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Superfluid-Like Stick−Slip Transition in Capillary Flow of Linear Polyethylene Melts. 1. General Features

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ABSTRACT: This paper explores rheological characteristics of and molecular mechanism for a superfluid-like stick−slip transition occurring under controlled pressure in capillary flow of a series of highly entangled linear polyethylene (PE) melts and establishes its connection with the spurt flow phenomenon. The transition is signified by a large discontinuity in the flow rate at a critical stress, resulting in a double value within the flow curve. The magnitude of the transition can be quantified in terms of an extrapolation length, *b*. In particular, the superfluid-like flow transition occurs throughout a range of temperatures from $T = 180$ to 260 °C as long as a critical stress, σ_c, is exceeded. It is found that σ_c increases linearly with *T*, and b_c at the transition remains around 1.7 mm at all the temperatures for the PE (MH20) of weight-average molecular weight $M_w = 316\,600$. Thus the observed remarkably large interfacial slip is believed to be due to complete disentanglement of the adsorbed chains from free chains at the melt/wall interface at and beyond the transition. The amount of wall slip, as described by *b*, diminishes quickly with decreasing M_w, in qualitative agreement with a simple scaling relation for noninteracting interfaces. The flow transition depends on the surface condition of the die wall and occurs at a considerably lower critical stress when the wall is treated by depositing a fluorocarbon elastomer to weaken the PE adsorption. Application of both controlled-pressure and controlled-piston speed conditions demonstrates that spurt flow instability originates from indeterminacy of the hydrodynamic boundary condition at the PE/die wall interfaces.

Introduction

Summary of Capillary Flow Characteristics. Highly entangled polymer melts, such as industrial polyethylene (PE) resins, exhibit a variety of “flow instabilities” during constant speed extrusion, as implied by the well-known extrudate irregularities. Extrudate distortions range from “sharkskin” at relatively low flow rates to large amplitude quasiperiodic oscillation in the extrudate diameter (spurt flow) and gross melt fraction at higher extrusion rates. The origins of these extrudate distortions and the corresponding rheological characteristics are not completely understood.[1−17] Wall slip is a central notion that may be involved in these complicated flow phenomena.[3−4,6−7,11−14] The melt/wall interfacial slip presumably arises from the strong dynamic structural discontinuity at a solid surface produced by high stresses under which either no polymer adsorption is present or disentanglement occurs between adsorbed and free chains at the interface, whereas the high molecular weight polymer chains strongly entangle in the bulk and produce an exceedingly high melt viscosity. The rheological consequence of vanishing polymer adsorption at a solid surface was first theoretically discussed by de Gennes[18] in 1979, and slip was thought to depend entirely on the existence of a noninteracting and nonadsorbing surface. Subsequent theoretical and experimental works again recognized the importance of polymer/wall interfacial interactions in determining the wall slip behavior of high molecular weight polymer melts.[3,9,19−21]

A very intringuing kind of PE melt flow behavior is a “flow instability” commonly termed “spurt flow” that occurs under controlled-piston speed over a range of relatively high extrusion rates in a capillary die.[4−5,12] At a sufficiently high piston speed, the pressure drop is found to oscillate substantially with time as measured by a “rate-controlled” capillary rheometer. The extrudate has a corresponding quasiperiodic variation in its diameter, reminiscent of bamboo. Search for the origin of the spurt flow phenomenon has been ongoing for at least 20 years.[1,2,5,12] Several mechanisms have been put forward to describe the spurt flow characteristics. Finite melt compressibility has been shown to produce the salient feature of pressure oscillation, provided that the rheological behavior of the polymer possesses an upper branch in the flow curve.[2,12] Another explanation of the spurt flow phenomenon, favored by many, claims that it is a manifestation of constitutive instabilities that are inherent bulk properties of polyethylene.[22−26] Wall slip appears to be a relevant component of the spurt flow behavior.[5] So far there have not been sufficient experimental data to differentiate these various possible sources for the spurt flow instability, and the precise mechanism remains an open question.

