Stick-Slip Transition at Polymer Melt/Solid Interfaces

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A striking superfluidlike stick-slip transition is studied and semiquantitatively analyzed for a series of highly entangled linear polyethylene melts subjected to capillary flow. The observed violation of the law of the stick hydrodynamic boundary condition is significant and unambiguous, and can be conveniently characterized by an extrapolation length b. It is shown that b at the transition is independent of temperature and sharply increases with molecular weight in confirmation with a simple scaling relation introduced by de Gennes.

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The stick hydrodynamic boundary condition (HBC) is usually an accurate description of viscous interactions at an interface between a solid surface and a liquid. The notion of slip HBC can be traced at least back to J.C. Maxwell according to Debye [1]. However, it has rarely received unambiguous experimental support. Highly entangled polymeric melts are a unique class of single-component liquids that may provide an exceptional example of slip behavior under certain experimental conditions. Such slip may originate from the strong dynamical structural discontinuity introduced by a solid surface where polymer-wall interfacial interactions diminish at high stresses. Thus, on the one hand, high molecular weight polymer chains interact strongly through chain entanglements in the bulk. On the other hand, when polymer adsorption is inhibited or disentanglement between adsorbed and free chains occurs in strong flow, the surface is essentially in contact with a molecularly thin layer of monomerlike or unentangled liquid, creating an extremely large disparity between the viscous interactions taking place across the interface and those taking place in the bulk. On a hydrodynamic length scale, this could amount to a finite slip velocity that invalidates the law of the stick HBC. The consequence of vanishing polymer adsorption at a solid surface was first discussed theoretically by de Gennes [2] in 1979 who rediscovered the concept of extrapolation length b.

For highly entangled polymer melts, significant deviation from the law of the stick hydrodynamic boundary condition may arise. The action of extremely high interfacial shear stress can produce massive disentanglement between adsorbed and free chains at a melt-solid interface. One anticipates that above a critical stress σ_c a large stick-slip transition may take place at the melt-solid interface. The possibility of wall slip in capillary flow involving polymer melts has been extensively studied [3–18]. It has been difficult to distinguish wall slip from the plausible occurrence of nonviscometric (or secondary) flows and other capillary-nonspecific flow instabilities such as constitutive instabilities [4,17].

In this Letter, we will semiquantitatively describe the simplest and most revealing aspect of polymer-solid flow interactions: a superfluidlike stick-slip transition phenomenon. Upon reaching a critical pressure, the flow rate may suddenly jump over one order of magnitude for various polymeric resins [9]. In our case, the capillary flow is clearly stable and exhibits smooth extrudate. The same polymers are found to exhibit spurt flow (i.e., pressure oscillation and bamboolike extrudate) under controlled rate in the same range of stress. The characteristics of this slip behavior are consistent with the condition of ideal slip and with the existence of a finite extrapolation length b.

The materials under investigation are linear high density polyethylenes from BP Chemicals, referred to as MH20 and MH07, having weight-average molecular weights of $M_w = 316\,600$ and $130\,500$, respectively. The different molecular weights permit us to illustrate the strong molecular weight dependence, as predicted by a scaling relation for the extrapolation length b. In order to study stress-induced slip, a pressure-controlled Monsanto Automatic Capillary Rheometer was employed, equipped with three orifices having length-to-diameter ratios L/Dof 15, 20, and 25, respectively. The diameters D of the orifices are 1.04, 0.787, and 0.635 mm, respectively. The variety of capillary diameters D allows us to demonstrate the sensitivity of the slip behavior to the characteristic length scale on which the hydrodynamic slip corrections are made. The experiments were conducted at two temperatures of 160 and 200 °C, respectively, in order to elucidate the temperature dependence of the stick-slip transition.

Throughout the explored range of stress, the extrudate remains smooth on macroscopic length scales, e.g., the surface roughness is much less than 1% of the extrudate diameter at the stick-slip transition. A critical wall shear stress σ_c for the stick-slip transition was found to be about 0.3 MPa at which the flow throughput Q becomes discontinuous, taking either the value expected for the stick HBC or a value which is an order of magnitude higher. The large amplitude slip can quantitatively be understood in terms of simple scaling arguments corresponding to the physical picture represented by Fig. 1, where the extrapolation length b is defined as the distance away from the polymer-wall interface where the velocity of the bulk fluid would be extrapolated to zero. Figure 2 shows the flow

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curves, consisting of the measured shear rate $\dot{\gamma}$ versus the applied shear stress σ , for the polyethylene MH20 (which has a melting point about 145 °C) at both 160 and 200 °C, obtained using the capillary die of aspect ratio L/D = 15 and D = 1.04 mm. Here the wall shear stress σ was converted from the *applied* pressure *P* according to $\sigma = (D/4L)P$ without the Bagley correction, and the wall shear rate $\dot{\gamma}$ was computed from the *measured* volumetric flow rate *Q* according to $\dot{\gamma} = 32Q/\pi D^3$ without the Rabinowitz correction.

