Annu. Rev. Fluid Mech. 2001. 33:265–87

EXTRUSION INSTABILITIES AND WALL SLIP

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Key Words melt fracture, sharkskin, slip-stick, adhesion, extrudate swell

■ **Abstract** Polymer melts exhibit extrusion instabilities at sufficiently high levels of stress, and they appear to exhibit wall slip. I explore the evidence for slip, the possible mechanisms of slip, and the relation between slip and extrusion instabilities.

INTRODUCTION

Many fabrication processes for polymeric objects include melt extrusion, in which the molten polymer is conveyed by a ram or a screw and the melt is then forced through a shaping die in continuous processing or into a mold for the manufacture of discrete molded parts. The properties of the fabricated solid object, including morphology developed during cooling and solidification, depend in part on the stresses and orientation induced during the melt shaping. Most polymers used for commercial processing are of sufficiently high molecular weight that the polymer chains are highly entangled in the melt, resulting in flow behavior that differs qualitatively from that of low-molecular-weight liquids. Obvious manifestations of the differences from classical Newtonian fluids are a strongly shear-dependent viscosity and finite stresses normal to the direction of shear in rectilinear flow, transients of the order of seconds for the buildup or relaxation of stresses following a change in shear rate, a finite phase angle between stress and shear rate in oscillatory shear, ratios of extensional to shear viscosities that are considerably greater than 3, and substantial extrudate swell on extrusion from a capillary or slit. These rheological characteristics of molten polymers have been reviewed in textbooks (e.g. Larson 1999, Macosko 1994); the recent research emphasis in rheology has been to establish meaningful constitutive models that incorporate chain behavior at a molecular level.

All polymer melts and concentrated solutions exhibit instabilities during extrusion when the stresses to which they are subjected become sufficiently high. The first manifestation of extrusion instability is usually the appearance of distortions on the extrudate surface, sometimes accompanied by oscillating flow. Gross distortion of the extrudate usually follows. The sequence of extrudate distortions

0066-4189/01/0115-000265$14.00

during continuous extrusion of a linear low-density polyethylene (LLDPE) at a controlled rate (in contrast to a controlled stress) through a long stainless steel capillary is shown in Figure 1. The surface of the extrudate becomes visibly rough at a wall shear stress level that is typically of the order of 0.1 MPa, with apparent periodicity in the small-amplitude distortion; this phenomenon is commonly called sharkskin. At a higher level of stress, typically of the order of 0.3 MPa, the flow becomes unsteady and the extrudate alternates between sharkskinned and smooth segments; this is commonly called slip-stick or spurt flow. At still higher stress levels, sometimes after a second region of spurt flow, the flow becomes steady. The extrudate surface is relatively smooth during the early part of this steady regime, with a long-wavelength distortion, but gross distortions occur at higher stresses; this regime is commonly called wavy or gross melt fracture. The term melt fracture is often used collectively for all extrusion instabilities. The behavior shown here is observed for many linear polymers (i.e. chains whose backbone elements are connected in a linear fashion, without large branches), with most observations having been made on high-density polyethylenes (HDPEs) and LLDPEs, polybutadiene, polyisoprene, and linear polysiloxanes (silicone polymers). Studies by El Kissi & Piau (1990, 1996) contain particularly fine photographs documenting the various regimes. Most commercial grades of branched polymers, such as low-density polyethylene and branched polysiloxane, do not exhibit sharkskin or spurt flow, but they do exhibit gross melt fracture, usually with a large-amplitude periodic distortion that appears to be accompanied by a swirling flow upstream of the entrance to the capillary. Distortions on the surface of injection-molded parts, which are not described in the literature, show similar periodicities and may be manifestations of the same phenomena.

Extrusion flow instabilities were apparently observed during World War II and were first reported in 1945. There is a good historical survey of extrusion instabilities in the text by Leonov & Prokunin (1994). The experimental observations through 1975 are described in a broad review of polymer flow instabilities by Petrie & Denn (1976), and it is fair to say that nearly everything phenomenological that is known today about extrusion instabilities had been reported in the literature by that time. There is a subsequent broad review of polymer flow instabilities by Larson (1992). The notion that a breakdown of the no-slip boundary condition might be linked to melt fracture is found in the early literature and has been a recurring theme; Denn (1990) identified the subject as one of the outstanding issues in viscoelastic fluid mechanics in an earlier review. Figure 2 is a flow curve obtained in a controlled-throughput experiment for an LLDPE; $8V/D$ is the nominal shear rate, where V is the average velocity and D is the capillary diameter. There is a small but reproducible change in the slope of the flow curve at the visual onset of sharkskin, which some authors have attributed to the onset of wall slip (e.g. see Kalika & Denn 1987); there is a discontinuity in the flow curve at the onset of the slip-stick regime, which is strongly suggestive of wall slip. Much of the research on instabilities in the past decade has been concerned with the relation between instabilities and slip.

