Effects of Surface Roughness and the Chemical Structure of Materials of Construction on Wall Slip Behavior of Linear Low Density Polyethylene in Capillary Flow*

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SYNOPSIS

The presence of wall slip during the flow of polymeric melts has significant ramifications on the melts' processability. In this study, the effects of materials of construction and surface roughness on the wall slip behavior of a linear low density polyethylene were investigated, using capillary flow. Capillaries, constructed from copper, stainless steel, aluminum, and glass, were used. The inner surface roughness of the capillaries were characterized by the employment of a profilometer and scanning electron microscopy. The roughness profiles of copper capillaries were also altered by the employment of chemical etching. Using Mooney's analysis, the wall slip velocity values were determined to be in the range of 0.09 to 1.34 mm/s. The wall slip velocity values were the highest for stainless steel and were negligible for aluminum. The relative work of adhesion values of polyethylene were the smallest for stainless steel and copper and the highest for glass. Overall, the wall slip velocity values increased with decreasing surface roughness of the capillaries and with decreasing work of adhesion. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In general, viscous fluids adhere to and attain the velocity of the boundary during flow. However, the presence of a relative velocity at the contact line between the fluid and the solid boundary during flow, that is, the "wall slip," is well documented for a variety of fluids and geometries. The experimental work on the wall slip behavior of various rubbers and commodity resins is summarized by Atwood and Schowalter.[1] Generally, the slip velocity is observed to be a function of the wall shear stress. The experimental work in the area of wall slip of suspensions was reviewed by Yilmazer and Kalyon[2] with extensive results reported on capillary and torsional flows of concentrated suspensions. In a study focusing on gels, Jiang et al.[3] determined that wall slip of gels occurs more readily in acrylic tubes, as compared to stainless steel tubes. The influence of materials of construction on the wall slip of rubber compounds was investigated by White et al.[4] Both a biconical rheometer and capillaries produced from different materials, including aluminum, brass, copper, steel, stainless steel, and poly(tetrafluorethylene), were used. Although wall slip velocities at the walls were not calculated, the data indicated that slip of the rubber compounds at the walls took place in both rheometers. Slip at the wall was found to decrease with increased applied pressure below 0.2 MPa. In the biconical rheometer and capillary flows, copper and brass gave rise to greater shear stress values than steel or stainless steel, with poly(tetrafluorethylene) generating the lowest shear stress values at the same rotational speed of the rotor in biconical rheometer flow.

In the area of wall slip of polyethylenes in capillary flows, Ramamurthy[5] reported the onset of slip

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around 0.14 MPa in capillary flows that involved stainless steel walls. The slip velocities of linear low density polyethylene were in the range of 0.61 to 9.23 mm/s for the 0.10 to 0.35 MPa wall shear stress range. These slip velocity values are significantly smaller than slip velocity values determined by Ramamurthy[6] for various other polymers, which reached values greater than 100 mm/s for plasticized poly(vinylchloride) and polypropylene, 30 mm/s for a linear low density polyethylene resin, and over 10 mm/s for a high density polyethylene resin. Blyler and Hart[7] also determined the wall slip velocity vs. wall shear stress behavior of linear polyethylenes using stainless steel capillaries. The wall slip velocities, which they reported on, were high and around 150–500 mm/s for the 0.15–0.45 MPa wall shear stress range.

The effects of temperature on wall slip of an ethylene–propylene copolymer were investigated by Vinogradov and Ivanova[8] and were modeled by Lau and Schowalter,[9] employing the concept of junctions at the conduit/polymer interface. Hatzikiriakos and Dealy[10–12] employed a sliding plate rheometer and capillary flow to characterize the wall slip behavior of high density polyethylenes. Wall slip velocities, in the range of 1 to 30 mm/s, corresponding to the shear stress range of 0.1 to 0.4 MPa, were determined. Melt slip occurred at a critical shear stress of around 0.09 MPa and depended especially on the polydispersity of the polyethylene. Wall slip was determined also to be a function of the stress component acting normal to the wall. The slip velocity of high density polyethylene remained a constant in capillary flows for dies with length/diameter ratios that were greater than 60. The wall slip velocities determined by the employment of a sliding plate rheometer were found to be greater than those characterized with the capillary rheometer. The nature of slip was thought to occur on the basis of adhesive failure at the interface or cohesive failure in the vicinity of the interface.[12]

