Influence of Carboxylic Acid Additives on the Flow Behavior of Molten Thermoplastics

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ABSTRACT: Following the suggestions of the behavior of carboxylic acid lubricants between steel surfaces and the wide usage of such acids in polymer compounds, we have considered their influence as an additive in polymer melts. An experimental study of the influence of carboxylic acid additives in various thermoplastics in rheometers is described. Capillary and cone-plate experiments are reported. A series of polymers of varying polarity, including polyethylene, poly(propylene), polystyrene, poly(methyl methacrylate), and polyamide-12, are compared. Both aliphatic fatty acids and aromatic carboxylic acids were used as additives. The aliphatic fatty acids include propionic acid, octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, eicosanoic acid, and commercial stearic acid (mixture of tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, and octadecanoic acid). The aromatic carboxylic acids include benzoic acid, *p*-toluic acid, and 3-phenylpropionic acid. The greatest effects were found with polyethylene and poly(propylene). Little or no effects were found with the other polymers. Aliphatic fatty acids were more effective than aromatic carboxylic acids. Mechanisms for this behavior are discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1555–1564, 2003

Key words: carboxylic acid additive; polyethylene (PE); poly(propylene) (PP); shear stress; slip velocity

INTRODUCTION

The mechanism of lubrication of steel machinery received considerable attention in the late 19th and early 20th centuries. Reynolds[1] showed that for relatively thick films (from a fraction of a millimeter to a few millimeters thick) Newtonian hydrodynamics is in the form of what we now call hydrodynamic lubrication. This phenomenon could be explained by the development of large pressures between small clearances. It was subsequently found by Hardy and Doubleday[2] that when the clearances between surfaces becomes quite small (~400 μm and smaller), the chemical nature of the lubricant becomes quite important. These authors found that aliphatic alcohols had lower coefficients of friction than paraffins and that aliphatic acids had still lower coefficients of friction. Generally, the coefficient of friction decreased with increasing molecular weight of the lubricant. In a subsequent paper,[3] they note that this behavior continues until higher temperatures are reached. The observations of Hardy and Doubleday were confirmed by Beare and Bowden,[4] Bowden and Leben,[5] and Bowden et al.[6] Subsequently, using artificial radioactive metal foils, Bowden and Moore[7] concluded that the source of the low friction of carboxylic acids with metals was a chemical reaction of the adjacent layer of the carboxylic acid with the metal surface.

In the polymer industry, fatty organic compounds have long been used, sometimes as processing aids, in compounds. Apparently, because of industrial secrecy and perhaps because of the complicated nature of recipes, which hide mechanisms, there seems little in the way of published systematic studies on these compounds. Stearic acid seems almost always to be included in recipes for rubber compounds, but its influence is usually ascribed to being involved in the vulcanization reaction. We note the work of Turner and Moore,[8] who seriously considered the influence of stearic acid on the extrusion of rubber compounds and hypothesized slippage. Recently, we made an investigation of the ability of various 18-carbon atom 'fatty' organic compounds to induce slippage.[9] Octadecanoic acid, zinc stearate, and octadecanamide were the most effective, and octadecanol, calcium stearate, and octadecane were relatively ineffective.

In the present article, we present a study comparing different carboxylic acids (both aliphatic and aromatic) as additives into various different thermoplastics and their influence on the flow characteristics. This critical study is the first of its type comparing the influence of different carboxylic acids on various thermoplastics.

EXPERIMENTAL

Materials

The five thermoplastics used in this investigation, polyethylene (PE), isotactic poly(propylene) (PP), atactic polystyrene (PS), atactic poly(methyl methac-

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TABLE I
Polymers Included in this Study

Name	Structural unit	T_g (°C)	T_m (°C)	Supplier	Grade
Polyethylene	$-[CH_2-CH_2]-_n$	—	111	Dow Plastics	Dow LDPE 6401
Isotactic polypropylene	$-[CH_2-CH(CH_3)]-_n$	−18	166	Equistar Chemical Company	Petrothene PP8000-GK
Atactic polystyrene	$-[CH_3-CH(C_6H_5)]-_n$	100	—	Dow Plastics	Styron 666D
Polymethyl metacrylate	$-[CH_2-C(CH_3)(COOCH_3)]-_n$	116	—	Rohm & Hass	Plexiglas V-825
Polyamide-12	$-[N(H)-(CH_2)_{11}-CH(=O)]-_n$	32	179	Ube Industries Inc.	3024U

rylate) (PMMA), and polyamide-12 (PA12), are listed in Table I with their structures, nominal characteristics and sources. These polymers were examined by differential scanning calorimetry (DSC). The DSC traces shown in Figure 1 indicate crystalline melting points (T_ms) for PE (111°C), PP (166°C), and PA12 (179°C) and glass transition temperatures (T_gs) for PS (100°C) and PMMA (116°C). All of these polymers are molten and processable in the temperature range 180–220°C.

Various aliphatic carboxylic acids were used as additives. The range of aliphatic carboxylic acids is from propionic acid (C_3H_5OOH) to eicosanoic acid ($C_{20}H_{37}OOH$). The various aromatic carboxylic acids used are summarized in Table II with their chemical structures and Tms.

