or shear stress (σ_{12}) as a function of apparent shear rate (Ω/α) are shown in Figure 6(a–d) for the various PE compounds. Figure 6(a) compares PE and PE/CB to the carboxylic acid containing carboxylic acid. Torque is increased by the addition of CB, but the carboxylic acid similarly re-

duces it for both PE and its compounds. Figure 6(b) is a similar comparison for the PE/(calcium carbonate) compound. The addition of calcium carbonate increases the torque of PE, but both are reduced by the addition of carboxylic acid. The extent of reduction of calcium carbonate is less than that of the CB compound. This behavior is also seen for zinc oxide and talc [Fig. 6(c,d)].

PS/particle/(carboxylic acid) compounds

Values of torque (M) or shear stress (σ_{12}) as a function of apparent shear rate (Ω/α) are presented for the various PS compounds in Figure 7(a–d). The addition of CB increases the torque, but when the carboxylic acid is introduced there is little change in torque for either the PS or the PS compounds [Fig. 7(a)]. The situation is different for the calcium carbonate compound. Here again the addition of carboxylic acid

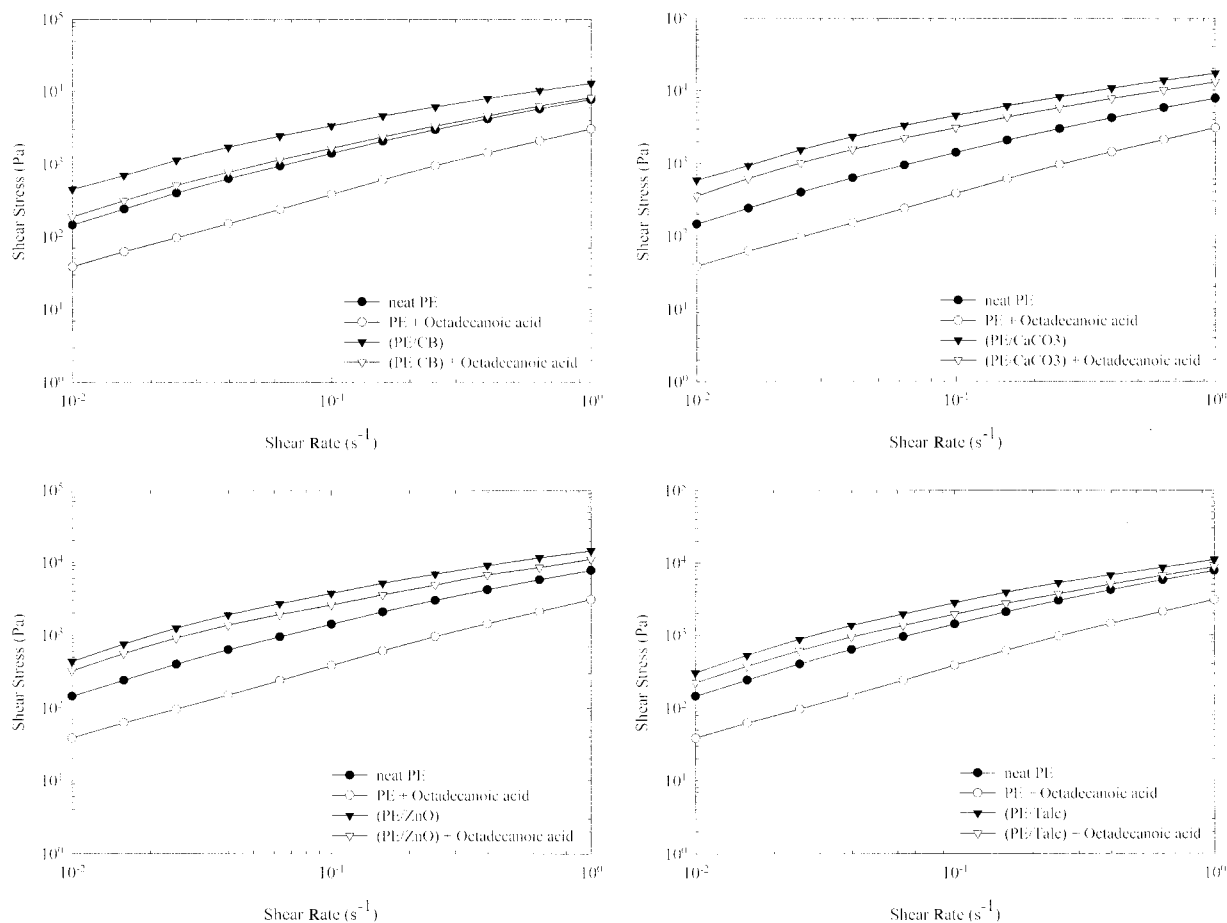


Figure 6 Shear stress as a function of Ω/α for polyethylene compounds: (a) polyethylene, polyethylene/(carbon black) (10 vol %), polyethylene/(carboxylic acid) (1 wt %) and polyethylene/(carbon black) (10 vol %)/(carboxylic acid) (1 wt %); (b) polyethylene, polyethylene/(calcium carbonate) (10 vol %), polyethylene/(carboxylic acid) (1 wt %) and polyethylene/(calcium carbonate) (10 vol %)/(carboxylic acid) (1 wt %); (c) polyethylene, polyethylene/(zinc oxide) (10 vol %), polyethylene/(carboxylic acid) (1 wt %) and polyethylene/(zinc oxide) (10 vol %)/(carboxylic acid) (1 wt %); (d) polyethylene, polyethylene/talc (10 vol %), polyethylene/(carboxylic acid) (1 wt %); and polyethylene/talc (10 vol %)/(carboxylic acid) (1 wt %). Temperature = 200°C.