One pertaining phenomenon involving these polyethylene resins has also been studied extensively in the past.[27−31] It was found that PE may undergo a discontinuous transition in capillary flow in the controlled-pressure mode at a critical stress at which the actual flow rate makes an abrupt jump. As noted in ref 12, several phenomena (e.g., wall slip and melt fracture) may occur concurrently; therefore the extrudate, especially of linear low-density polyethylene, was often highly distorted even under controlled-pressure following the transition,[27−29] with few exceptions.[32] On the basis of a variety of experimental data, it has been suggested many times[27,29,12] that the transition involved an adhesive-to-cohesive failure transition near the PE/wall interface. However, the molecular mechanism for the transition has remained elusive.

Objectives of This Work. In short, the hydrodynamic mechanism and molecular origin of the spurt flow phenomenon remain to be explicitly elucidated. A

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quantitative characterization of the stick–slip transition needs to be carried out. The objective of this paper is to explore the molecular origin of the stick–slip transition, to reveal the interplay between this interfacial transition and the spurt flow phenomenon, and to put forward a more coherent proposal for the mechanism of sput flow. By performing capillary flow experiments using both controlled-piston speed and controlled-pressure modes and comparing respectively the corresponding extrudate appearance and rheological characteristics, we aim to disclose the interfacial nature of the spurt flow phenomenon and illustrate the molecular mechanism for the stick–slip transition.

In summary, the capillary flow of a series of PE melts is found to be rheologically *stable* and free of extrudate distortion and to display an abrupt stick–slip transition at a critical stress. On the other hand, typical spurt flow features are observed under controlled-piston speed, including the appearance of bamboo-looking extrudate distortion in contrast to the smooth extrudate obtained in the controlled-pressure mode. The sharp distinction of the rheological bheavior, observed under the different driving conditions, discloses that oscillation of the PE/wall interfacial condition between its *stick* and *slip* states occurs in controlled-piston speed and produces the familiar symptoms of spurt flow. The temperature dependence of the stick–slip transition characteristics indicates that the transition is most likely a flow-induced chain entanglement–disentanglement transition occurring at the first interfacial molecular layer. The same PE is found to undergo the stick–slip transition at an appreciably lower $\sigma_c' < \sigma_c$ when the steel die wall surface is coated with a fluorocarbon elastomer. This observation not only demonstrates the interfacial nature of the transition but also lends supporting evidence for a recent theoretical proposal for interfacial slip.[19]

Experimental Section

The materials under investigation were linear high-density PEs supplied by BP Chemicals and referred to as MH20 and MH07, having weight-average molecular weights (M_w) of 316 600 and 130 500, respectively. The different molecular weights permitted us to illustrate the strong molecular weight dependence, as predicted by a scaling relation for the extrapolation length, *b*, to be introduced in the following. A pressure-controlled Monsanto automatic capillary rheometer was employed, equipped with three orifices having length-to-diameter ratios, L/D, of 15, 20, and 25, respectively. The diameters, *D*, of the orifices were respectively 1.04, 0.79, and 0.63 mm. The $L/D = 20$ orifice also received surface treatment, where the inner wall was deposited with a fluorocarbon elastomer, Dynamar 9613 (a 3M product). The deposition procedure was similar to that previously described.[9] The variety of capillary die diameters, *D*, and modification of die wall surface allowed us to delineate the sensitivity of the hydrodynamic slip correction to the characteristic length scale *D* and the surface condition and to demonstrate the irrelevance of constitutive instabilities and melt compressibility to the observed stick–slip transition. The experiments were conducted at a number of temperatures between 180 and 260 °C in order to elucidate the temperature dependence of the flow transition. Thermal oxidation is inconsequential and does not affect extrusion of the PEs even at $T = 260$ °C, since there is little air allowed into the barrel and orifice of the capillary rheometer during measurements.

Throughout the explored stress range, both the *in situ* molten and room-temperature solid extrudates were smooth on macroscopic length scales, with the surface roughness <1% of the extrudate diameter. However, under controlled-piston speed, we found using a "rate-controlled" Instron capillary rheometer that extrudate distortion appears, characteristic of spurt flow "fracture". In all that follows, the wall shear stress, σ, is computed from the *applied* pressure, *P*, according to $\sigma = (D/4L)P$ without the Bagley correction, and the wall shear rate, $\dot{\gamma}$, is computed from the *measured* volumetric flow rate, *Q*, according to $\dot{\gamma} = 32Q/\pi D^3$ without the Rabinowitz correction. For the present purpose, it is unnecessary to apply these corrections to the raw data.