Shear viscosity

The shear viscosities of the five neat thermoplastics were determined at low shear rates in a Rheometrics
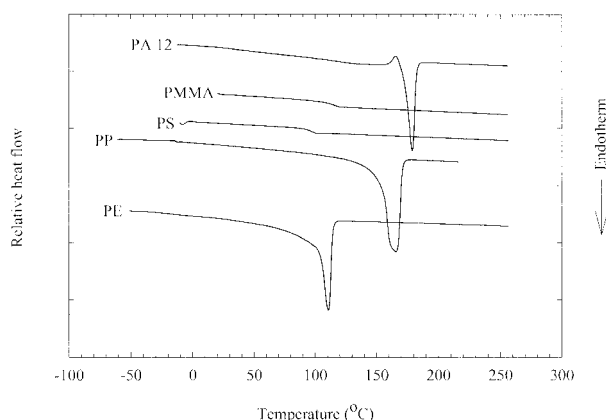

Figure 1 DSC traces for the polymers included in this study (heating rate = 10°C/min).

Mechanical Spectrometer (RMS 800) and at higher shear rates in an Instron Capillary Rheometer (Instron 3211). A temperature of 200°C was used.

Blend process

The various carboxylic acids (1.0 wt %) 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.

Rheological measurements

The five neat thermoplastics were rheologically characterized over a wide range of shear rates. Measurements at low shear rates, made in the cone-plate mode with a mechanical spectrometer at 200°C, were used to calculate shear stress, σ_{12}, as[10]

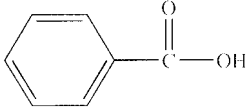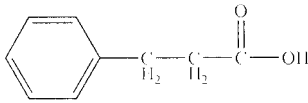$$\sigma_{12} = \frac{3M}{2\pi R^3} \quad (1)$$

where M is torque and R is the radius of the cone or plate. In the absence of slip, the shear rate is given by

$$\dot{\gamma} = \frac{\Omega}{\alpha} \quad (2)$$

where Ω is the rotation rate and α is the cone angle. Equations (1) and (2) were used to obtain the shear viscosity, $\eta = (\sigma_{12}/\dot{\gamma})$.

Measurements at higher shear rates, made in a capillary instrument, were used to determine shear stress by the method of Bagley,[11] with total pressure, p_T, calculated by

TABLE II
Carboxylic Acids Investigated in this Study

Carboxylic acid type	Chemical name[a]	Structure	M_w (g/mol)	Melting point (°C)
Aliphatic	Propionic acid	$CH_3(CH_2)CO_2H$	74.08	−24
	Octanoic acid	$CH_3(CH_2)_6CO_2H$	142.22	16
	Decanoic acid	$CH_3(CH_2)_8CO_2H$	172.27	30–32
	Dodecanoic acid	$CH_3(CH_2)_{10}CO_2H$	200.32	44
	Tetradecanoic acid	$CH_3(CH_2)_{12}CO_2H$	228.38	54–55
	Hexadecanoic acid	$CH_3(CH_2)_{14}CO_2H$	256.43	61–62
	Octadecanoic acid	$CH_3(CH_2)_{16}CO_2H$	284.48	67–69
	Eicosanoic acid	$CH_3(CH_2)_{18}CO_2H$	312.54	74–76
	Stearic acid	$CH_3(CH_2)_{12\approx16}CO_2H$	268.77	70
Aromatic	Benzoic acid		122.12	122–123
	3-Phenylpropionic acid		150.18	47–49
	p-Toluic acid		136.15	180–182

[a] All chemicals supplied by Aldrich except stearic acid, which was supplied by Akrochem Company.

$$p_T = 2\sigma_{12}(R)\frac{L}{R} + \Delta p_{ends} \quad (3)$$

The shear rate at the die wall is derived from the work of Weissenberg[12] and Mooney[13] who showed that

$$\frac{Q}{\pi R^3} = \frac{1}{(\sigma_{12})_w^3}\int_0^{(\sigma_{12})_w}\sigma_{12}^2\left(-\frac{dv_1}{dr}\right)d\sigma_{12} + \frac{v_s}{R} \quad (4)$$

where v_s is the slip velocity.

If slip is neglected ($v_s = 0$), one may evaluate the wall shear rate by differentiating eq. (4) with respect to $(\sigma_{12})_w$. This procedure leads to

$$\dot\gamma = \left(-\frac{dv_1}{dr}\right)_w = \frac{4Q}{\pi R^3}\left(\frac{3n'+1}{4n'}\right) \quad (5)$$

with

$$n' = \frac{d\log\sigma_w}{d\log(4Q/\pi R^3)} \quad (6)$$

A series of capillary dies of length/diameter (l/d) ratios of 9.3, 19.3, and 28.5 and diameter of 1.59 mm were used to obtain the die wall shear stress, shear rate, and viscosity (η).

Capillary rheometer measurements on thermoplastic–carboxylic acid additives

Long-time extrusion experiments were made on the various compounds and corresponding neat thermoplastics. The applied pressure, p_T, of eq. (4) 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 end pressure losses were 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. This extrusion rate was chosen because it accentuates the extrusion pressure reduction in a reasonable time.