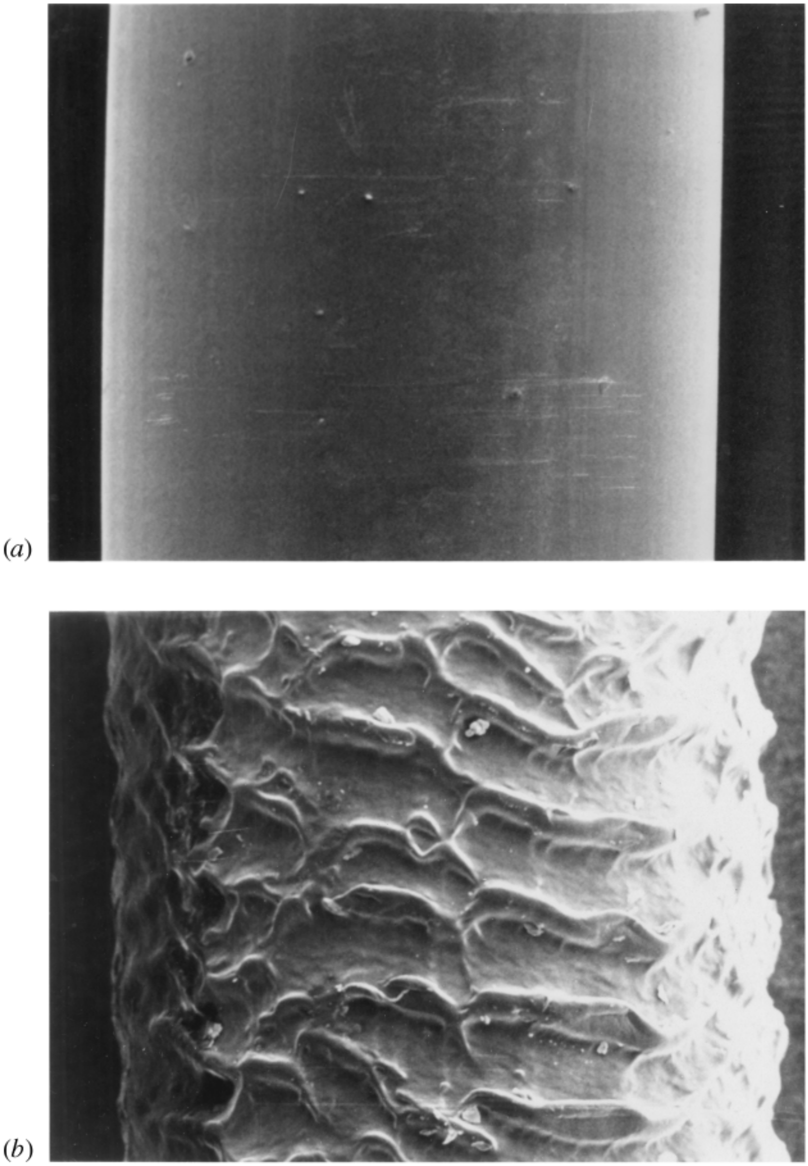

Figure 1 Extrudates of linear low-density polyethylene from controlled-rate experiments: (*a*) stable; (*b*) sharkskin; (*c*) slip-stick, showing alternating smooth and sharkskin regions; (*d*) wavy, initial portion of the upper branch of the flow curve; (*e*) Gross melt fracture. (*a*–*d*) From Pudjijanto & Denn (1994); (*e*) from Kalika & Denn (1987), with permission of the *Journal of Rheology*.

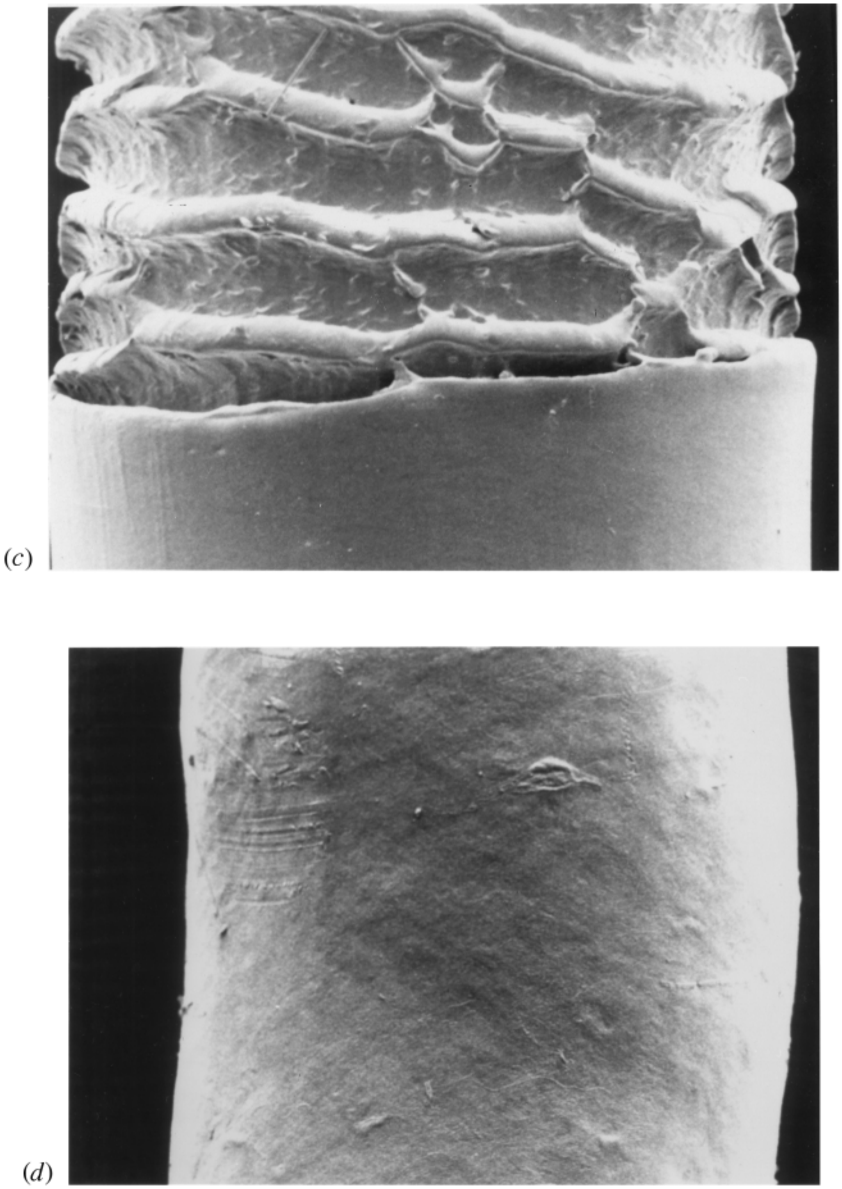

Figure 1 (*Continued*)