The objective of this study is to evaluate experimentally the role played by the materials of construction and wall surface roughness on the wall slip behavior. Our own earlier work in concentrated suspensions, the study of White et al.[4] in rubbers, and Ramamurthy's work in blown film extrusion[5] have revealed that the materials of construction play a significant role in the processing behavior of various polymers. However, such effects were not quantified. In this study, capillaries made of glass, steel, aluminum, and copper were used to investigate the effects of the materials of construction on the wall slip of polyethylene. The copper capillaries were further etched in acid solutions to investigate the effect of surface roughness on slip, assuming that the chemical structure of the metal remains unchanged during varying periods of chemical etching. The relative adhesional strength between the linear low density polyethylene and the capillary wall was measured by contact angle experiments of the polymer melt on the corresponding substrates. This study is part of a broader investigation, in which the interplay between the material science (construction of the conduits involving the base metal, possible coatings, surface quality, and surface roughness) and the rheological behavior of polymeric melts is elucidated.

EXPERIMENTAL MATERIALS

The resin used in this study was a commercial blown film extrusion grade linear low density polyethylene, LLDPE, produced by Union Carbide, Canada. It is a comonomer of butene with ethylene, its solid density (ASTM D 1505) is 918 kg/m^3, and its melt index, MI (ASTM D 1238), is 1 g/10 min. The weight average molecular weight, M_w, number average molecular weight, M_n, and polydispersity, M_w/M_n, of this resin are 94336, 25614, and 3.68, respectively. The number of short chain branches per 1000 carbon atoms is 18–19. The primary characteristics and the rheological behavior of this resin were determined in an earlier study, in which this resin was designated as "Resin A."[13,14] However, in this earlier study, no attempt was made to characterize the wall slip behavior of this resin.

The capillary tubes were fabricated from aluminum (type 122), copper (type 3003-H14), stainless steel (type 303), and glass (Fisher borosilicate glass). The dimensions of the capillaries are shown in Table I. The interior surface roughness factors of these capillary tubes were characterized by ex-

Table I Dimensions of the Dies Used in Capillary Flow

Capillary Material	Diameter (mm)		
	Capillary 1	Capillary 2	Capillary 3
Glass	1	1.4	2.6
Stainless steel	1.3	1.6	2
Aluminum	1	1.6	2.5
Copper	0.9	1.6	2.5

Note: (1) The entry angle is 120° for all capillaries. (2) The length over diameter ratio, L/D is 57.6 for all capillaries.

posing the inner surface area of the capillaries and employing a Sloan Dektak Profilometer with a fast leveling module to determine the roughness distribution. Longitudinal and transverse scans were performed. Denoting the height, h, of a single unit of roughness, a relative roughness parameter, k, can be defined as $k = h/D$, where D is the capillary diameter. The characteristic length for roughness is defined as the distance between grooves or peaks. As shown in Table II, the dimensionless roughness factor, k, values ranged between 2×10^{-6} for glass to 0.02 for stainless steel capillaries. The roughness factors for copper and aluminum were similar to one another.

The polyethylene was characterized by the employment of capillary flows at the apparent shear rate at the wall values, $\dot{\gamma}_a$, ranging from 2 to 3000 s^{-1} at 170°C. The reported results were restricted to wall shear stress values, at which no gross extrudate surface irregularities were observed. The occurrence of gross surface irregularities suggests that the flow dynamics under such flow instabilities are complicated enough to render the Mooney correction, used here, inapplicable. For capillary flow experiments, an Instron Capillary Rheometer was used. It is a constant extrusion rate apparatus, with the shear rate determined by the rate of plunger travel and capillary dimensions. It was employed in conjunction with four sets of capillaries, produced from different materials of construction. Each set contained three capillaries. In each set, the capillaries had the same length over diameter ratio of 57.6, but the capillaries differed in their diameters.

Sufficiently long capillaries were used to eliminate the use of the Bagley correction, which requires the employment of multiple capillaries with constant diameters, but varying length/diameter ratios. Hatzikiriakos and Dealy[11] have shown that wall slip also depends on the stress component acting normal to the capillary wall and, hence, on the length/diameter of the capillary. However, their results also indicate that in capillary flow, the slip velocity is constant for capillaries with length/diameter ratios of 60 and greater. This result seems to be because of the sufficiently high pressure over a substantial length of the capillary, thus, the slip velocity varies little with pressure in this range.[11]

For capillary flow, the apparent shear stress at the capillary wall, τ_w, is given by

$$\tau_w = \frac{\Delta P D}{4L} \tag{1}$$

where ΔP is the pressure drop for fully developed flow, D is the capillary diameter, and L is the length. The apparent shear rate at the capillary wall, $\dot{\gamma}_a$, is

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} = \frac{8V}{D} \tag{2}$$

where Q is the volumetric flow rate, R is the radius of capillary, and V is the average velocity of the fluid.