Slippage experiments

When particular additives induced shear pressure reductions, the magnitude of die wall slippage was determined by the procedure of Mooney,[13] using dies of different diameter. According to Mooney, if slip occurs in a capillary rheometer, the extrusion rate Q may be written in the form of eq. (4). The first term on the left-hand side of this equation depends on $(\sigma_{12})_w$ only. If we differentiate eq. (4) with respect to $(1/R)$ at constant $(\sigma_{12})_w$, we obtain
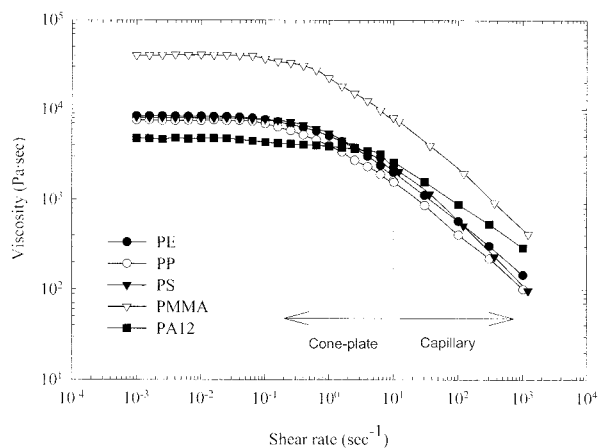
Figure 2 Shear viscosity versus shear rate data for the neat polymers included in this study (measuring temperature = 200°C).

$$\left.\frac{\partial\left(\dfrac{Q}{\pi R^3}\right)}{\partial\left(\dfrac{1}{R}\right)}\right|_{(\sigma_{12})_w} = v_s \qquad (7)$$

Equation (7) represents the basis of Mooney's method for determining die wall slip. 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.

RESULTS

Shear viscosity of neat thermoplastics

The shear viscosity data for the neat thermoplastics used in this study are shown in Figure 2. All the melts exhibit zero shear viscosities at low shear rates and decreasing shear viscosities at higher shear rates. Experiments with capillaries of different diameter gave no indication of slip.

Capillary rheometer pressure–time traces

The capillary rheometer pressure–time traces for the various polymer melts and their carboxylic acid compounds (listed in Table II) are shown in Figures 3 and 4. The characteristics of pressure versus time for PE and its compounds with various carboxylic acids [Figs. 3(a) and 4(a)] include a discontinuity in pressure that is associated with refilling the rheometer barrel. For the neat PE, the pressure builds up to a steady state and then maintains that value. For the compounds, the pressure builds up to a steady value and then decreases gradually to a newer steady state. The compounds contain aliphatic carboxylic acids such as propionic acid, octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid,

hexadecanoic acid, octadecanoic acid, and eicosanoic acid. We include commercial stearic acid (Akrochem Company), which is a mixture of ~52% hexadecanoic acid, 44% octadecanoic acid, 2.5% heptadecanoic acid, 1% tetradecanoic acid, and 0.5% pentadecanoic acid. We also include other carboxylic acids, notably the aromatic carboxylic acids: benzoic acid, *p*-toluic acid, and 3-phenylpropionic acid. It is evident that the aliphatic and the aromatic carboxylic acids both produce significant reductions in pressure and therefore shear stress.

The behavior of PP in this experiment is shown in Figures 3b and 4b. As in the case of PE, the pressure build up shows an overshoot and then goes to a steady state for neat PP. For the compounds, the pressure reaches a maximum and then decreases to a new lower steady state. The greatest reductions of shear stress are for the aliphatic fatty acids. The aromatic carboxylic acids have little effect.

The pressures for the neat PS, PMMA, and PA12, shown in Figures 3(c), (d), and (e), respectively, all exhibit pressure buildup overshoot and steady state. The compounds with aliphatic carboxylic acids, also shown in Figures 3(c), (d), and (e), have much smaller levels of pressure reduction for PS, PMMA, and PA12. Of these three melt systems, the additives show the greatest reductions with PMMA and the least with PA12. The results of measurements of these thermoplastics with aromatic acids, shown in Figures 4(c), (d), and (e), are again the greatest with PMMA and the least with PA12.

Cone-plate shear stresses of carboxylic acid–polymer melt compounds

The apparent shear stresses ($3M/2\pi R^3$) from cone-plate experiments of the five neat thermoplastics with 1% carboxylic acid levels were determined. Large levels of shear stress reduction are found for the PE and PP compounds, as shown in Figures 5(a, b) and 6(a,b), respectively The levels of reduction are much smaller for the PS, PMMA, and PA12. The behavior of PS is shown in Figures 5(c) and 6(c).

For both the PE and PP, the greatest shear stress reductions are for the aliphatic carboxylic acids. The aromatic carboxylic acids are also effective, especially for the PE but not for the PP.