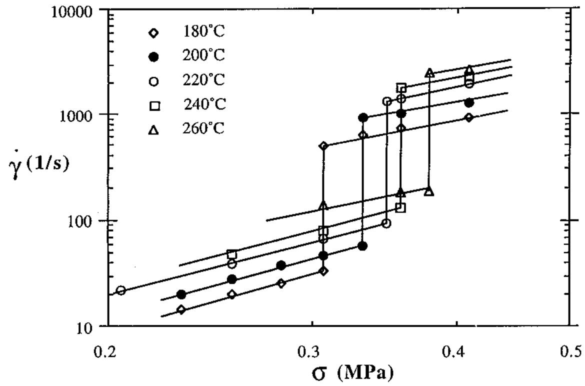

Figure 1. Apparent wall shear rate, $\dot{\gamma}$, versus the applied wall stress, σ, at $T = 180$, 200, 220, 240, and 260 °C for the polyethylene MH20, using $L/D = 15$ die.

Typically a constant driving *P* was applied, corresponding to a σ range from 0.1 to 0.5 MPa, and the *Q* was measured four times in each of such constant pressure experiments. In general, there ubiquitously exists a very narrow range of stresses within which the measured *Q* may jump from its value Q_C, expected for the stick hydrodynamic boundary condition (HBC), to an apparent value Q_A that is often over 1 order of magnitude higher. This superfluid-like flow transition occurred at all the experimental temperatures tested and is sensitive to the surface condition of the orifice wall (bare versus elastomer-coated). Below we define the critical stress, σ_c, to be the value at which the PE resins have 50% probability to slip at the PE/wall boundary. Furthermore in all the subsequent analyses and calculations, except for those involving the surface modification, we note that wall slip is negligible before the transition.

Results

We found for the first time that the quantitative characteristics of the stick–slip transition do not change with temperature. In other words, the transition always takes place at the point where polymer chains are found to experience the same extent of chain stretching, γ_c, and the magnitude of wall slip at the transition is the same at all the temperatures from 180 to 260 °C. Figure 1 shows this flow behavior of the highly entangled polyethylene MH20 at different temperatures, where the critical stress, σ_c, shifts upward linearly with temperature, *T*, and the magnitude of the transition, as approximately quantified by the length of the vertical lines, is essentially the same at the various temperatures. Since σ_c/T is a constant, the transition is evidently not an activation (i.e., chain debonding) process which would require a lower onset stress at a higher temperature.

Figure 2 shows the superposition of all data at different temperatures when plotted as the rescaled stress σ/T versus the reduced shear rate $a_T\dot{\gamma}$, where a_T is the WLF shift factor depicting the temperature dependence of the chain relaxation time, τ (see Table 1). We see from Figure 2 that the stick–slip transition always occurs at a critical chain deformation, $\gamma_c = a_T\dot{\gamma}$, at all temperatures. Furthermore, Figure 2 indicates that the strength of melt/wall interfacial interactions (i.e., the strength and extent of chain adsorption)

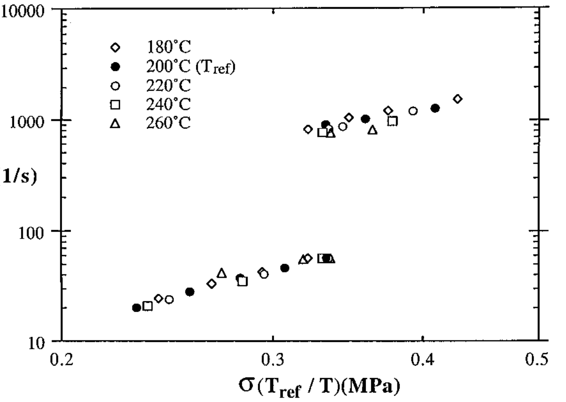

Figure 2. Reduced shear rate, $a_T\,\dot{\gamma}$, versus the rescaled shear stress, $\sigma(T_{ref}/T)$, with T_{ref} = 200 °C for the polyethylene MH20.