The analysis proposed by Mooney[15] for fully developed, incompressible, isothermal, and laminar flow in circular tubes, with a slip velocity of u_s at the wall, yields:

$$\frac{8V}{D} = \frac{4}{\tau_w^3} \int_0^{\tau_w} \tau^2 \dot{\gamma} d\tau + \frac{8u_s}{D} \tag{3}$$

where τ is the shear stress and $\dot{\gamma}$ is the shear rate. Differentiating the last equation with respect to $1/D$ at constant shear stress at the wall, τ_w, one obtains:

$$\left. \frac{\partial(8V/D)}{\partial(1/D)} \right|_{\tau_w} = 8u_s \tag{4}$$

Thus, the plot of the apparent shear rate, $(8V/D) = \dot{\gamma}_a$, vs. $1/D$ at constant τ_w should yield a straight line with a slope of $8u_s$.

Table II The Interior Surface Roughness of Various Capillaries

Material	Longitudinal Direction, Roughness Parameter (k)	Longitudinal Characteristic Length (μm)	Transverse Direction, Roughness Parameter (k)
Glass	2×10^{-6}	150	[a]
Stainless steel	0.02	500	0.00005
Aluminum	0.004	50	0.002
Copper	0.002	300	0.0006

[a] Extremely small to be measurable with profilometer.

From shear stress vs. shear rate plots, $\dot{\gamma}_a$, was read at constant τ_w for each diameter of the same capillary construction and $\dot{\gamma}_a$, vs. $1/D$ was plotted at constant τ_w, as implied by eq. (4). A least-square linear regression analysis of the data points was carried out. The correlation coefficients for linear regression, R^2, were determined to be around 0.8 for all capillaries. The relatively low value of the correlation coefficient suggests nonlinear behavior and dependence on diameter, which were ignored in this study to compare the wall slip behavior associated with different materials of construction and roughness.

An error analysis procedure[16] was followed to assess the experimental uncertainties before each experiment was made. Both the apparent shear stress at the wall and the apparent shear rate were found to be subject to uncertainties of ±2%. These uncertainties were the result of the propagation of errors related to load cell accuracy, capillary dimension, and crosshead speed. The 95% confidence intervals for the data were determined according to Student's t-distribution.

CONTACT ANGLE MEASUREMENTS

The contact angles of the linear low density polyethylene melt on the plates that were manufactured from the same materials were measured by the sessile-drop technique. Copper, steel, aluminum, and borosilicate glass plates were prepared and cleaned in the same manner as were the capillaries. The chamber was maintained at 200°C for at least one hour prior to the experiment. The polyethylene resin was available in the form of cylindrical pellets, weighing around 12 mg, which were then placed on the plates inside the isothermal chamber. In this method, an advancing contact angle is achieved for the polyethylene-solid substrate system. The high viscosity of the melt and the surface rugosities of the substrate prevent the attainment of the equilibrium contact angle value in relatively short durations (hours). Thus, only the relative wetting behavior of various substrates could be characterized. The novelty of this method is that mainly the vertical motion of the melt from the initially hemispherical shape is achieved. This minimizes the three phase contact line (TPL) motion on the substrate. The work of Bayramli et al.[17,18] shows that the TPL motion gives rise to contact angle hysteresis, even with low viscosity liquids. The relaxed contact angles may still be arrested at metastable positions.[19]

The schematic diagram of the set-up is shown in Figure 1. The chamber is continuously flushed with a continuous stream of argon to prevent the oxidative degradation of the melt. The apparatus includes computerized image analysis with Automatix II software and hardware, a charge-coupled-device-based video camera, equipped with a Melles-Griot 20× magnification telescope and the apparatus was mounted on vibration damping legs. The system allows the vertical and horizontal alignment of the components. The image analysis performs frame grabbing and image digitization with 640 by 480 pixel arrays. The temperature of the sessile-drop chamber is controlled by the use of a Moore Proportional Integral Derivative (PID) temperature controller, within 0.5°C.