Mooney slippage measurements

The results shown in Figures 3–6 suggest the existence of slippage at the walls of both the capillary and cone-plate rheometer when the additives are present. This suggestion led us to carry out experiments with capillary dies of varying diameter. Following the method of Mooney,[13] $Q/\pi R^3$ versus $1/R$ at constant $(\sigma_{12})_w$ is plotted in Figure 7 for PE and its compounds with various carboxylic acids (given in
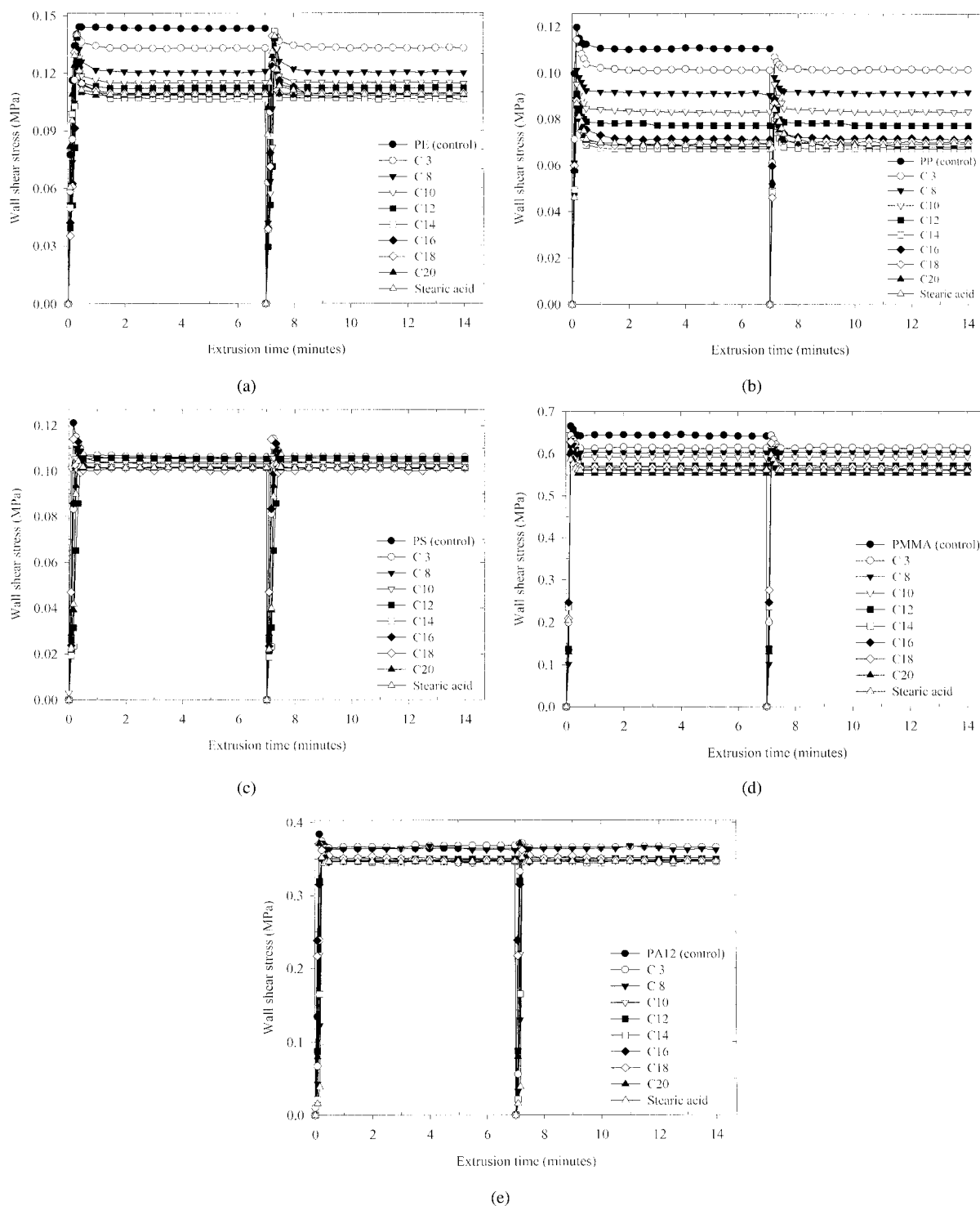
Figure 3 Wall shear stress as a function of time for extrusion from capillary rheometer of (a) polyethylene, (b) poly(propylene), (c) polystyrene, (d) poly(methyl methacrylate), and (e) polyamide-12 containing aliphatic carboxylic acid additives at 1% level (diameter of capillary = 1.04 mm, l/d = 30.2; temperature = 200°C).

Table II). Large slopes indicating slippage are observed. Similar behavior is shown for PP, but PS, PMMA, and PA12 show little or no slippage.