significantly reduces the torque [Fig. 7(b)]. There is little torque reduction for the zinc oxide and talc compounds [Fig. 7(c,d)].

Slippage studies

We have experimentally measured slippage for the various polymer/(particle filler)/(carboxylic acid) binary and ternary compounds. Figure 8 plots $(4Q/\pi R^3)$ against $(1/R)$ at constant wall shear stress $(\sigma_{12})_w$ for PE, PE/CB, PE/(carboxylic acid) and ternary PE/CB/(carboxylic acid) compound.

We have calculated slip velocities from data, such as those in Figure 9, for the various compounds considered in this article. Generally, PE, PS and their binary compounds with particle fillers exhibit no die wall slip. When carboxylic acid is introduced, the situation changes for PE compounds. PS compounds with carboxylic acid exhibit no slippage. In Figure 9, we plot

slip velocity for the PE/CB/(carboxylic acid) system. PE and its CB compound exhibit no slip, but both systems with the carboxylic acid do exhibit slip.

The levels of slip in the PE/(octadecanoic acid)/(CaCO₃, ZnO, or talc) systems are less than those found in the PE and PE/CB systems. The differences are summarized in Table II, where we present the slip velocities for PE/(carboxylic acid) and various ternary systems with particulates.

Discussion

We have found in this study, as has been found by previous investigators,¹⁶⁻¹⁹ that carbon black, calcium carbonate, talc, and zinc oxide all increase the viscosity of PE and PS melts. We have made a comparative study of the influence of octadecanoic acid on the flow properties of the neat polymer and its compounds. It was found that octadecanoic acid reduces the appar-