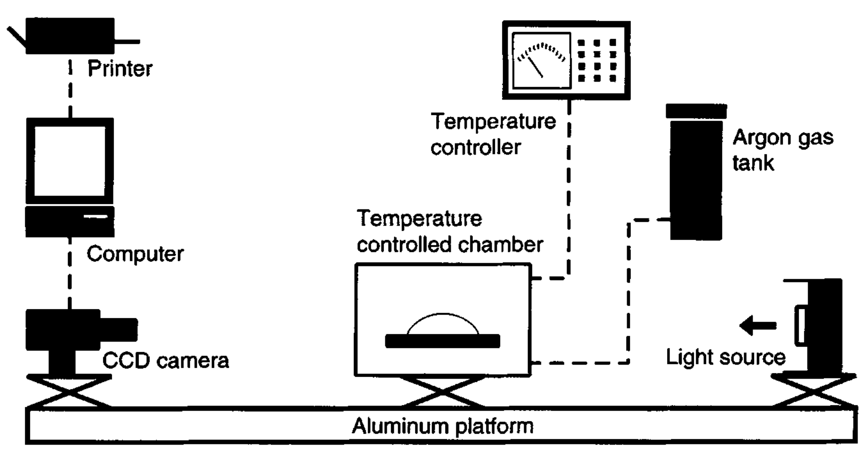

Figure 1 Schematic diagram of sessile drop analysis apparatus.

Table III The Slopes of Mooney Plots for Various Capillaries (Unit: mm/s)

Shear Stress at the Wall	Copper	Stainless Steel	Glass	Aluminum
0.04 MPa	0.9	2.1	0.7	0.0
0.06 MPa	1.6	3.8	1.2	0.0
0.08 MPa	2.3	5.2	1.5	0.1
0.10 MPa	2.4	8.3	1.9	0.2
0.12 MPa	2.2	10.7	2.7	0.8

CONTROLLED ROUGHNESS EXPERIMENTS

In a second set of experiments, the roughness profiles of the inner surface of the copper capillaries were intentionally altered, using a chemical polishing technique. In this technique, the internal roughness of sets of capillaries were systematically modified by circulating an etching solution (20% nitric acid, 25% glacial acetic acid, 54.5% phosphoric acid, and 0.5% hydrochloric acid) through the capillary at the rate of 4 cm^3/min at 60°C. Different durations of exposure time (10 to 20 min) were used to achieve different roughness factors. The roughness values varied between 0.0006 and 0.002.

RESULTS AND DISCUSSION

Rheology and Wall Slip

The slopes of the Mooney plots, which were calculated by the least-square regression fits, are presented in Table III. For the aluminum capillaries, the slopes of the Mooney plots are small, and are in the range of 0 to 0.8 mm/s. Significantly higher slopes are obtained with stainless steel capillaries (2.1 to 10.7 mm/s). The slip velocity values, calculated from the slopes of Mooney plots [i.e., from eq. (4)] are shown in Figure 2. The dependence of slip velocity at the wall, u_s, on the wall shear stress, τ_w, is similar for glass and copper capillaries. However, the wall slip behavior is significantly different with stainless steel. Overall, the slip velocities are in the range of 0.11 to 0.30 mm/s for copper, 0.27 to 1.34 mm/s for stainless steel, and 0.09 to 0.34 mm/s for glass in the range of wall shear stress values between 0.04 and 0.12 MPa.

These results indicate that linear low density polyethylene exhibits observable wall slip with certain materials of construction, that is, copper, stainless steel, and glass, but not with aluminum up to 100 kPa. Thus, the critical shear stress value, above which wall slip occurs, depends on the material of construction.[20] The presence of wall slip of polyethylenes at such relatively low wall shear stress values, however, is not reported in the literature. The greater slip velocities associated with stainless steel, in comparison to copper and aluminum, is consistent with the qualitative results of White et al.[4] on rubbers, which determined that greater wall slip of styrene–butadiene rubber and its compounds occurred with the stainless steel rotor, in comparison to rotors manufactured from copper and aluminum.