Slip velocities (v_s) versus shear stress for PE and PP are contained in Figures 8(a) and 8(b), respectively. It is evident that the aliphatic carboxylic acids with >10 carbon atoms induce the greatest slippage for PE and PP. The aromatic carboxylic acids also induce noticeable slippage for PE and PP, as shown in Figures 9(a) and 9(b). The level of slippage for PA12 is nonexistent. The levels of slippage for PS and PMMA are small. However, slippage clearly exists for aliphatic carboxylic acids in PMMA and PS.
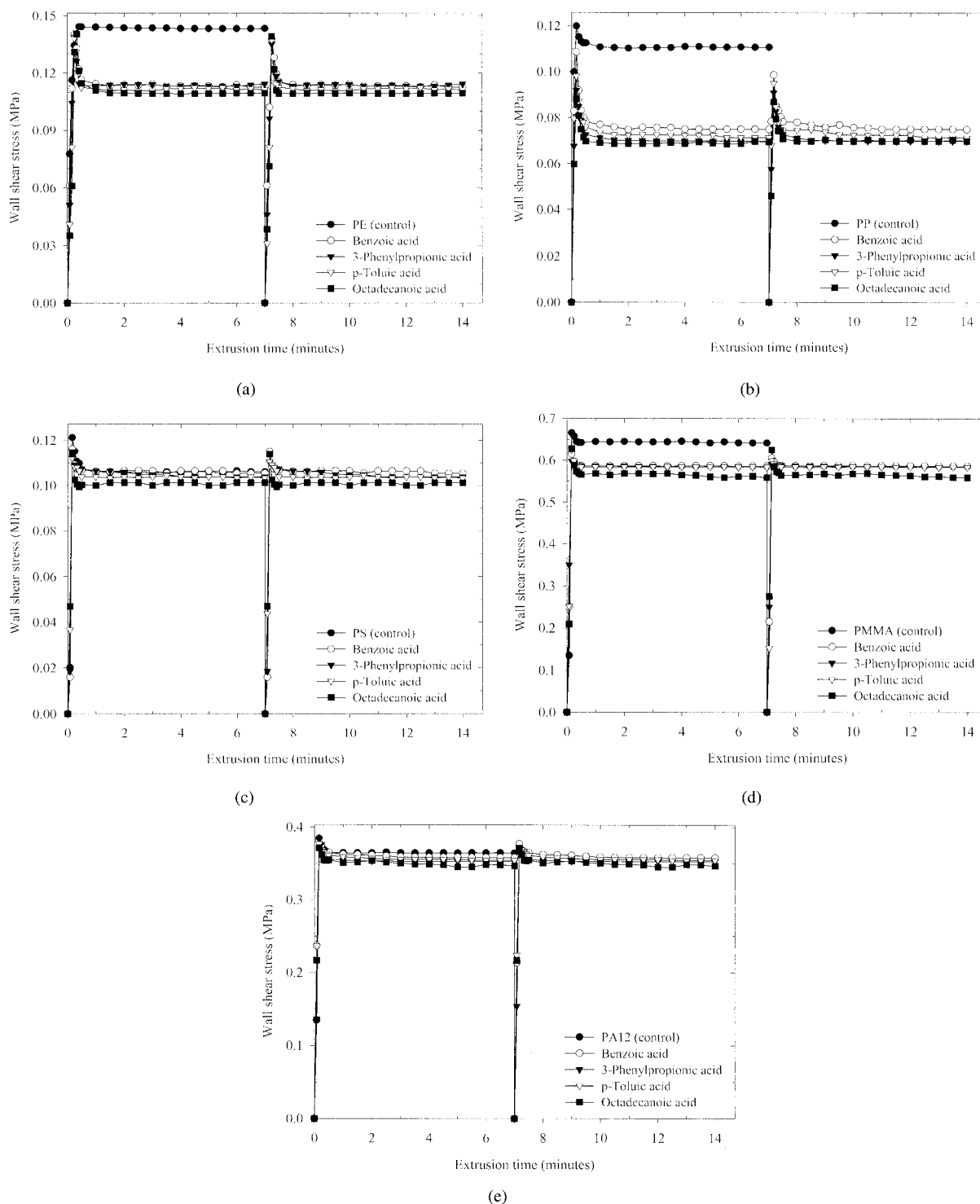
Figure 4 Wall shear stress as a function of time for extrusion from capillary rheometer of (a) polyethylene, (b) poly(propylene), (c) polystyrene, (d) poly(methyl methacrylate), and (e) polyamide-12 containing aromatic carboxylic acid additives at 1% level (diameter of capillary = 1.04 mm; l/d = 30.2; temperature = 200°C).

DISCUSSION

Occurrence of slippage

Observations of slippage in extrusion of polymer melts began in the 1960s with studies of fluoropolymers[14] and high-density PEs.[14,15] These observations are connected with unstable flow. The literature has had a rebirth in the late 1980s and 1990s, with several articles about linear low-density PEs.[16-18] Vinogradov et al.[19,20] have observed slip in polyisoprene and polybutadiene under similar conditions. It was also observed that elastomers at low applied pressures exhibited slip.[21,22]