The discontinuity in Q at the critical driving pressure P_c is strong evidence for a stick-slip transition. The two states at the critical stress σ_c , designated by $\dot{\gamma}_{\text{stick}}$ and $\dot{\gamma}_{\text{slip}}$, respectively, in Fig. 2, involve the same degree of flow deformation as shown in Figs. 1(a) and 1(b), and possess similar smooth extrudates. At $\dot{\gamma}_{\text{stick}}$, sufficient entanglement is present between the adsorbed and free chains at the polymer-wall interface, and the stick hydrodynamic boundary condition applies, as illustrated by Fig. 1(a). At $\dot{\gamma}_{slip}$, the interfacial layer experiences a structural transition that may be thought of as flow-induced disentanglement between adsorbed and free chains at the melt-wall interface, resulting in an interfacial layer free of chain entanglement and in an extremely low interfacial shear viscosity η_i in comparison to the shear viscosity η_m away from the interfacial layer.

The difference $\dot{\gamma}_{slip} - \dot{\gamma}_{stick}$ at the critical stress σ_c is related to the slip velocity v_s at the melt-wall interface by



FIG. 1. (a) Velocity field at the stick-slip transition in the capillary corresponding to the "stick" state, with sufficient chain entanglement denoted by the dots and with zero slip velocity. (b) Velocity field at the transition corresponding to the "slip" state, with the exaggerated depiction of zero chain entanglements in the interfacial layer and a much larger apparent flow throughput due to a finite slip velocity v_s .

the Mooney relation [19]

$$\dot{\gamma}_{\rm slip} - \dot{\gamma}_{\rm stick} = 8v_s/D$$
, (1)

where *D* is the orifice diameter of the capillary instrument. Using (1), the slip velocity v_s at the transition was calculated for both T = 160 and 200 °C. Table I summarizes all the results evaluated from Fig. 2, including the critical stress σ_c , the shear viscosity η_m , and the wall shear rate $\dot{\gamma}_{\text{stick}}$ and the slip velocity v_s at the critical point of the transition. Since the stress across the slipping interface is given by $\sigma_c = \beta_i v_s$ at the stick-slip transition, the increase of v_s with temperature *T* indicates that the friction coefficient β_i decreases rapidly with increasing *T*. This means that the viscosity η_i of the unentangled interfacial layer may have an Arrhenius-like temperature dependence. For such an interface, the friction coefficient $\beta_i = \eta_i/a$ [2], where *a* is the thickness of the molecularly thin interfacial layer as shown in Fig. 1(b).

The extrapolation length *b* given by

$$b = v_s / \dot{\gamma}_{\text{stick}} = [\dot{\gamma}_{\text{slip}} - \dot{\gamma}_{\text{stick}} / \dot{\gamma}_{\text{stick}}]D/8 \quad (2)$$

can be evaluated readily from the data in Table I for T = 160 and 200 °C. In contrast to the temperature dependence of v_s , the extrapolation length b is found in Table I to remain constant at the stick-slip transition with respect to temperature T. Furthermore, σ_c increases linearly with T, and the transition obeys the time-temperature superposition principle [20(a)].This surprising result has persuaded us to conclude that the interfacial transition arises most likely from chain disentanglement and not chain desorption, and indicates that b is a material property of the melt-solid interface. From the definition (2) and $\sigma_c = \beta_i v_s = \eta_m \dot{\gamma}_{stick}$, one readily arrives at a simple scaling relation $b = \eta_m / \beta_i = (\eta_m / \eta_i) a$. Since the shear viscosity η_m of the bulk polymer has the same temperature dependence as that of η_i , the extrapolation length b is essentially independent of temperature, in



FIG. 2. The apparent wall shear rate versus the applied wall stress at T = 160 and 200 °C for polyethylene MH20 indicates a discontinuous jump in the measured flow rate from $\dot{\gamma}_{stick}$ to $\dot{\gamma}_{slip}$.

IABLE I. Temperature and molecular weight dependence.								
Т	$\dot{\gamma}_{\rm slip}~({ m s}^{-1})$	$\dot{\gamma}_{ m stick}~({ m s}^{-1})$	$v_s \ (cm/s)$	σ_c (MPa)	η_m (Pas)	<i>b</i> (mm)		
160 °C (MH20)	148	8.5	1.8	0.256	30118	2.11		
200 °C (MH20)	788	47	9.6	0.307	6532	2.05		
160 °C (MH07)	1744	682	13.8	0.337	494	0.20		
200 °C (MH07)	-	-	_	>0.46	_			

agreement with the experimental data of Fig. 2. The magnitude of b is macroscopically large (on the order of millimeters), leading to a tremendous surge in the flow rate upon the transition. However, it reflects a physical process taking place only at the microscopic length scale a within the interfacial layer. This large b arises from the extraordinarily large ratio of the bulk viscosity η_m (of a highly entangled liquid) to the interfacial viscosity η_i (of an unentangled liquid).