The slip velocity at the wall values increase with increasing shear stress at the wall, consistent with earlier findings.[2,3,6,7,11,21] The contribution of slip to the total volumetric flow rate, i.e. the ratio of flow due to slip, Q_s, over the total flow rate, Q, is given as:

$$(Q_s/Q) = (u_s/V) = (8\,u_s/D\dot{\gamma}_a) \tag{5}$$

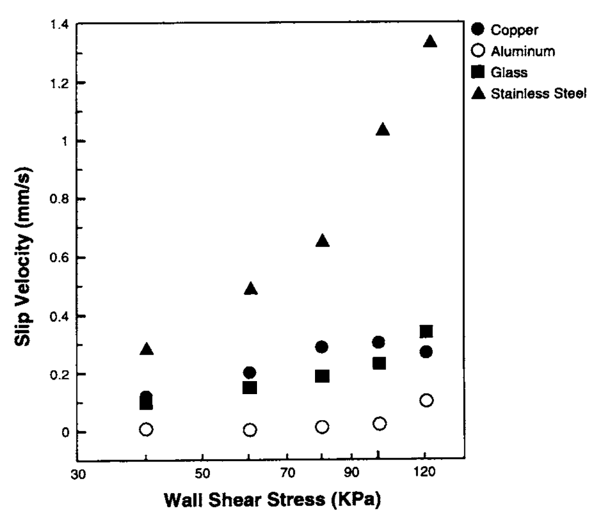

Figure 2 The slip velocity vs. shear stress of LLDPE melt, flow through various capillaries at 170°C with L/D of 57.6.

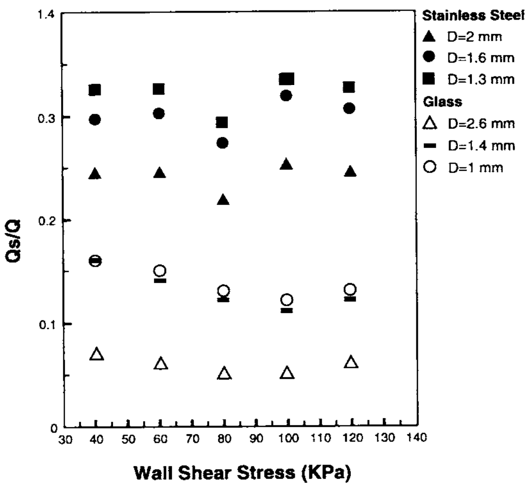

Figure 3 The ratio of (Q_s/Q) vs. shear stress at the wall for stainless steel and glass capillaries with L/D of 57.6.

Q_s/Q values were determined by Kalika and Denn[22] to be in the range of 0.15 to 0.9 and, for the wall shear stress, range of 0.25 to 0.6 MPa for a low density polyethylene in the range of shear rates where flow instabilities were present. Our results regarding the contribution of the wall slip to the total flow rate for stainless steel and glass capillaries are shown in Figure 3. The Q_s/Q values appear to be constant, that is, insensitive to the wall shear stress up to a critical wall shear stress of 0.1 MPa.

These results of Q_s/Q values indicate that the contribution of slip to the total flow rate is dependent on the capillary diameter. For example, for the stainless steel capillary, Q_s/Q increases from 0.24 to 0.33 with decreasing capillary diameter from 2 mm to 1.3 mm, at the wall shear stress value of 0.12 MPa. For the glass capillary, Q_s/Q increases from 0.06 to 0.13 as the capillary diameter decreases from 2.6 mm to 1 mm, at the wall shear stress value of