There has been a limited literature on additives inducing slippage in the literature. We have already
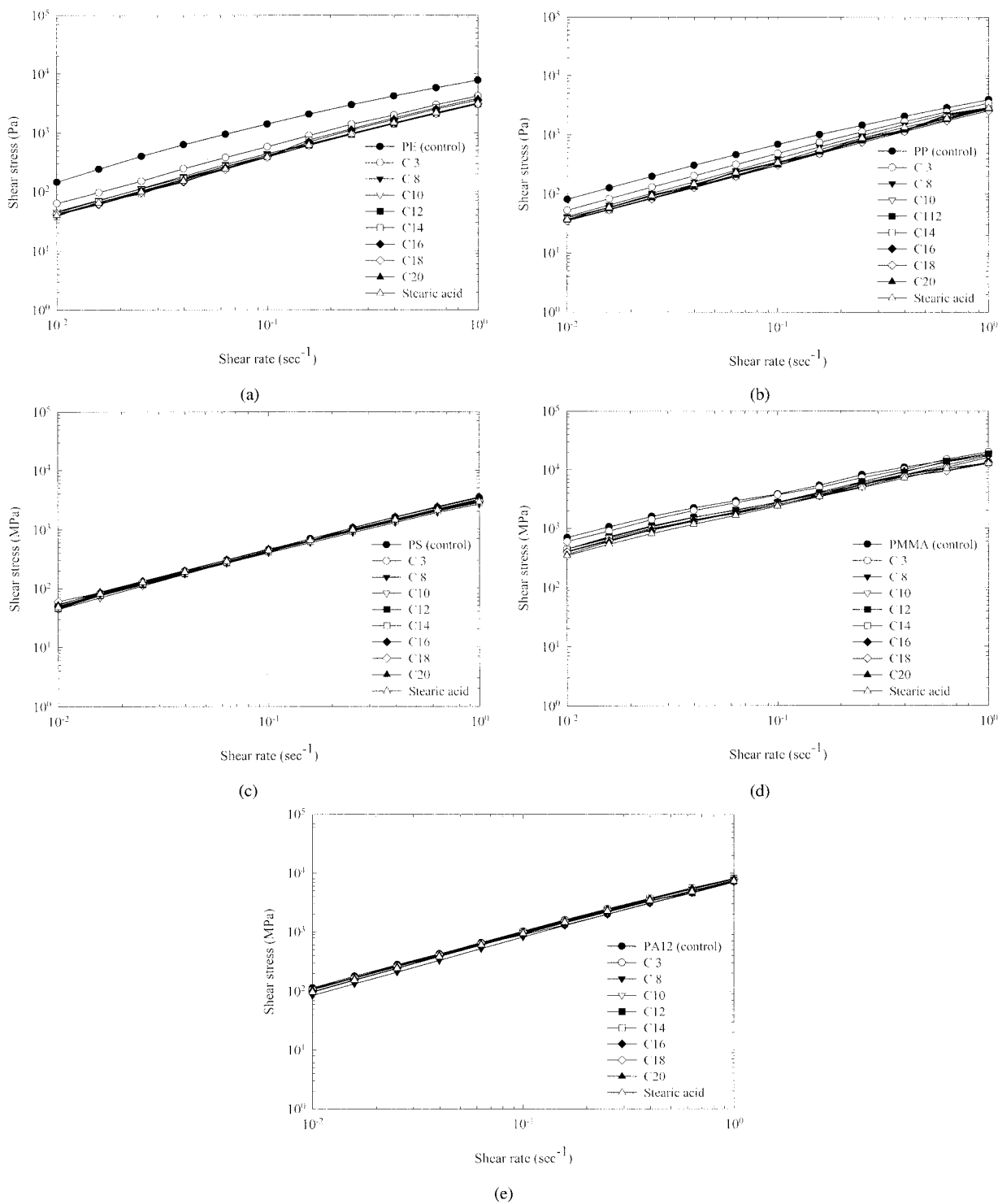
Figure 5 a Reduction in apparent shear stress in cone-plate instrument of (a) polyethylene, (b) poly(propylene), (c) polystyrene, (d) poly(methyl methacrylate), and (e) polyamide-12 containing aliphatic carboxylic acids at 1% level (measuring temperature = 200°C).

mentioned the work of Turner and Moore[8] with stearic acid in rubber compounds. The precipitation of fluoropolymers on die surfaces and its ability to induce slip in PE over a very wide range of conditions has been described by various authors[23–27] in recent years. Reports of slippage with polymers other than

PE are scarce. Lee and White[25,26] found fluoropolymer additives were effective for PE but not for PS or PA12.