Table 1. Temperature Dependence for Polyethylene MH20 (L/D = 15)

T (°C)	$\dot{\gamma}_A$ (s^{-1})	$\dot{\gamma}_C$ (s^{-1})	v_s^c (cm/s)	σ_c (MPa)	a_T	b_c (mm)
180	489	34	5.9	0.307	1.67	1.74
200	914	57	11.1	0.332	1.00	1.95
220	1343	92	16.3	0.348	0.67	1.77
240	1776	132	21.4	0.358	0.45	1.62
260	2489	186	29.9	0.373	0.31	1.61

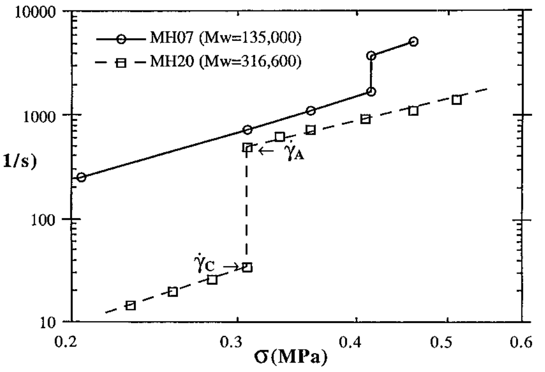

Figure 3. Comparison between polyethylenes MH20 and MH07 of molecular weight 316 600 and 130 500, respectively, at T = 180 °C, using L/D = 15, where $\dot{\gamma}_C$ corresponds to the critical shear rate and $\dot{\gamma}_A$ represents the apparent shear rate just over the transition.

remains sufficiently strong within the experimental temperature range from 180 to 260 °C. Thus the striking transition most probably arises from a chain disentanglement transition that naturally obeys the time−temperature superposition principle. It is important to note that σ_c does not obey σ_c/T = constant for $T \le$ 180 °C, perhaps suggesting flow-induced mesophase at the wall. Future work will focus on the flow transition at $T \le$ 180 °C in greater detail.

One dominant feature of the stick−slip transition is its molecular weight dependence. Specifically, the magnitude of the wall slip diminishes as the molecular weight decreases. Our experiments show that the MH07 polyethylene (M_w = 130 500) exhibits a much smaller stick−slip transition at 180 °C (i.e., a much smaller ratio $\dot{\gamma}_A/\dot{\gamma}_C$ in comparison to that displayed by the MH20 PE (M_w = 316 600) at the same temperature), as shown in Figure 3. This observation agrees with previous studies on the molecular weight dependence.[29] The σ_c for MH07 is found to be higher than that for MH20. The analysis of Figure 3 is given in Table 2. There is no obvious explanation of the M_w dependence of σ_c. More systematic molecular weight dependence studies will be done in future work.

Table 2. Molecular Weight Dependence at T = 180 °C (L/D = 15)

M_w	$\dot{\gamma}_A$ (s^{-1})	$\dot{\gamma}_C$ (s^{-1})	v_s^c (cm/s)	σ_c (MPa)	b_c (mm)
130 5000	3819	1693	27.6	0.414	0.16
316 600	489	34	5.9	0.307	1.74

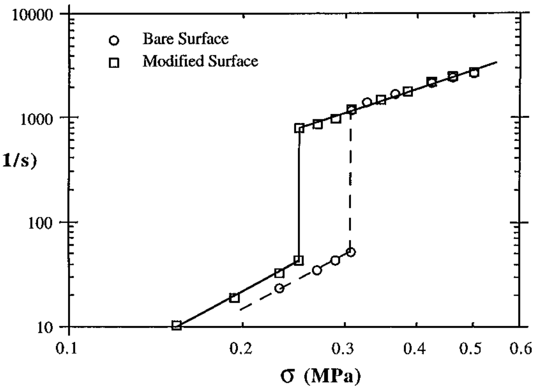

Figure 4. Surface effects on the stick−slip transition at T = 200 °C for the polyethylene MH20, using L/D = 20 die.

A key experiment to perform is one that varies the surface condition of the die wall to explore the microscopic nature of the transition and determine whether the transition is strictly *interfacial*. If the transition is due to the disentanglement process, as we are inclined to believe based on the existence of the master curve Figure 2, the theory of Brochard and de Gennes[19] indicates that σ_c should be lower for a less adsorbing surface with fewer adsorbed chains, ν', per unit area. If the melt flow transition was a manifestation of the theoretically hypothesized constitutive instabilities[13,22−26] and therefore a bulk flow phenomenon, the values of $\dot{\gamma}_A$ and $\dot{\gamma}_C$, as well as σ_c, would not change as the surface condition of the capillary wall is modified. To distinguish these two possibilities, we compare in Figure 4 the flow curves obtained using respectively the bare steel die and the elastomer-coated steel die. The deposition of the fluorocarbon elastomer (Dynamar) is expected to reduce the adsorbed chain density, ν, on the modified die wall. The Dynamar did actually reduce the critical stress for the transition, as the data in Figure 4 indicate. Thus the transition must involve a molecular process at the melt/wall interface. More discussion of the features of Figure 4 will be presented in the next section.