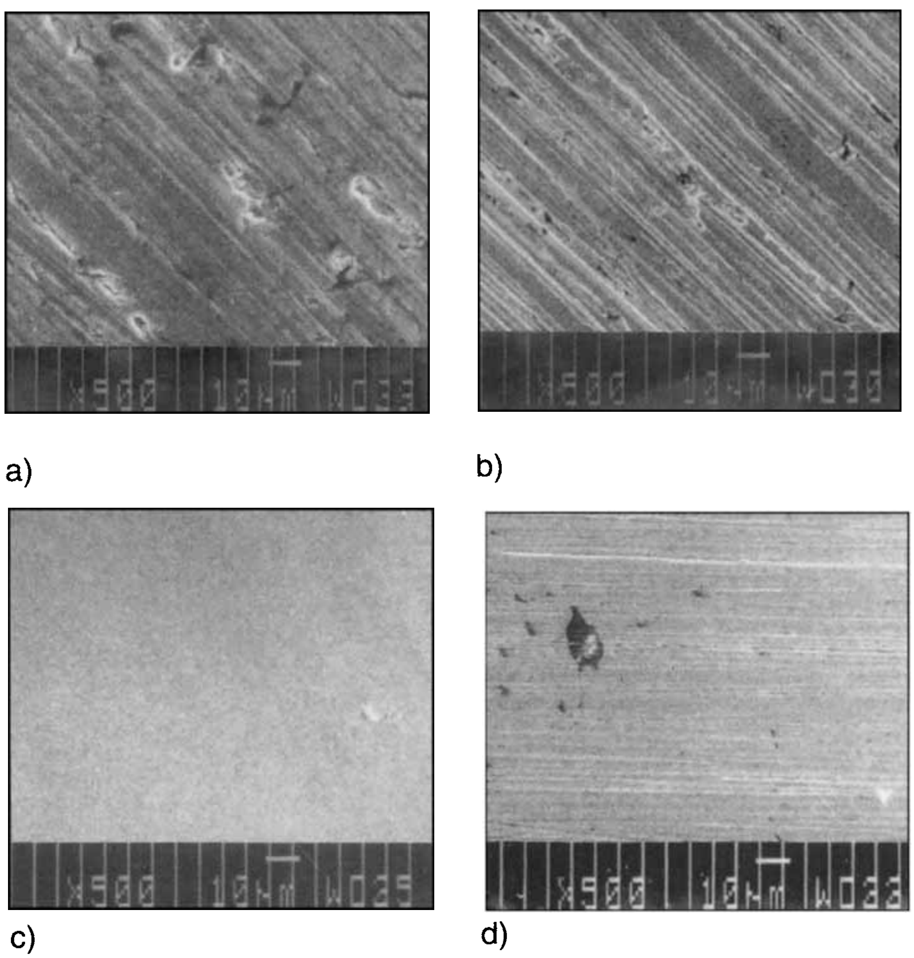

Figure 4 The SEM Micrograph of (a) aluminum, (b) copper, (c) glass, and (d) steel substrates at 500× magnification.

0.12 MPa. Therefore, the slip contribution is more significant with conduits with smaller diameters at constant length/diameter, L/D ratio. This behavior may be expected, since, with increasing diameter (at constant L/D), the surface to volume ratio decreases, thus reducing the effect of the wall slip.

Surface Roughness and Wetting

It is known that the adhesion at a melt metal interface is influenced by both the roughness and the chemical nature of the surface.[23] Thus, wall slip is expected to be affected by both the roughness and the chemical nature of the wall of the viscometer. The scanning electron micrographs of the surfaces of the various substrates that were used are shown in Figure 4. The micrographs indicate that the surface of glass substrates exhibit the smallest roughness. The typical roughness profile of the surface of untreated copper capillary (before chemical treatment) is shown in Figure 5. The profile is recorded with the profilometer tip moving along the capillary axis (longitudinal) and around the capillary axis (transverse). In all of the capillary surfaces investigated, the transverse roughness values were smaller than the longitudinal values (Table II).

The longitudinal profiles of the etched copper surfaces are presented in Figure 6. There is considerable decrease in both the magnitude and the frequency of the roughness upon etching, as compared to the roughness distribution of the surfaces of the copper capillaries prior to chemical treatment. The effects of the surface roughness on the wall slip behavior of copper capillaries are shown in Figure 7. With the smoother capillary wall surfaces (with roughness parameter, k, of 0.0006), the wall slip

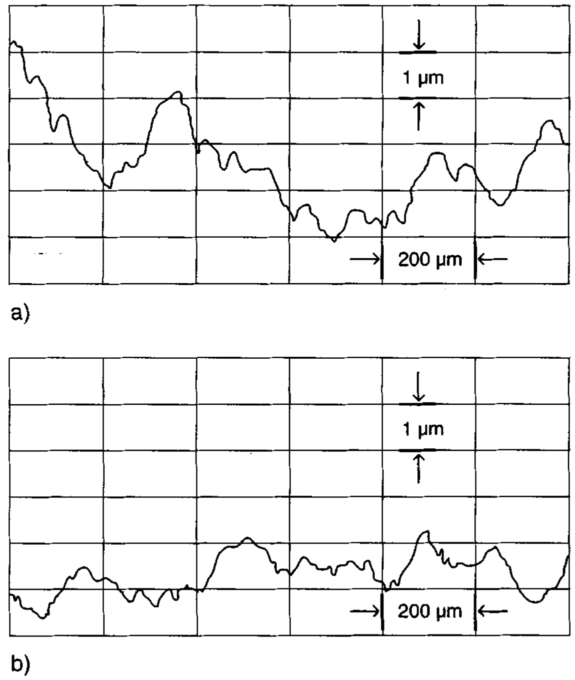

Figure 6 The typical longitudinal roughness profiles of chemically treated copper. (a) k = 0.0016 and (b) k = 0.0006.