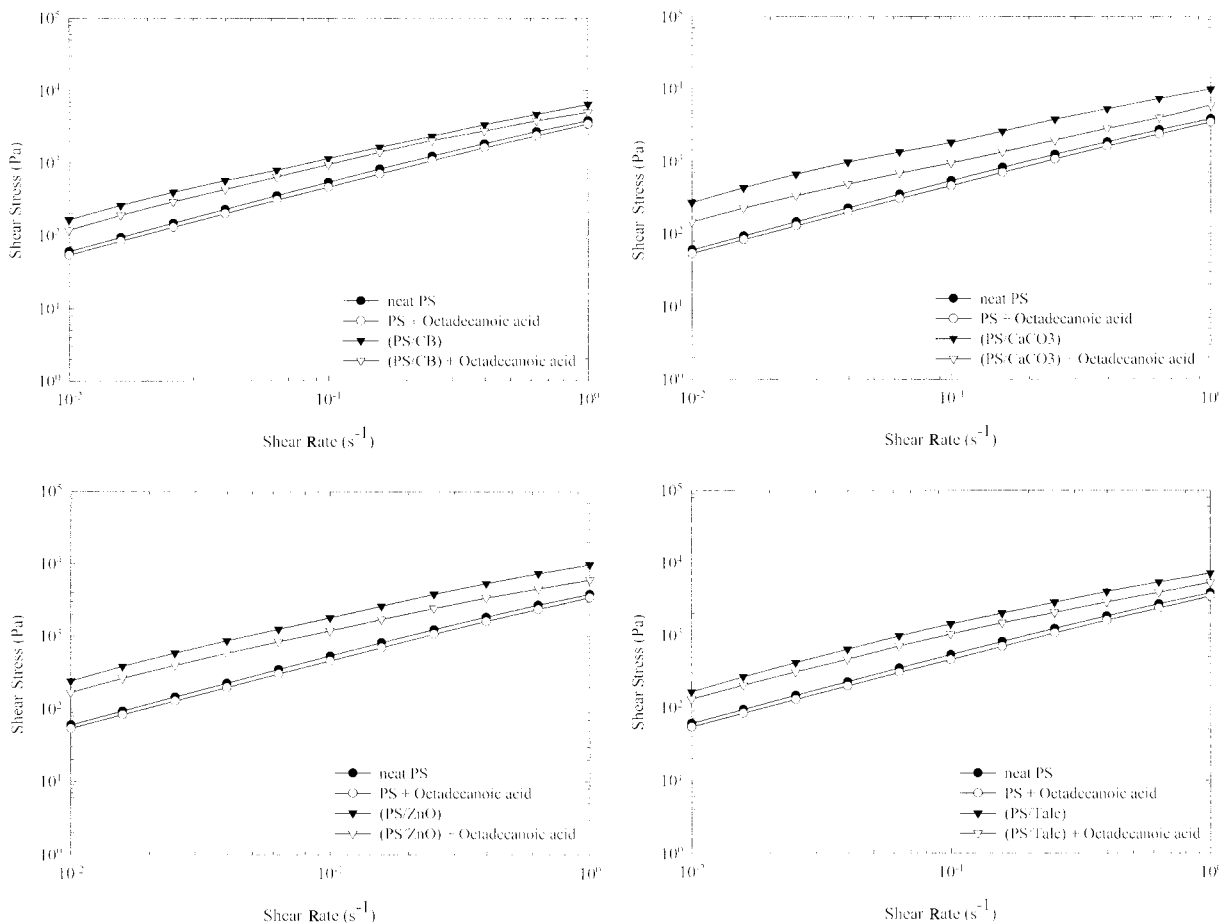


Figure 7 Shear stress as a function of Ω/α for polystyrene compounds: (a) polystyrene, polystyrene/(carbon black) (10 vol %), polystyrene/(carboxylic acid) (1 wt %) and polystyrene/(carbon black) (10 vol %)/(carboxylic acid) (1 wt %); (b) polystyrene, polystyrene/(calcium carbonate) (10 vol %), polystyrene/(carboxylic acid) (1 wt %) and polystyrene/(calcium carbonate) (10 vol %)/(carboxylic acid) (1 wt %); (c) polystyrene, polystyrene/(zinc oxide) (10 vol %), polystyrene/(carboxylic acid) (1 wt %) and polystyrene/(zinc oxide) (10 vol %)/(carboxylic acid) (1 wt %); (d) polystyrene, polystyrene/talc (10 vol %), polystyrene/(carboxylic acid) (1 wt %); and polystyrene/talc (10 vol %)/(carboxylic acid) (1 wt %). Temperature = 200°C.

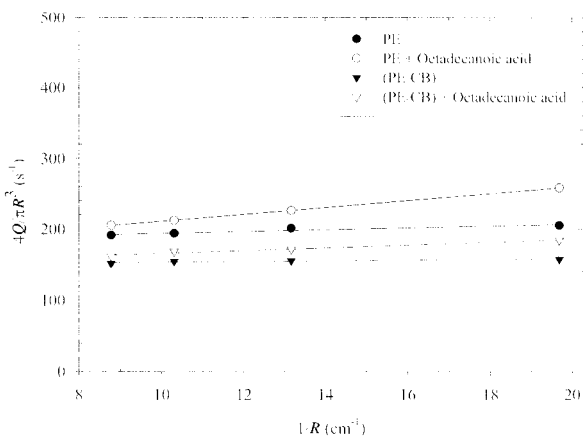


Figure 8 $(4Q/\pi R^3)$ versus $(1/R)$ data from capillary dies of varying diameter for polyethylene, polyethylene/(carbon black) (10 vol %), polyethylene/(carboxylic acid) (1 wt %), and polyethylene/(carbon black) (10 vol %)/(carboxylic acid) (1 wt %) at constant stress (0.1 MPa). Temperature: 200°C.