The mechanism of slippage in the flow of polymer melts through dies is the loss of adhesion to the die wall. This mechanism has been proposed by various researchers.[23,24,28] It would therefore seem reasonable that the
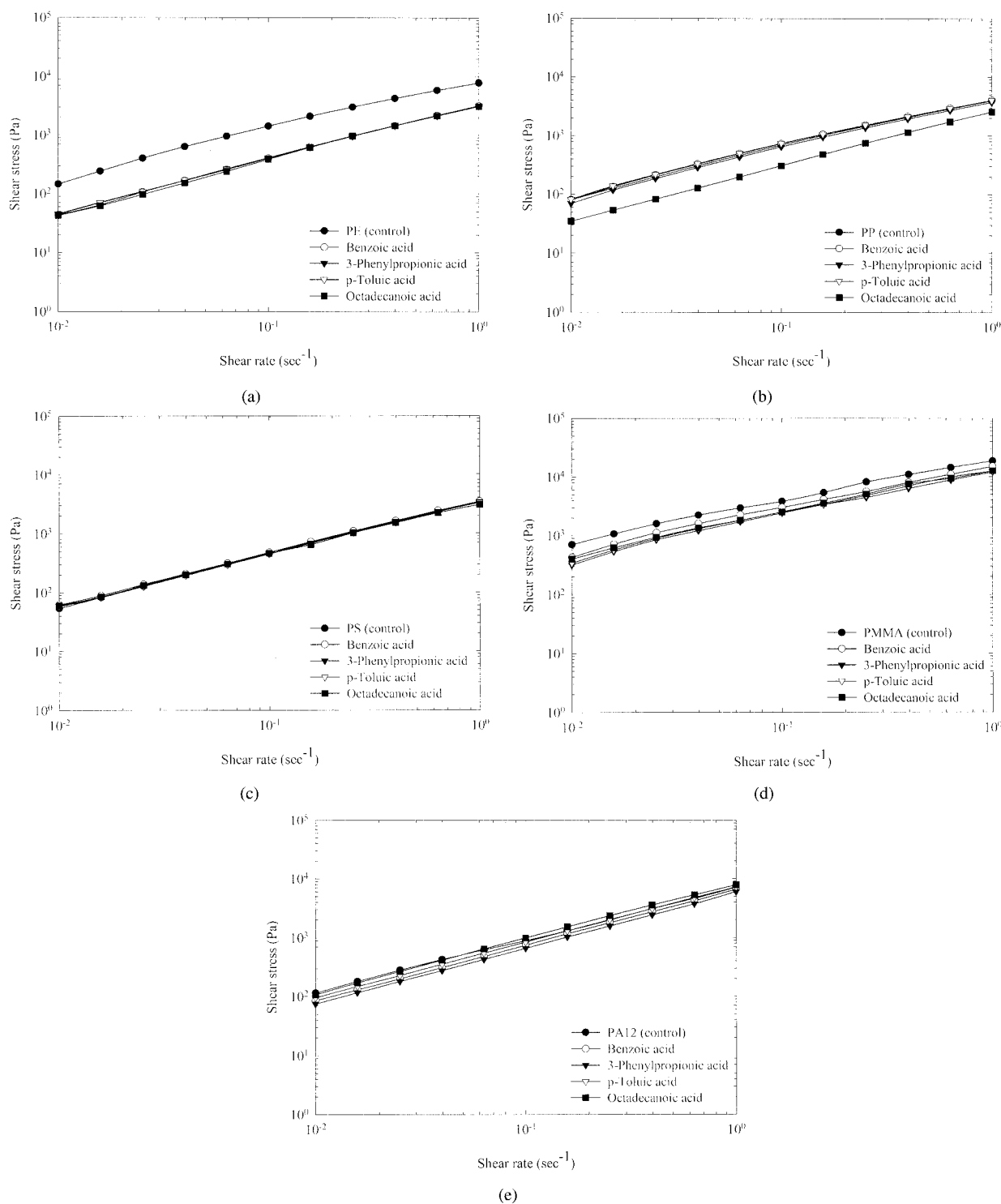
Figure 6　Reduction in apparent shear stress in cone-plate instrument of (a) polyethylene, (b) poly(propylene), (c) polystyrene, (d) poly(methyl methacrylate), and (e) polyamide-12 containing aromatic carboxylic acids at 1% level (measuring temperature = 200°C).

low polarity of PE would lead to low adhesion levels to steel compared with that to polar thermoplastics.

Mechanism of carboxylic acids

It is of interest to compare quantitatively the levels of shear stress reduction and slip velocity in the different polymer melt–additive systems. There are only large effects for PE and PP. The additives producing these effects are the aliphatic carboxylic acids with 3 to 20 carbon atoms. Some aromatic carboxylic acids with phenyl rings have the same or a lesser effect.

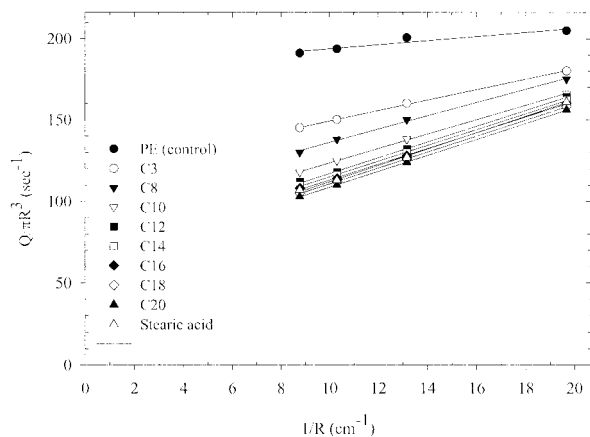It would seem clear that carboxylic acid additives migrate to the steel walls of the capillary and cone-
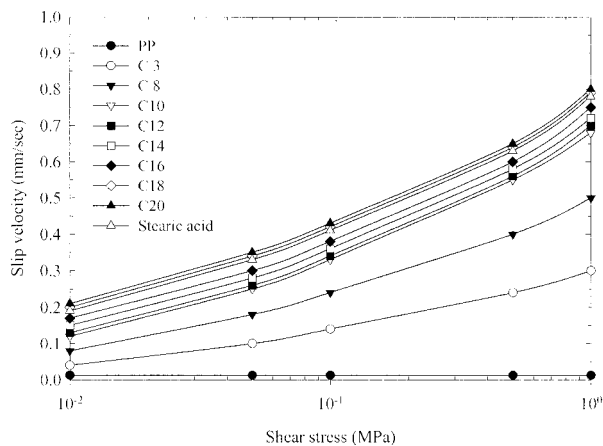
Figure 7 The $4Q/\pi R^3$ versus $1/R$ data from capillary dies of varying diameter for polyethylene with 1% aliphatic carboxylic acid level at constant stress of 0.1 MPa (measuring temperature = 200°C).