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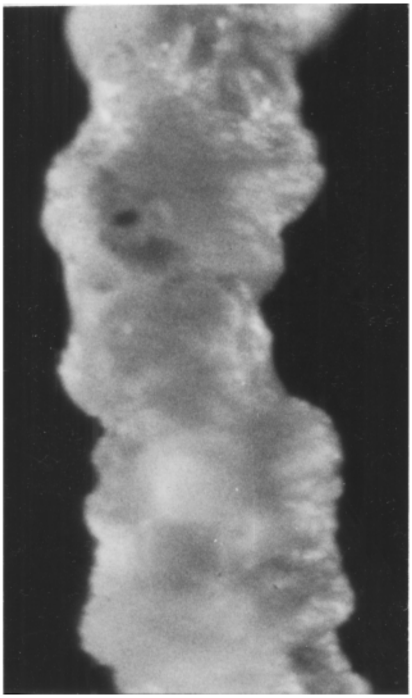

Figure 1 (*Continued*)

THE NO-SLIP CONDITION

The no-slip boundary condition is a core concept in fluid mechanics, and it is usually introduced in textbooks as though it were intuitively obvious. It is not intuitively obvious to the beginner, nor was it intuitively obvious to the founders of the discipline. Goldstein (1938, 1969) describes the early history of the concept, including the various opinions and supporting evidence, and Schowalter (1988) has written a more recent review. Navier's concept of slip is often quoted today; he proposed that the fluid velocity relative to the adjacent surface (the slip velocity), ν_s, is proportional to the shear stress at the wall, τ_w:

$$\eta \nu_s = b \tau_w. \tag{1}$$

Here η is the shear viscosity and *b* is a characteristic length equal to the distance that the velocity profile at the wall must be extrapolated to reach zero; *b* would presumably be a material parameter characteristic of the fluid-solid pair. The no-slip condition was ultimately accepted based on its agreement with experiments conducted with Newtonian fluids, especially the sensitive fourth-power dependence of flow rate on diameter in capillary flow.

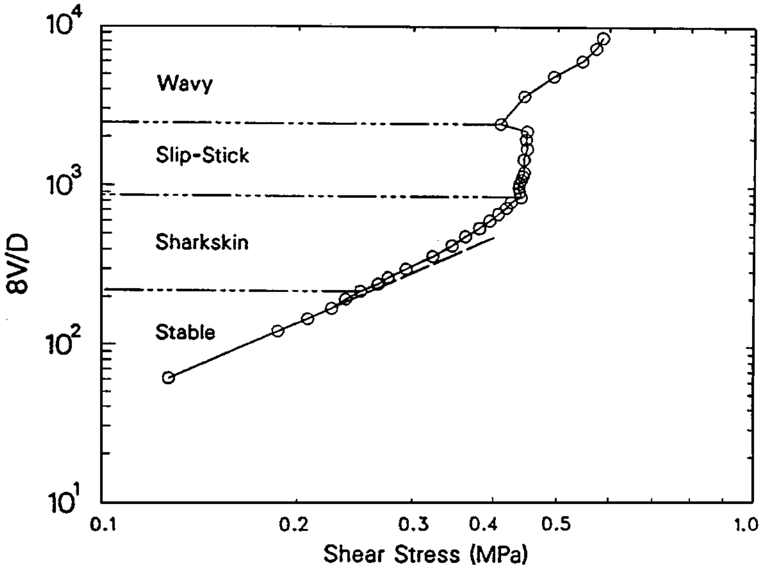

Figure 2 Shear rate vs shear stress for a linear low-density polyethylene in a controlled rate experiment. Here $8V/D$ is the nominal shear rate, V is the average velocity, and D is the capillary diameter. From Kalika & Denn (1987), with permission of the *Journal of Rheology*.

Goldstein's (1938) acceptance of the no-slip condition is tentative; he states, "At the present time it appears to be definitely settled that for practical purposes the fluid immediately in contact with a solid body may be taken as having no velocity relative to the solid, at any rate for nearly all fluids; but the exact conditions on a molecular scale remain still in doubt."

There are also very careful modern experiments with Newtonian fluids that keep the issue unresolved. Schowalter (1988) calls attention to apparent slip in gas-phase experiments by Chen & Emrich (1963), "... the results of which do not seem explicable in terms of conventional continuum or molecular mean–free path arguments." Bulkley's (1931) work at the National Bureau of Standards is of particular interest. Bulkley was studying the possibility of adsorption effects in fine capillaries, but in 11-μm-diameter glass capillaries he found a systematic "... discrepancy between the measured and calculated values for the radius ... equivalent to an error of about 9 per cent in the viscosity of a liquid" in the direction of apparent slip. Bulkley noted, however, that the error was within the limits of measurement uncertainty of the capillary diameters. Debye & Cleland (1958) reported discrepancies from the expected throughput for liquid hydrocarbons in well-characterized porous glass, which they attributed to "a slipping absorbed layer of molecular thickness at the wall."

The issue of wall slip for Newtonian fluids has seemed to be of limited interest, because phenomena that act over distances of molecular size, or even a fraction of a micrometer, generally have a negligible effect on macroscopic behavior. Bulkley's observations do raise a cautionary note with regard to flow and transport in micro devices, however, where channels with dimensions comparable to Bulkley's capillaries are used. Indeed, there have been reports of reduced frictional drag in the laminar flow of liquids in microchannels intended for heat exchange, although it is not clear if the observations can be explained in terms of wall slip (Pfahler et al 1991). Wall effects extending over lengths of the order of molecular dimensions or fractions of a micrometer could have measurable consequences for polymeric materials.

WALL SLIP IN POLYMER MELTS

The first published report of apparent wall slip in polymer melts seems to be by Rielly & Price (1961), who marked the face of a mold cavity with a colored wax crayon and injected molten HDPE at a high rate. The color appeared on the molded part at the place marked on the mold, as expected, but it also appeared on the opposite face at a downstream distance corresponding to three times the channel thickness. This behavior was observed with HDPE in molds of a variety of shapes and marking locations; it was not observed for polystyrene or cellulose acetate.