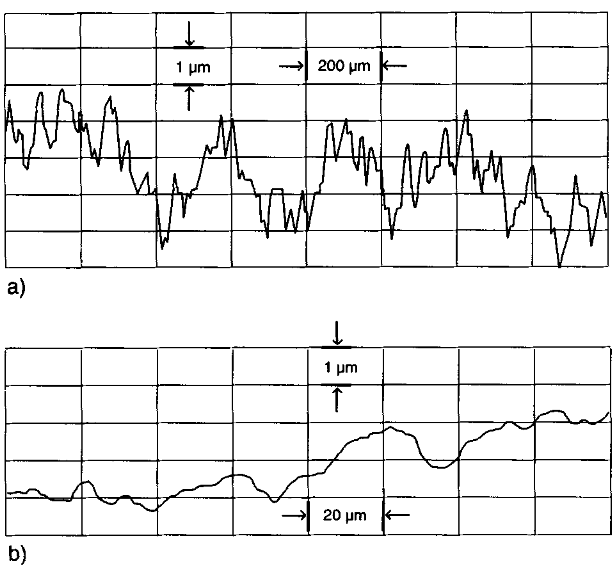

Figure 5 The typical roughness profiles of untreated copper (k = 0.0020) capillary. (a) longitudinal and (b) transverse direction.

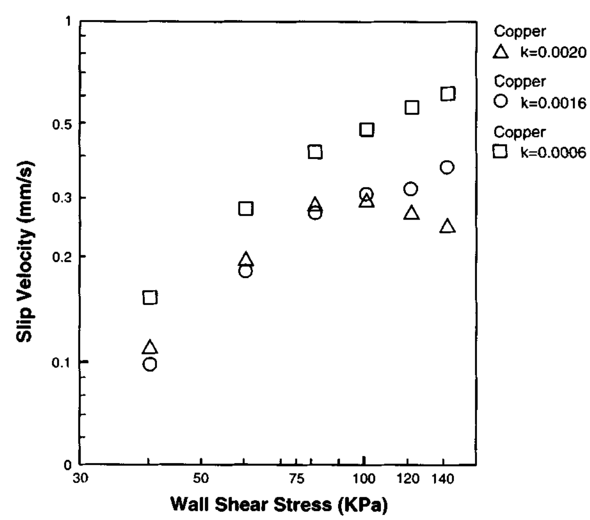

Figure 7 The slip velocity vs. shear stress of LLDPE melt, flow through various capillaries at 170°C with L/D of 57.6.

velocities are about 50% to 150% greater than those observed with capillaries, which exhibited greater roughness, k, values, which were in the range of 0.0016–0.0020. This finding is consistent with the earlier studies of Kraynik and Schowalter[24] on aqueous solutions, which indicated that the wall slip of aqueous solutions decreases with increasing roughness of the die surface. Jiang et al.[3] also observed, with hydroxypropyl guar gels, that wall slip occurs more readily in tubes with smooth surfaces.

The work of adhesion, W_a, of the melt (the reversible work required to separate unit area of liquid from the substrate), with respect to the capillary surface, can be calculated from the Young–Dupré equation,

$$W_a = \gamma_{LV}(1 + \cos\theta) \quad (6)$$

where γ_{LV} is the surface tension of the linear low density polyethylene, which is 25.4 mN m^{-1} at 200°C and θ is the contact angle. For systems with basically dispersive interactions across an interface, such as polyethylene, the employment of eq. (6) is theoretically justified.[25] The work of adhesion values of the linear low density polyethylene on the substrates used in this study are presented in Table IV, together with the measured contact angle values. Polyethylene on glass shows the greatest degree of adhesion, which is about twice that of the steel–polyethylene adhesion. The glass capillaries exhibit smaller slip velocity values as compared to steel (Fig. 2). This should be associated with the greater adhesion of polyethylene to glass, which appears to offset the relative smoothness of the glass surface. The wall slip behavior is, therefore, determined by two opposing effects: (i) the relatively high adhesion of linear low density polyethylene to glass and (ii) the smoothness of the glass surface. Copper and glass exhibit similar values of wall slip velocities. The relatively low adhesion of polyethylene on copper appears to be offset by the greater roughness of the copper surface. As shown earlier, as the roughness factor decreases, one observes greater slip velocities for copper capillaries (Fig. 7). Slip effects for copper are smaller than for steel. Copper exhibits a similar adhesional strength to polyethylene and a rougher surface in the transverse direction when compared to the steel surfaces used in this study.