Hydrodynamic corrections due to interfacial slip would also strongly depend on the characteristic dimension of the experimental apparatus (i.e., D). Figure 5 confirms this, lending further evidence to confirm the *interfacial* nature of the stick−slip transition. At each value of wall stress, the apparent wall shear rate was measured using three different die length to diameter ratios, L/D, and die diameters, D. The ratio $\dot{\gamma}_A/\dot{\gamma}_C$, representing the slip correction, increases strongly with decreasing D as shown in Figure 5. The overlapping of the data points below the transition indicates that there is no geometry (i.e., L/D) dependence. As mentioned above, many believe that there might be constitutive instabilities in 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 and a range of shear rates where highly entangled melts exhibit “instability” with a high-shear rate state coexisting with a low-shear rate state.[22−26] The observed D dependence in Figure 5 shows that the stick−slip is not

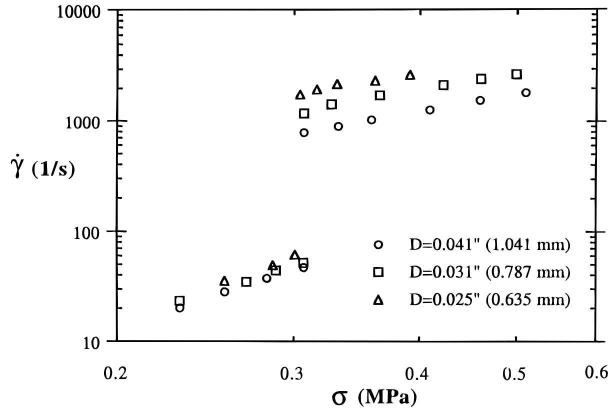

Figure 5. Stick–slip transition of the polyethylene MH20 at T = 200 °C as measured by three different orifices with diameters equal to 1.04, 0.79, and 0.63 mm, respectively.

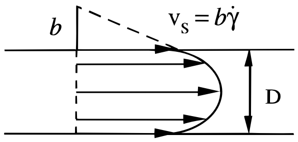

Figure 6. Velocity field in a capillary following transition to the "slip state", where D is the die diameter and b, the extrapolation length, is related to the shear rate at the wall and the apparent slip velocity, v_s, as shown.

a bulk phenomenon, and constitutive instabilities are not pertinent.

Discussion

Transition Characteristics. The previous section described an experimental study of the stick–slip transition phenomenon in capillary flow of PE melts. The flow under controlled pressure was found to be stable in terms of both steady flow rates and extrudate smoothness both below and above the transition. The transition from $\dot{\gamma}_C$ to $\dot{\gamma}_A$ (cf. Figure 3) implies an enormous hydrodynamic slip at the melt/wall interface. At and beyond the critical pressure, P_c, the volumetric flow rate, Q, jumps from Q_C, which is expected for the stick hydrodynamic boundary condition, to Q_A where

$$Q_A = Q_C + (\pi D^2/4)v_s, \qquad (1a)$$

indicating the appearance of a slip velocity, v_s, at the interface. At the transition, (1a) can be rewritten in the well-known Mooney form, in terms of the shear rates $\dot{\gamma}_C$ and $\dot{\gamma}_A$

$$\dot{\gamma}_A/\dot{\gamma}_C - 1 = 8b^c/D \qquad (1b)$$

where $\dot{\gamma}_{A,C} = 32Q_{A,C}/\pi D^3$ and the slip velocity, v_s^c, at the transition was combined with the shear rate $\dot{\gamma}_C$ to introduce a length scale called the *extrapolation length*, $b_c = v_s^c/\dot{\gamma}_C$, that is a material property of the PE/wall interface. See Figure 6 for an illustration of the relation between b and v_s. Both v_s^c and b_c are computed for all of the temperatures from T = 180 to 260 °C according to (1a) and (1b) based on Figure 1 and are tabulated in Table 1. The concept of the extrapolation length, b, can be utilized to quantify the superfluid-like stick-slip transition as observed in Figures 1–5. It is highly remarkable to note from Table 1 that b_c remains essentially *constant* from T = 180 to 260 °C within experimental error and the stick–slip transition always happens at the same reduced critical shear rate and stress (cf. Figure 2). This means the critical condition for the stick–slip transition is invariant and transition occurs through a chain disentanglement process that satisfies the time–temperature superposition. To our knowledge, this important property of the transition has never been demonstrated before.