Petrie & Denn (1976) reviewed the early literature on polymer slip, and Joshi and coworkers (2000) recently tabulated more than 20 experimental studies of apparent slip in melt flow. One early study deserving of particular mention is that of Benbow & Lamb (1963), who performed a variety of experiments with different polymers and die materials; these included using dies constructed of different materials and following colored markers at the die wall during extrusion. Their conclusions below foreshadow much of the research of the most recent decade.

> (*a*) Melt instability originates at the die wall near the entry to the die.
>
> (*b*) When the melt flow is unstable, slipping occurs along the die wall.
>
> (*c*) The material from which the die is constructed affects the onset of instability.
>
> (*d*) Flow birefringence experiments suggest that the stress changes in a manner consistent with a stick-slip motion.
>
> (*e*) Interpretation of the onset of melt instability as being due to a breakdown of adhesion between the polymer and the die wall is supported by the known dependence of σ crit. [the critical stress] on molecular properties and external conditions (Benbow & Lamb 1963).

Ramamurthy (1986) initiated the "modern" period of studies of slip in polymers and the relation between slip and extrusion instabilities when he reported that the flow instabilities illustrated in Figure 1 can be eliminated by extruding linear polymers through an α-brass die under conditions identical to those in which instabilities are observed when a conventional chrome-plated stainless steel die is used. This work attracted considerable attention and focused research on the issue of slip. Ramamurthy believed that the vanishing of the instabilities was a consequence of improved adhesion, but he did not report flow curves. He noted that the observed phenomena required an induction period, and based on observations of a color change on the die surface, he speculated that "the formation of either clean nascent metallic copper or some chemical form of copper (for example, oxide of copper) during the induction time under processing conditions, is responsible for improved adhesion in the die land region with CDA-360 surfaces." Ramamurthy's work was controversial, in part because of the claim that improved adhesion was required to eliminate the instabilities, whereas the industrial practice was (and remains) to add what were believed to be "slip promoters" to delay the onset of instabilities.

Ramamurthy's claim that the instabilities in LLDPE can be eliminated by using an α-brass die was first validated independently by Ghanta and coworkers (1999), who found that it was necessary to extrude an olefin containing an abrasive through the die prior to extrusion of the polyethylene, probably to remove any oxide layer, and to start the system up under a nitrogen blanket to minimize oxidation. The flow curves obtained by Ghanta and coworkers using identical brass and stainless steel dies are shown in Figure 3; the vertical lines reflect the range of pressure oscillations. Sharkskin and slip-stick flow were observed with the stainless steel die, whereas smooth extrudates and a gradual transition to the upper branch of the flow curve were obtained following initial transients with the brass die. One notable feature of these data is that the throughput at a fixed stress is higher for

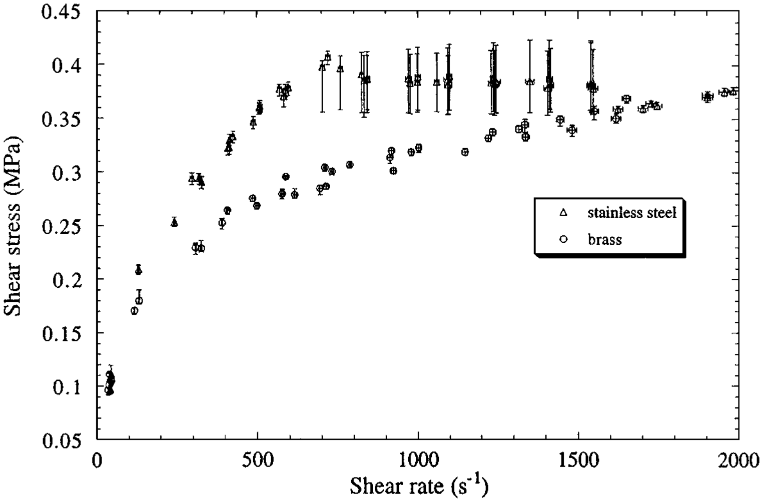

Figure 3 Steady-state flow curves for the continuous extrusion of a linear low-density polyethylene through identical stainless steel (triangles) and α-brass (circles) capillaries. The vertical lines reflect the range of pressure oscillations at a given throughput. From Ghanta et al (1999), with permission of the *Journal of Rheology*.

the brass die, suggesting, in contrast to Ramamurthy, that wall slip, not improved adhesion, suppresses the instabilities.

Chen and coworkers (1993) studied the extrusion of an LLDPE through long capillaries fabricated from four different materials, with three diameters each: copper, stainless steel, aluminum, and glass. The copper was etched to different degrees of surface roughness. Slip velocities were deduced from the diameter dependence of the flow curves. The largest apparent slip velocities were observed with stainless steel, whereas no slip was seen with aluminum. Chen and coworkers concluded that both the material and the roughness contribute to the magnitude of the slip. A similar conclusion was reached by Person & Denn (1997), as well as by El Kissi and coworkers (1994) in a study of flow of polydimethylsiloxane (PDMS) through slit dies of steel, silica, and fluorinated silica. The fluorinated surface was particularly effective in promoting apparent slip and delaying the onset of extrudate defects.

Many authors have studied extrusion through capillaries or slits with fluoropolymer surfaces. The general conclusion is that there is substantial apparent slip, and instabilities are eliminated or reduced in intensity. Typical results can be found in the reviews by El Kissi & Piau (1996) and Wang & Drda (1997). Figure 4 shows a smooth, transparent extrudate from the fluoropolymer-coated center portion of a slit die, whereas surface distortions remain on the uncoated portions.