plate instruments and induce slippage by the formation of a lubricating layer. As we mentioned earlier, Hardy and Doubleday[2,3] and Bowden and his co-
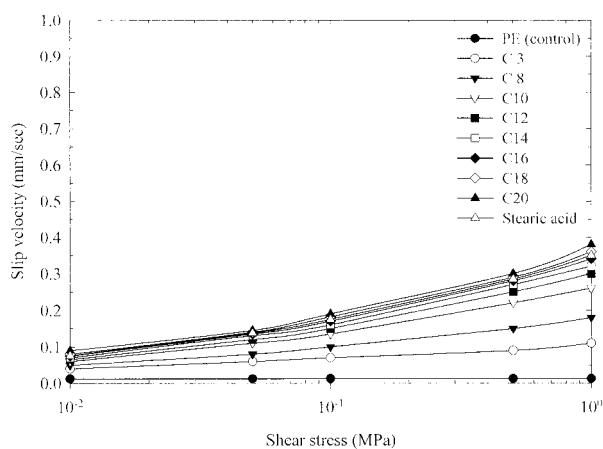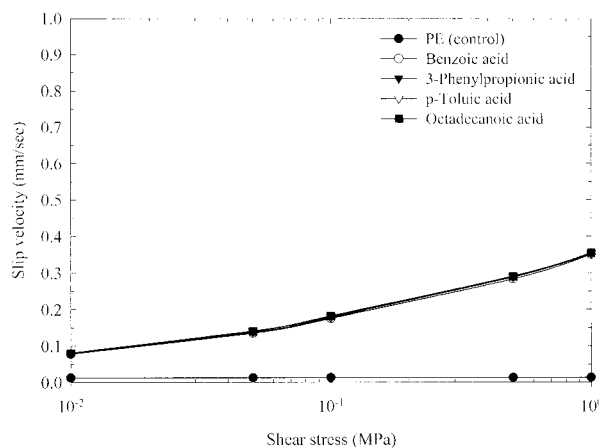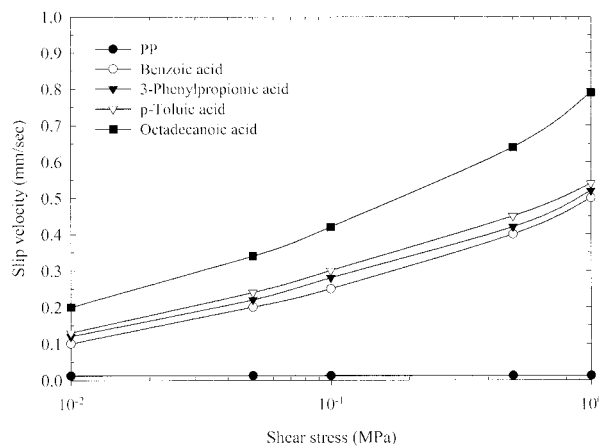

(a)

(b)

Figure 8 Slip velocity versus wall shear stress from a capillary rheometer for (a) polyethylene and (b) poly(propylene) with 1% aliphatic carboxylic acid levels at 200°C.

(a)

(b)

Figure 9 Slip velocity versus wall shear stress from a capillary rheometer for (a) polyethylene and (b) poly(propylene) with 1% aromatic carboxylic acid levels at 200°C.

workers[4–6] investigated the efficiency of lubrication between metal objects with fatty acids and found enhanced lubrication for the fatty acids compared with other organic compounds. Bowden and Moore[7] conducted experiments with various reactive metals and, by studying the fatty acids so treated that the enhanced lubrication, they found a chemical reaction between the metal and the fatty acid. One is led to believe as already suggested that polyolefins have very weak adhesion to the steel walls and are readily replaced by the reaction products of the carboxylic acids and metals and additional carboxylic acid. The aliphatic carboxylic acids and some aromatic carboxylic acids presumably form chemical bonds with the steel wall, which produces a stable slip layer. The lack of slippage in polyamides is presumably because amide chain ends in the polyamides react with acidic end groups as they do in reactive extrusion process. The situation with PS and PMMA is not clear. Based on the conclusions just cited, one would expect this carboxylic acid-induced slippage in other commercial

polyolefins, such as syndiotactic PP, isotactic poly-butene-1, and poly-4-methyl pentene-1.

The results presented here parallel an earlier paper,[9] which considered various 18-carbon amphiphilic ω-compounds. The effects were again strong for PE, much weaker for PS, and nonexistent for PA-12. All the experiments in this paper were for the various carboxylic acids. Lower molecular weight carboxylic acids in the C_3 to C_{10} range are less effective because they are probably too volatile during processing. Aromatic carboxylic acids with benzene rings are also less effective because of the steric hindrance effect of benzene ring. It would seem clear that carboxylic acids react with a metal such as steel so as to produce a stable slip layer of metal soap during processing. Some metals may be nonreactive. Metals with different distributions of electrons and chemical reactivity need more study.

CONCLUSIONS

An experimental study of slippage induced in various thermoplastics in rheometers by the presence of small amount of carboxylic acid additives shows large levels of shear stress reduction and slip velocity in PE and PP melts. Aliphatic carboxylic acids with >10 carbon atoms and some aromatic carboxylic acids with a phenyl ring have a large effect.

It is clear that carboxylic acid additives migrate to the steel walls of the rheometers and induce slippage by the formation of a lubricating layer. It seems that polyolefins have weak adhesion to steel walls and are readily replaced by the reaction products of the carboxylic acids and metals and additional carboxylic acid. However, the effects are much weaker for PS and nonexistent for PA-12. The lack of slippage in poly-amides is presumably because amide chain ends in the polyamides react with acidic end groups. It seems clear that carboxylic acids react with the metal so as to produce a stable slip layer.

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