There is a strong molecular weight dependence of the magnitude of the interfacial slip. Figure 3 shows that the magnitude of wall slip is much smaller for the polyethylene MH07 of M_w = 130 500 than that for the polyethylene MH20 of M_w = 316 600. The extrapolation length b_c = 0.16 mm for MH07 in comparison to b_c = 1.74 mm for MH20 at 180 °C. The origin of the molecular weight dependence of slip arises from the strong molecular weight dependence of the melt viscosity, η_m, in the entanglement regime. It is easy to show[19] that $b = (\eta_m/\eta_i)a$, where η_i is an effective interfacial viscosity that is essentially independent of M_w beyond the stick–slip transition and a is a molecular length. Given the molecular weight difference between MH20 and MH07, it is not surprising that b_c of MH07 is less than one-tenth of that of MH20.

Hydrodynamic Origin of Spurt Flow. The spurt flow phenomenon, observed under the condition of controlled rate, has been a most perplexing rheological property of the commodity polyethylene resins. When the polyethylene is extruded at a *fixed* piston speed, corresponding to an apparent wall shear rate, $\dot{\gamma}$, between $\dot{\gamma}_A$ and $\dot{\gamma}_C$, extrudate distortion occurs and the measured pressure drop oscillates with time. There are two "exceptions". (a) Sometimes introducing additives,[33] using Teflon capillary die,[34,35] or modifying the die wall surface[35] to reduce the surface energy has been shown to minimize the spurt flow instability for polyethylene. (b) For other less entangled polymers such as polystyrene (PS) and poly(dimethylsiloxane) (PDMS) of comparable molecular weight, the spurt flow characteristics are nowhere to be found under controlled speed, and no flow discontinuity transition is observed under controlled stress either.[36] What is common in both cases is the lack of a large stick–slip transition. In case a, the complete wall slip is already present throughout the typical shear rate range (where spurt flow would occur without the surface modification) due to elimination of the adsorbed chains by surface modification, and therefore there is no longer a large stick–slip transition to destabilize the capillary flow under the condition of constant speeds. In case b, available PS and PDMS are not sufficiently entangled to produce a large interfacial slip that would yield a great difference between the applied shear rate and the actual shear rate present in the capillary die, leading to an indeterminate state of the hydrodynamic boundary condition.

Here we describe the origin of the spurt flow instability in terms of the flow-induced stick–slip transition. In constant piston speed mode, for a given piston speed, V^*, if it produces a flow in the capillary die that generates a σ lower than the σ_c for the stick–slip transition, no slip occurs ($v_s = 0$) and the extrusion will continue. Upon application of a sufficiently high V^*, the initial mass flow rate, Q, out of the die is smaller than the externally applied flow rate, $Q_{ext} = V^*\pi R_b^2$, where R_b is the barrel radius. The difference, $Q_{ext} - Q$, causes pressure buildup in the barrel and melt compression until P reaches the point P' at the die entry that begins to produce a wall stress $\sigma > \sigma_c$. At this point, the stress-induced stick–slip transition occurs and Q jumps to Q_A given by (1a) where Q_C corresponds to the pressure P'.

Now $Q_A > Q_{ext}$, causing decompression and rapid pressure drop. The pressure in the barrel drops until the stress on the die wall allows the hydrodynamic boundary condition to restore its stick state where the absorbed chains re-entangle with the unbound chains and v_s in (1a) goes to zero. At this point, the mass flow leaves the barrel at rate $Q < Q_{ext}$. Subsequently the cycle begins again and will repeat indefinitely, marked by periodic oscillation in the measured pressure drop and fluctuation in the actual wall shear stress. The periodicity turns out to be proportional to the volume of melt in the barrel and inversely proportional to Q_{ext}.[4,12] Since the actual wall stress and shear rate in the capillary die fluctuate in time, the degree of die swell also oscillates in time, giving rise to the familiar bamboo-like appearance of the extrudate which is often termed spurt melt fracture, although it is not a true melt fracture. Indeed we found that the polyethylene MH20 showed bamboo-looking extrudate under controlled-piston speed. The same polymer exhibits *smooth* extrudate when extruded under controlled pressure. The striking contrast between constant rate and constant pressure experiments shows that the stress-induced stick−slip transition is the origin of the spurt flow behavior of highly entangled linear polyethylene.