Most reports of slip in polymer melts and concentrated solutions have utilized mechanical measurements, like the studies mentioned above, and hence have been indirect measurements. Leger and coworkers (Migler et al 1993, Leger et al 1997)

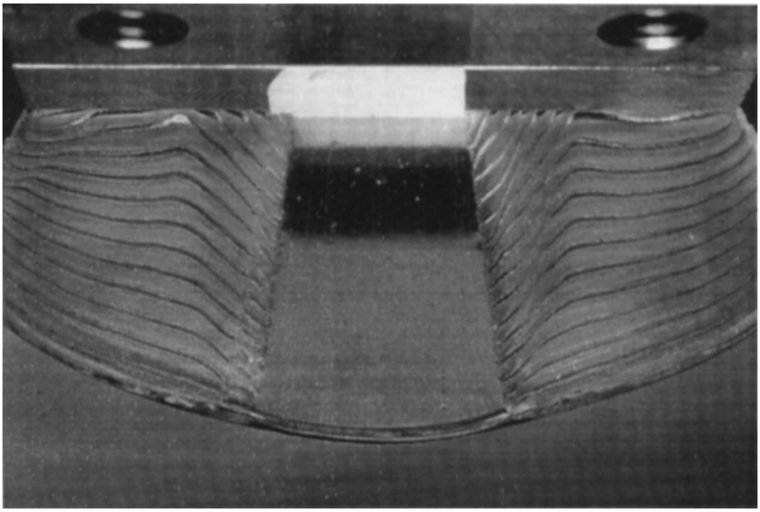

Figure 4 Polydimethylsiloxane flowing from a film die with a 2-mm gap. The center portions of the upper and lower die faces have a fluorinated coating. From El Kissi & Piau (1996), with permission of Elsevier Science BV.

used near-field laser velocimetry, which combines optical evanescent wave spectroscopy with photobleaching of fluorescent tracer molecules, to carry out direct observations of motion in plane Couette flow of PDMS within 100 nm of a polished silica surface. They reported a regime of small slip, with $b \sim 0.2\ \mu$m, followed by a transition to macroscopic slip with values of b of the order of several hundred micrometers. The transition was identified with a coil-stretch transition of bound surface chains. Legrand and coworkers (1998) applied a modification of the same technique to pressure-driven flow of PDMS over a steel surface. They placed a small amount of PDMS containing fluorescent chains on the channel wall, and the intensity decay was recorded after the flow was started. A small slip velocity was observed prior to the onset of unstable flow; macroscopic slip was observed following the onset of a flow instability, with an apparent slip plane located within the polymer. Related work is reviewed by Leger and coworkers (1999).

Wise and coworkers (2000) modified an infrared evanescent wave spectroscopy technique developed by Dietsche and coworkers (1995) to monitor the disappearance of a sample of deuterated polybutadiene displaced in a channel by unlabeled polybutadiene of the same molecular weight over surfaces of zinc selenide and copper- and fluoropolymer-coated zinc selenide. Absorbance decay data for a highly entangled melt are shown in Figure 5. Data for normalized absorbance of

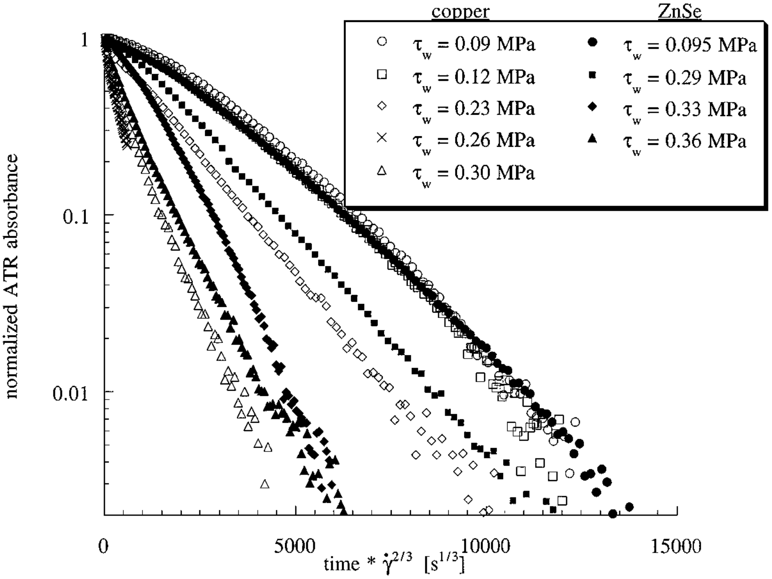

Figure 5 Normalized infrared absorption versus reduced time for a 120,000-molecular-weight polybutadiene over zinc selenide (solid symbols) and copper (open symbols) surfaces, where τ_w is the wall shear rate. Note the superposition of the data at the lower stresses. From Wise et al (2000), with permission of the *Journal of Rheology*.

the labeled polymer, plotted as a function of time multiplied by the two-thirds power of shear rate, will superimpose for convective diffusion with a constant diffusivity and no wall slip, and such a superposition is observed with both unentangled and slightly entangled melts (Wise et al 1998); the data superimpose at the lower stress levels, whereas the increased decay rate as a function of normalized time with increasing stress and the surface sensitivity suggest apparent slip. Slip lengths *b* of the order of 0.5 μm were inferred from simulations of the flow, together with reduced chain mobility near the surface, but finite slip lengths could be discriminated in the data analysis only at stress levels above those at which the onset of sharkskin became visible in capillary extrusion experiments. Massive slip was sometimes observed at stress levels typical of slip-stick flow. It is worth noting that linear PDMS and polybutadiene are used for studies of this type because they exhibit the full range of instabilities illustrated in Figure 1 at or near room temperature. In addition, polybutadiene can be synthesized with a narrow-molecular-weight distribution, which is important in chain mobility studies because of the strong dependence of polymer diffusivity on molecular weight.

Callaghan and coworkers (e.g. Britton & Callaghan 1997, Britton et al 1999) have used nuclear magnetic resonance spectroscopy to image velocity distributions in shear and capillary flow. They have observed apparent slip in polymer solutions, as well as "shear banding" in wormlike surfactant solutions. It is likely that the apparent slip they observed in solutions is a consequence of the development of a solvent-rich layer of reduced viscosity near the wall and is different from the mechanism(s) in melt flow, but the technique is a promising candidate for further studies on melts. As with the two evanescent wave spectroscopic techniques, resolution at a molecular scale is not possible with nuclear magnetic resonance imaging.