The comparison of wall slip, occurring in capillaries manufactured from different materials of construction, is thus difficult, due to the overlapping effects of the surface roughness and adhesion on wall slip. In the case of aluminum capillaries, which gave rise to the no-slip condition at the wall below 0.1 MPa, the results may be due to several factors. First, all aluminum surfaces have porous Al_2O_3 surface layers and the diffusion of the polymer molecules into these pores may act as anchoring points for the melt. Aluminum surfaces also appear to be jagged with an average distance of 50 μm between longitudinal rugosities. Finally, polyethylene has a greater affinity to adhesion to aluminum than do steel and copper, as shown in Table IV.

The greatest slip velocities at the wall are observed for steel capillaries, which exhibit the least amount of rugosities on the surface in the transverse direction, except for glass, which shows no observable roughness. For steel, large rugosities are separated from each other by almost 500 μm with a smooth profile between (Fig. 8). The relatively smooth nature of stainless steel in the transverse direction, coupled with its relatively low work of adhesion with polyethylene, that is, 12.7 m N/m, should give rise to the observed high wall slip velocities in steel capillaries.

CONCLUSIONS

The effects of surface roughness and the chemical structure of materials of construction on the wall slip behavior of polyethylene were investigated. The critical shear stress, above which wall slip of polyethylene melt occurs, was related to materials for construction, with wall slip observed for copper, stainless steel, and glass capillaries and with no slip for aluminum for wall shear stress values smaller

Table IV The Work of Adhesion, W_a, (mN m^{-1}) and the Contact Angle, θ, of Linear Low Density Polyethylene on Various Substrates at 200°C, Obtained on the Basis of 20 Runs[a]

Capillary Material	Glass	Copper (Untreated)	Aluminum	Stainless Steel
W_a	24	11.1	17.6	12.7
θ	93.2 ± 2.5	124.3 ± 3.3	107.8 ± 3.4	120 ± 2.1

[a] The reported ranges are the 95% confidence intervals determined according to Student's-t-distribution.

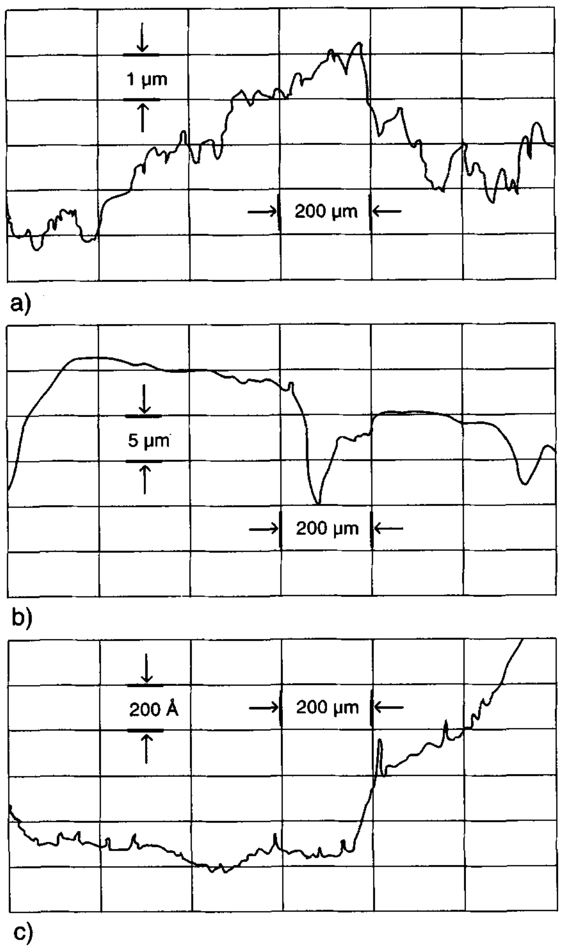

Figure 8 The typical roughness profiles of (a) aluminum, (b) stainless steel, and (c) glass, in the longitudinal direction.

than 0.10 MPa. The wall slip velocity values decreased with increasing surface roughness of the capillary. The relative slip behavior of polyethylene, in various capillaries, is related to the competing effects of surface roughness and work of adhesion. The highest wall slip velocities were observed with stainless steel, which exhibited relatively small work of adhesion and capillary surface roughness transverse to the flow direction. The no-slip condition, observed for aluminum, is related to the porous nature and the relatively higher roughness of the aluminum surface and the moderate adhesion of polyethylene to aluminum.

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