Molecular Processes at the Stick−Slip Transition. The stick−slip transition appears to occur only for relatively strong melt/wall interfaces, so that there is sufficient chain adsorption to assure the stick HBC up to the transition when the adsorbed chains disentangle from the unbound free chains. Violation of the stick HBC following the transition is an extraordinary property of highly entangled polymeric liquids such as the PE studied in this work. The extraordinarily large interfacial slip observed at the stick−slip transition could also, in principle, originate from flow-induced chain debonding. In the literature of polymer interfacial adhesion,[37] often no distinction is made between chain debonding and chain disentanglement. Our observation of the temperature dependence of the stick−slip transition rules out the possibility of chain debonding and favors a previously proposed theoretical picture of interfacial chain disentanglement.[19]

Many studies have been carried out in the past to interrogate the phenomena of spurt flow “instability” and flow discontinuity, observed respectively under controlled-piston speed[3−4,12,14−16] and controlled pressure.[27−31] The most recent theoretical proposal is the disentanglement transition mechanism of Brochard and de Gennes.[19] Our data represent the first experimental evidence supporting this picture of the disentanglement taking place in the first molecular layer at melt/solid interfaces. This theoretical picture of a coil−stretch transition of the adsorbed chains at the PE/wall interface clarifies all previous speculations[12,27b,29] about the molecular origin of the stick−slip transition that always center around the question of whether the transition involves cohesive or adhesive breakdown.

The idea of elastic strain energy has also been proposed many times in the past. A modern version is that of Hill et al.[38] Based on energy balance between the elastic strain energy and work of adhesion, which is an argument drawing analogy between adhesive failure of peel experiments[39] and the apparent adhesive failure in melt flow, an adhesion failure mechanism involving chain debonding at PE/metal interfaces was *hypothesized* for slip and unsteady flow.[38] Our data do not appear to support this proposed mechanism for strong interfaces such as those between PE melt and metallic die walls.

Table 3. Surface Effect on Transition of MH20 at $T = 200$ °C ($L/D = 20$)

surface condition	$\dot{\gamma}_A$ (s^{-1})	$\dot{\gamma}_C$ (s^{-1})	σ_c (MPa)	b_c (mm)
bare	1178	52	0.307	2.13
Dynamar	805	43	0.250	2.32

Table 4. Stick−Slip Transition of MH20 at $T = 200$ °C in Different Orifices

L/D	D (mm)	$\dot{\gamma}_A/\dot{\gamma}_C$	$\dot{\gamma}_C$ (s^{-1})	v_S^c (cm/s)	b_c (mm)
15	1.049	16.8	47	9.6	2.11
20	0.79	22.7	52	11.1	2.13
25	0.63	28.7	61	13.2	2.16

Data in Figure 4 further indicate that the stick−slip transition is strictly interfacial and not cohesive. The phenomenon can be understood in terms of the recent theory of Brochard and de Gennes.[19] Not only is the predicted scaling for $\sigma_c \propto T$ consistent with our experimental data but also in agreement is the dependence of σ_c on the interfacial condition, i.e., on the adsorbed chain density, ν. Coating the die wall with the fluorocarbon elastomer (Dynamar 9613) reduced ν to $\nu' < \nu$. The die wall with less chain adsorption allowed the stick−slip transition to occur at a lower $\sigma_c' < \sigma_c$ as shown in Figure 4. Table 3 summarizes the difference due to the surface modification, where the b for the surface-modified die was calculated by taking into account the correction due to the pretransitional slip.