Mhetar & Archer (1998b) used a tracer particle velocimetry method described by Archer and coworkers (1995) to study slip in a series of polybutadiene melts sheared between clean silica surfaces. They found three regions of slip: "weak slip," where the slip velocity is proportional to the stress and *b* is a constant (i.e. Navier slip); "stick slip," observed only in samples above a minimum molecular weight, where the shear stress oscillates; and "strong slip," with values of *b* between 100 and 1500 μm. The values of *b* measured in the weak-slip regime for three molecular weights were very close to those deduced from mechanical torsional shear measurements. Particle-tracking experiments indicative of slip were reported as early as 1964 (Galt & Maxwell 1964), but the particle size was such that the apparent slip could have been simply a consequence of the velocity gradient across the particles; the particles used by Archer and coworkers were sufficiently small that this mechanism could not explain the data.

Münstedt and coworkers (2000) employed laser Doppler velocimetry to measure velocity profiles in slit flow of a HDPE. Figure 6*a* shows profiles prior to the onset of extrudate distortions, whereas Figure 6*b* shows profiles at the maximum and minimum pressures in the oscillatory slip-stick regime. Extrapolation to the wall clearly indicates slip in both flow regimes; similar measurements on a branched low-density polyethylene extrapolated to a zero velocity at the wall.

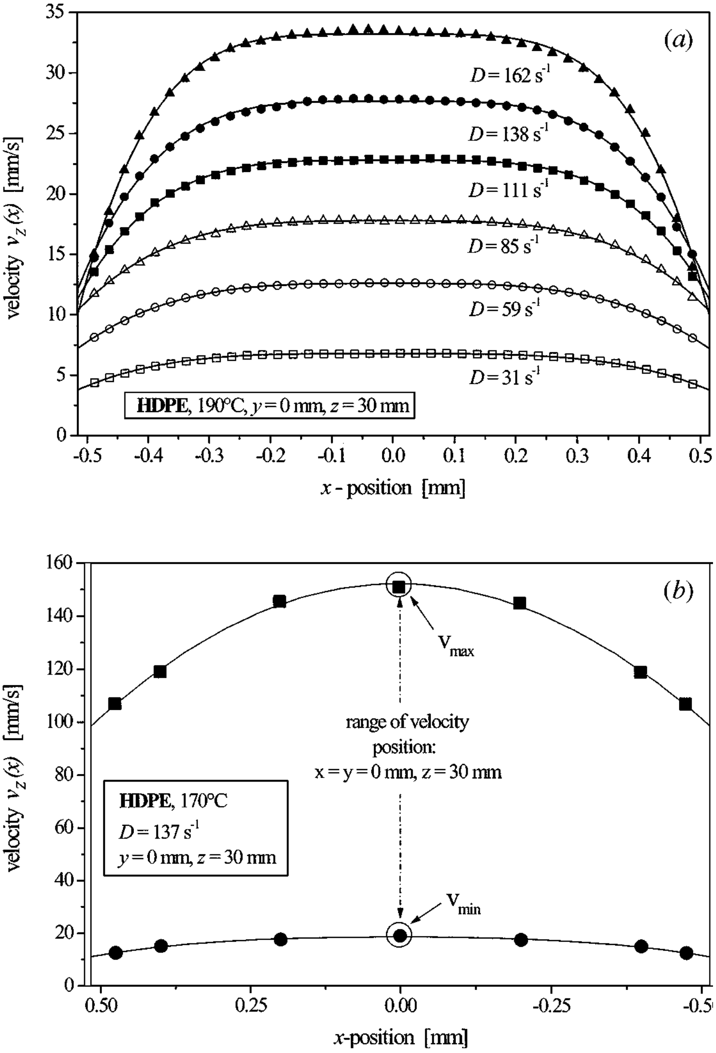

Figure 6 Velocity profiles for a high-density polyethylene (HDPE) melt. (*a*) Prior to the onset of extrudate distortions. (*b*) In the slip-stick regime, corresponding to the maximum and minimum throughputs. $V_{\max}$, maximum velocity; $V_{\min}$, minimum velocity. From Münstedt et al (2000), with permission of the *Journal of Rheology*.

The melt studies cited here were selected because they illustrate the major observations; the work of other research groups, some extremely prolific, can be found in the references of the papers and the reviews cited above and those that follow. In particular, significant experimental contributions by Vinogradov and coworkers are discussed by Petrie & Denn (1976), Denn (1990), and Leonov & Prokunin (1994). The general conclusion that can be reached is that apparent slip is observed for some highly entangled linear polymers, whereas it has not been observed for branched polymers or for linear polymers with an insufficient number of entanglements per chain. The most sensitive methods of measurement indicate the appearance of slip at stresses below those at which the onset of extrudate distortion becomes visible. The slip behavior at stresses characteristic of slip-stick and the upper branch of the flow curve appears to be qualitatively different from that at stresses characteristic of sharkskin and below.

THEORIES OF SLIP

There are three broad pictures of wall slip in polymer melts and concentrated solutions. It is likely that different models apply (if at all) in different regimes, and perhaps even apply simultaneously. One view holds that slip is the result of an adhesive failure of the polymer chains at the solid surface. A second holds that slip is a cohesive failure resulting from disentanglement of chains in the bulk from chains adsorbed at the wall, with the polymer slipping over an adsorbed "brush." A third is that there is a lubricated layer at the wall, perhaps the result of a stress-induced transition to a low-viscosity mesophase.