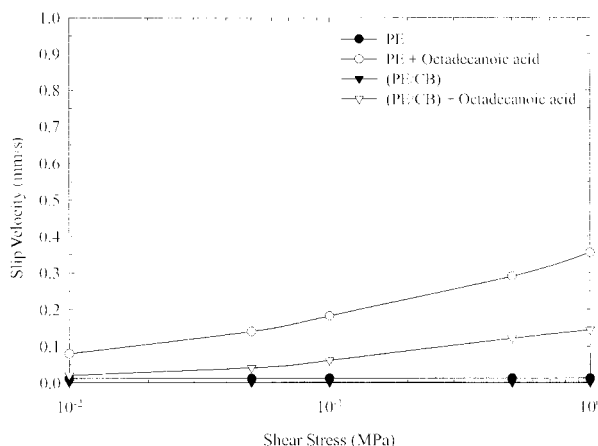


Figure 9 Slip velocity versus wall shear stress from a capillary rheometer for polyethylene, polyethylene/(carbon black) (10 vol %), polyethylene/(carboxylic acid) (1 wt %), and polyethylene/(carbon black) (10 vol %)/(carboxylic acid) (1 wt %) at 200°C.

TABLE II
Slip Velocities for Polyethylene and Polystyrene
Compounds with Octadecanoic Acid ($\sigma = 0.1$ MPa).

Systems	Slip velocity (mm/s)
Polyethylene	0
Polystyrene	0
Polyethylene/C ₁₇ H ₃₅ COOH	0.182
Polystyrene/C ₁₇ H ₃₅ COOH	0
Polyethylene/(carbon black)/C ₁₇ H ₃₅ COOH	0.061
Polyethylene/CaCO ₃ /C ₁₇ H ₃₅ COOH	0.036
Polyethylene/ZnO/C ₁₇ H ₃₅ COOH	0.038
Polyethylene/talc/C ₁₇ H ₃₅ COOH	0.042
Polystyrene/(carbon black)/C ₁₇ H ₃₅ COOH	0
Polystyrene/CaCO ₃ /C ₁₇ H ₃₅ COOH	0
Polystyrene/ZnO/C ₁₇ H ₃₅ COOH	0
Polystyrene/talc/C ₁₇ H ₃₅ COOH	0

ent shear viscosity of PE and PE/CB compounds significantly and, to a lesser extent, that of CaCO₃, ZnO, and talc compounds as well. The octadecanoic acid had no effect on the apparent viscosity of PS or its CB compounds. The CaCO₃/PS notably and, to a lesser extent, the ZnO and talc compounds, exhibited apparent viscosity reductions with the introduction of octadecanoic acid. These results for PE and PS and their compounds are intriguing in their apparent contradictions. There is evidence to support the migration of octadecanoic acid to the die walls in polymers, and there is also the evidence to support the interference of fillers with migration, as shown in Figures 4, 5, 6, and 7.

It had been shown in our previous studies^{7,8} that the addition of octadecanoic acid (and other carboxylic acids, amides, and zinc stearate) induce die wall slippage in PE but not in PS. This development of slippage in PE must be due to the migration of octadecanoic acid into the die walls. The results shown in Table II

thus strongly suggest that compounds with fillers, notably CaCO₃, ZnO, and talc, interfere with the migration of octadecanoic acid through PE into the die wall. Thus, they must reduce slippage.

The reduction in viscosity of the PS compounds, notably with CaCO₃, but also with ZnO and talc, would seem to elucidate this interference. The octadecanoic acid seems to associate itself with these well-dispersed minerals as a surfactant. Interparticle networks are broken up by the octadecanoic acid surfactant.

Octadecanoic acid and similar substances such as stearic acid seem to act as agents outside the control of the compound designer. They can act in some cases to induce slip and in others to break up particle networks, as shown here and elsewhere.^{16,18} They may also act as emulsifying agents in blends.²⁰

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