The nature of the stick−slip transition can be further demonstrated by examining it using different capillary L/D and different D. Figure 5 shows the dependence of the slip correction (i.e., magnitude of the discontinuity in the wall shear rate) on the orifice D. At the transition, the ratio $\dot{\gamma}_A/\dot{\gamma}_C$ varies from 16.8 for $D = 1.04$ mm to 28.7 for $D = 0.63$ mm as presented in Table 4, where b_c’s calculated from Figure 5 for the three L/D ratios are also listed. The inverse relation between $\dot{\gamma}_A/\dot{\gamma}_C$ and D is consistent with (1b). Similar observations have been reported before.[29]

Conclusion

We have characterized a superfluid-like interfacial transition phenomenon as a function of temperature, molecular weight, and surface condition and proposed a plausible molecular mechanism for the stick−slip transition. A universal feature is that the flow transition occurs ubiquitously over a wide range of experimental temperatures, T, unlike the superfluidity transition in liquid helium. The critical stress, σ_c, for the interfacial transition turns out to linearly increase with T. The master curve in Figure 2 shows *for the first time to our knowledge* that the stick−slip transition occurs at the *same* reduced stress and corresponding critical chain deformation. The magnitude of the flow transition, as measured by the extrapolation length, b, is *demonstrated for the first time* to be essentially independent of T. Thus b is a materials property and a much more useful concept than the conventional notion of slip velocity that is merely a kinematic quantity. All of the evidence indicates that *chain disentanglement* at the *first molecular melt/wall interfacial layer* is most likely the molecular process taking place following the transition. At the transition, the interfacial interactions suddenly diminish as the adsorbed chains disentangle from the surrounding free chains. The slip occurring at the melt/wall interface appears to be unrelated to any other possible molecular processes such as chain debonding, although such a process would require little energy dissipation in comparison to the viscous dissipation. This conclusion implies that the superfluid-like stick–slip transition may not be sensitive to the type of metallic walls, as long as the melt/wall interfacial interactions are sufficiently strong. It is worth noting that the proposed disentanglement mechanism is consistent with a recent spectroscopic study[40] of polyethylene/melt interfaces that revealed the presence of a molecular layer of PE on the metal surfaces after peeling. Furthermore, the coil–stretch mechanism for the stick–slip transition also illustrates the molecular origin of the hysteresis associated with the flow discontinuity.[27–31] If the PE/wall interface can be made sufficiently weak so that PE chains can only interact with the die wall via van der Waals interactions, one may anticipate a stress-induced chain-debonding process to replace the disentanglement mechanism for interfacial slip. In an intermediate case, we observed the influence of the surface condition of the die wall on the onset of the transition. This feature is consistent with the proposed disentanglement mechanism for the transition.[19]

The molecular weight dependence is an exquisite feature of the superfluid-like flow transition. It underscores the molecular origin of the transition and illustrates a peculiar example of interfacial phenomena where the interfacial behavior depends directly on the bulk properties—degree of chain entanglement in the bulk. The expression $b = (\eta_m/\eta_i)a$ provides a qualitative description of the M_w dependence of the stick–slip transition without explicitly describing the actual microscopic interfacial process occurring at the transition. A more precise theoretical treatment is needed to specify the hypothetical interfacial viscosity, η_i, in terms of the dynamic interfacial structures.

Since the nature of the hydrodynamic boundary condition (HBC) depends on the wall shear stress, the HBC is indeterminate when capillary flow is driven under controlled-piston speed in a region where the adsorbed chains switch back and forth between their entangled (coil) and disentangled (stretch) states. It is this HBC indeterminacy that produces the observed spurt flow symptoms during extrusion under the specific condition of controlled-piston speed, where temporal oscillation of pressure drop and bamboo-like extrudate take place. In other words, the fluctuations in the actual wall stress and shear rate due to the interfacial stick–slip transition produce oscillations in the die swell, so that the extrudate *appears* to be "melt fractured". This extrudate distortion is clearly not a manifestation of an intrinsic bulk flow instability, nor is it a representation of an inherent gross melt fracture. Furthermore, our experiments systematically eliminate the suggestion of constitutive instabilities as the origin of the spurt flow "instability".

In summary, the results of this work suggest: (a) the interfacial flow transition characteristics satisfy the time–temperature superposition, (b) the molecular origin of the stick–slip transition may be *interfacial* chain disentanglement, (c) the spurt flow rheology and the associated extrudate irregularities arises from the indeterminacy of the hydrodynamic boundary condition under controlled-piston speed due to the stress-induced stick–slip transition, and (d) the extrapolation length, *b*, is a preferred quantity for characterizing wall slip. Future studies must attempt to further verify the molecular processes involved in the flow-induced stick–slip transition and further establish the interfacial nature of the stick–slip transition phenomena.

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