Hill and coworkers (1990) proposed a continuum model of slip based on an extension of results for the adhesion of elastomers; the slip velocity in this theory is analogous to the velocity of crack propagation as the elastomer is peeled from the substrate. A number of authors have formulated theories based on adsorption/desorption kinetic models of surface chains, in some cases accounting for the mechanics of chain entanglement in the near-surface region; recent formulations, with references to the earlier literature, are given by Yarin & Graham (1998) and Joshi and coworkers (2000). The adhesive-failure theories are unlikely to apply in the sharkskin regime, and perhaps may not even apply elsewhere. Bergem (1976) showed that a surface layer of colored HDPE in a corrugated capillary die remained in place despite the occurrence of surface sharkskin and spurt flow. An experiment using the displacement of a colored linear polyethylene by the same polymer without pigment to study the wall effect, first described by Cogswell (1977), is the subject of an amusing exchange between "Watson" and "Inspector Lestrade" (Watson et al 1999), but the protagonists do not agree on the interpretation. Hill and coworkers (1994) carried out peel experiments with deuterated polyethylene from copper, aluminum, and brass substrates and analyzed the post-fracture metal and polymer surfaces using X-ray photoelectron and secondary-ion mass spectroscopies. Optical microscopy indicated apparent adhesive failure, but the spectroscopy showed the presence of residual polymer on all metal surfaces; the depths of the residual polymer layers were estimated from electron microscopy and ellipsometry to be of the order of 6 nm and probably uneven in depth, and there were indications of interfacial chemistry between the polymer and metal. The spatial resolution was insufficient to determine if the failure was always in the interior or if it was sometimes at the phase boundary. The infrared spectroscopy experiments of Wise and coworkers (2000) shown in Figure 5 require a simulation for quantitative interpretation, but the results at stress levels characteristic of the initiation of sharkskin seem to be inconsistent with a slip velocity at the channel wall. In the slip-stick region, on the other hand, their results suggest the possibility of an adhesive failure over at least a portion of the surface, resulting in massive slip and nonreproducible decay curves. The issue is far from settled, however. Kanoh and coworkers (1996) found a correlation between wall slip measurements and the thermodynamic work of adhesion as measured by a sessile drop technique for two polymers and three surfaces, and Anastasiadis & Hatzikiriakos (1998) showed a linear correlation between the work of adhesion and the critical stress needed to produce the onset of apparent slip for four linear polyethylenes and three surfaces. The sensitivity of the flow curve to the surface composition of metallic dies, such as that shown by Ghanta and coworkers (1999) in Figure 3, Ramamurthy (1986), and, to a lesser extent, Benbow & Lamb (1961), Chen et al (1993), and Person & Denn (1997), is difficult to explain on the basis of phenomena occurring in the polymer bulk, because the electronic properties of the surface are masked within atomic distances.

Bergem (1976) seems to have first proposed the notion that slip in a polymer melt is a consequence of disentanglement between chains adsorbed to the wall and those in the polymer bulk. The theoretical foundation was developed by Brochard & de Gennes (1992), who imagined entanglement between adsorbed chains at the surface and nearby chains in the polymer bulk and relate the transition to “strong slip” to a transition from a coil to an extended-chain conformation [see also the reviews by Leger et al (1997, 1999)]. Similar theories have been developed by Mhetar & Archer (1998a) and Yarin & Graham (1998). The Brochard & de Gennes theory is consistent with the experiments of Migler and coworkers (1993), and the theory has been applied extensively by Wang and coworkers, whose work is summarized by Wang (1999). Experiments of Mhetar & Archer (1998b) are consistent with their own version of the theory in the weak and transition regions, but not in the region of strong slip. Experiments by Mackay and coworkers (Mackay & Henson 1998, Awati et al 2000) are qualitatively consistent with a disentanglement mechanism, but do not agree quantitatively. The infrared experiments of Wise and coworkers (2000) in Figure 5 appear to follow a disentanglement mechanism, but the slip planes inferred from simulations are too far from the polymer/solid interface to be consistent with the molecular picture that forms the foundation of the Brochard & de Gennes model. The strong sensitivity of some polymer flow curves to the materials of construction of the die seems to be reconcilable with the disentanglement model only if it is assumed that a significantly lower density of chains adsorbs stronger to a brass die than to a stainless steel or oxide-coated wall;

this is perhaps equivalent to the picture of stress-induced desorption proposed by Awati et al (2000) and contained in some earlier models cited therein.

The idea that apparent slip is a lubrication phenomenon has several variants and is not always clearly distinct from the disentanglement model. Joseph (1997) noted that the wave forms observed on melt extrudates are like those seen in interfacial instabilities in two-phase systems, but he does not argue for a specific mechanism, citing diffusion of low-molecular-weight species to the wall as one possible cause and Schallamach "waves of detachment" (Roberts 1992, Leonov & Prokunin 1994) as another. The former mechanism is certainly the cause of apparent slip in some polymer solutions, where the exclusion of long chains from the wall results in a region of low concentration and reduced viscosity, and it may be the cause of slip in melts containing fluoropolymer additives (e.g. Lo et al 1999), but the mechanism is more problematic for highly viscous melts without additives. The mechanism by which Schallamach waves would form in a melt is unclear; Joseph seems to assume a mechanism that leaves a molecular-scale lubricating layer behind (perhaps by a disentanglement mechanism), whereas Awati et al (2000) assume a desorption mechanism. [The first suggestion that sharkskin might be mechanically equivalent to what are now known as Schallamach waves is contained in a comprehensive and informative paper by Howells & Benbow (1962), who show a photograph of the sharkskinlike structure caused by dragging a slider across the surface of a pool of a sharkskin-prone PDMS.]

A different lubrication mechanism follows from observations by Keller and coworkers of a temperature "window" in linear polyethylenes, in which there is a dramatic drop in the extrusion pressure and a smooth extrudate is obtained under conditions in which one would expect surface distortions; the series of papers is summarized in Kolnaar & Keller (1997). This phenomenon is likely to be the same as the stable "island" with reduced extrusion pressure in the slip-stick region observed by Pudjijanto & Denn (1994; also see Watson et al 1994) for an LLDPE, and it may be related to the region of "easy flow" observed by Perez-Gonzalez and coworkers (2000) for a metallocene-catalyzed LLDPE. Keller and coworkers hypothesized a stress-induced phase change to a structured mesophase, which they identified through in situ X-ray diffraction as the mobile hexagonal phase of polyethylene. The mesophase would have a lower viscosity than the bulk polyethylene and would form a lubricating layer along the wall. The most likely mechanism for formation of the mesophase in a shear flow is chain extension resulting from disentanglement. This phenomenon is almost certainly limited to crystallizable polymers, possibly only to polyethylene.