One dominant feature of the stick-slip phenomenon is its molecular weight dependence. Our experiments show that the polyethylene MH07 exhibits a much smaller stick-slip transition at 160 °C and does not undergo such a transition at 200 °C within the stress range of our instrument. The detailed molecular weight and temperature dependence of σ_c is currently under further investigation [Refs. 20(a) and 20(b)]. The extrapolation length b at the stick-slip transition for the polyethylene MH07 ($M_w = 130500$) is found to be only one-tenth that for the polyethlene MH20 $(M_w = 316\,600)$. This result is consistent with the relative magnitude of η_m just before the transition: According to the data in Table I, $\eta_m = 6532$ Pas for MH20 which is over 10 times higher than $\eta_m = 494$ Pas for MH07. Further studies show that b scales with M_w to the familiar 3.4 power at 200°C [20(b)].

It is widely believed that there may be constitutive instabilities associated with the bulk flow of highly entangled polymer melts. The Doi-Edwards theory and its variations predict a maximum in the stress versus shear rate curve for highly entangled melts and a region of instability beyond the maximum [21-24]. In the flow instability region, shear bands are expected to form because of alternating shear at low and high rates, respectively [24]. To our knowledge, there are no successful observations of such shear bands in the stress neighborhood below 1 MPa [25]. Although much experimental data on melt flow behavior at high rates might be consistent with the possibility of constitutive instabilities, our observations are clearly not in confirmation of such a theoretical speculation.

The unique character of the interfacial slip is its strong dependence on the dimension of the experimental apparatus. If the two states denoted by $\dot{\gamma}_{\text{stick}}$ and $\dot{\gamma}_{\text{slip}}$ in Fig. 2 would correspond to two stable bulk flow states as suggested by the theoretical hypothesis of constitutive instabilities, the magnitude of the jump $(\dot{\gamma}_{slip} - \dot{\gamma}_{stick})$ in the apparent wall shear rate would be constant regardless of the die diameter D used to obtain the data. On the contrary, according to the Mooney relation (1), the difference $(\dot{\gamma}_{slip} - \dot{\gamma}_{stick})$ is expected to scale with the capillary die diameter D as D^{-1} . Figure 3 shows the measured apparent wall shear rate upon ramping up the wall stress, using three different die length-to-diameter ratios L/D and die diameters D. The difference $(\dot{\gamma}_{slip} - \dot{\gamma}_{stick})$ increased considerably with decreasing D and did not remain constant, as can be seen from Table II. To describe the slip behavior quantitatively, we calculate the extrapolation length b. Table II indicates that, within experimental error, the measured extrapolation lengths b are identical for all three capillary dies. Finally, it is absolutely important to note that the transition phenomenon is sensitive to surface modification of the capillary wall. Reduction of adsorbed chain density by depositing some fluorocarbon elastomer on the wall resulted in a considerable decrease in the critical stress [20(a)]. Thus all the evidence indicates that the possibility of a constitutive instability can be ruled out.

In conclusion, flow behavior and liquid-solid interfacial interactions of linear polyethylene melts have been studied under controlled stress using capillary rheometry. The striking superfluidlike stick-slip transition can be understood in terms of simple scaling arguments. The extrapolation length b is indeed the proper material parameter that characterizes the interfacial slip behavior. The transformation from Fig. 1(a) to 1(b), corresponding to the stick-slip transition shown in Fig. 2 from $\dot{\gamma}_{stick}$ to $\dot{\gamma}_{slip}$, can be shown to arise from flow-induced massive chain disentanglement [20(a)]. Had the breakdown of interfacial interactions been due to stress-induced chain desorption, the critical stress σ_c would have decreased with



FIG. 3. The stick-slip transition at T = 200 °C as measured by three different orifices with diameters equal to 1.04, 0.79, 0.625 mm, respectively. For clarity, the transition point is indicated by full circles only on data obtained with $L/\dot{D} = 15$.

L/D	D (mm)	$\dot{\gamma}_{ m slip} = \dot{\gamma}_{ m stick} \ ({ m s}^{-1})$	$\dot{\gamma}_{stick} \ (s^{-1})$	v_s (cm/s)	<i>b</i> (mm)
15	1.04	741	47	9.6	2.11
20	0.79	1126	52	11.1	2.14
25	0.625	1692	61	13.2	2.16

TABLE II. Slip of MH20 evaluated with different orifices.

increasing temperature for such an activation process [20(c)]. According to the recent theory of Brochard and de Gennes [28], a disentanglement process requires a preexisting uniform slip velocity field v_s in the first molecular layer of the interface. It is conceivable that the observed stick-slip transition develops in two stages: chain desorption first, leaving only the strongly adsorbed chains at the capillary wall, and then followed by a coil-stretch transition of the remaining tethered chains.

The polyethylenes (PE), MH20 and MH07, studied in this work exhibit neither any flow instability nor any form of extrudate irregularities around the stick-slip transition under the extrusion condition of *controlled stress*. This enabled us to explore and analyze the remarkable stressinduced stick-slip phenomenon of highly entangled polymer melts, as a function temperature, molecular weight, dimension of the capillary apparatus, and wall surface condition, without instigating any unknown flow processes leading to extrusion instabilities. Under controlled rate, the same PE develops the "flow instability" known as spurt flow, evidenced by the appearance of significant extrudate distortion. Thus the present work reveals that the long-researched spurt flow phenomenon originates from the stick-slip transition at melt-wall interfaces.

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