SLIP AND INSTABILITIES

There is a preponderance of evidence that slip occurs above the slip-stick transition in highly entangled linear polymers and a reasonable amount of evidence that slip accompanies and even precedes sharkskin. Whether there is a cause-and-effect relationship between slip and extrudate instabilities is not established, however.

The association of sharkskin with the onset of slip was heightened by the experiments of Ramamurthy (1986), together with the observation that there is a break in the flow curve coincident with the visual onset of sharkskin (Kurtz 1984; Kalika & Denn 1987). El Kissi & Piau (1994), however, used superposition of data taken at different temperatures to argue that the shape of the flow curve for an LLDPE similar to that used by Kalika & Denn is unrelated to slip. Some theories of slip, such as those of Yarin & Graham (1998) and Shore and coworkers (1997), lead to an unstable multivalued flow curve. (The theory of Shore et al is based on a linearized stress-constitutive equation that is not properly invariant.) Any sharkskin mechanism associated with adhesive failure, such as that of Hill and coworkers (1994), or the formation of Schallamach waves (Joseph 1997), is, of course, based on slip. There is universal agreement that sharkskin is initiated at the die exit, but this fact does not imply a mechanism; adhesion theories like those of Hill and coworkers (1990) and Hatzikiriakos & Dealy (1992) include a dependence on pressure that will cause slip to occur first at the die exit and then to propagate back into the die with increasing throughput. That sharkskin vanishes when apparent slip is induced by the use of a brass or fluoropolymer die also does not imply a physical mechanism, because a smooth transition to slip at low stresses could simply vitiate a more drastic failure that would manifest itself as a surface distortion. [Experiments by Moynihan et al (1990), Piau et al (1995), Wang et al (1996), and Inn et al (1998) that demonstrated the absence of sharkskin when only the exit region of the die is coated with a slip agent are instructive, but a coating that induces slip over an exit region that is equal to as little as one die gap spacing could be sufficient to change the near-wall mechanics.]

The most likely cause of sharkskin is incorporated in a mechanism proposed in large part by Bergem (1976) and Cogswell (1977). The melt leaving the die in the neighborhood of the wall experiences a large, rapid, tensile deformation as the velocity field adjusts from the no-slip boundary condition to the free-surface condition. Polymer chains are stretched during this tensile deformation, which causes the highly entangled polymer to respond like a rubber. The large stresses on the free surface cause cracks to open, probably by an undefined slip-stick mechanism analogous to the formation of Schallamach detachment waves in a rubber. [The crack formation process has been nicely photographed by El Kissi and coworkers (1997) and Inn and coworkers (1998), with the former including stress birefringence measurements; early photographs by Howells & Benbow (1962) are also very informative, as are images of extrudate cross-sections by Venet & Vergnes (1997).] The periodicity is associated with retraction and stress recovery between crack openings, and thus it should be of the order of the mean time for viscoelastic stress relaxation, as observed experimentally (Wang et al 1996). Slip induced by wall treatment or addition of a fluorocarbon additive serves to lower the stress at the die exit and, perhaps more important, to lessen the tensile deformation at the surface in the exit region by reducing the velocity gradient and hence the required amount of stretch. Coating only the exit region with a fluoropolymer should serve simply to move the inception of stretching to a point further upstream in the die, but in the experiments reported to date the exit-region coating seems to be adequate to reduce the tensile stresses to a level below that required to form the rubbery state and to open cracks. The "interfacial molecular instability" mechanism proposed by Barone and coworkers (1998) is a specific manifestation of this conceptual model, with the plausible assumption that a coil-stretch transition accompanied by disentanglement of near-wall chains in the exit region is the local cause of the slip-stick mechanism.

The upper branch of the flow curve is almost certainly associated with an interfacial failure and slip throughout the die. It is likely that the discontinuous transition to the upper branch of the flow curve reflects a disentanglement mechanism accompanied by a coil-stretch transition. The absence of a slip-stick transition in the brass-die experiments of Ghanta et al (1999), where there is a smooth, sharkskin-free progression to the upper branch of the flow curve, is best explained in terms of slip that increases smoothly with stress. It is not obvious how to incorporate the dependence on the materials of die construction into a model of disentanglement, however, unless the density of adsorbed surface chains decreases at a sufficient rate with increasing stress on the brass surface; the relevant experiments (probably spectroscopic) have not been done. The evanescent-wave infrared spectroscopy experiments of Wise et al (2000) on narrow-distribution polybutadiene at stresses above the slip-stick transition are consistent with a slip plane located at the surface, or within one polymer-chain radius of gyration (about 13 nm) of the surface, but reproducibility in this regime is poor and some of the data may reflect more complex behavior, possibly a slip plane that is initially far from the surface in some regions of the channel. The mechanism for pressure and flow oscillations between the upper and lower branches of the flow curve in a controlled-rate experiment has long been accepted as a capacitance effect that results from a small amount of melt compressibility, and this mechanism has been exploited in simulations of the relaxation oscillations (e.g. Ranganathan et al 1999, den Doelder et al 1998, and references therein). The nature of the wall slip is not required for these simulations, however; only the experimental upper and lower branches of the flow curve are used, together with compressibility data. A recent experiment by Perez-Gonzalez and coworkers (2000) that shows a period of 17 min for cycling between the upper and lower branches of the flow curve of a metallocene-catalyzed LLDPE is enigmatic, but the capacitance model for oscillations is unlikely to be incorrect.

The extrudate along the initial portion of the upper branch of the flow curve is often relatively smooth, and it has been known for at least four decades that this is an area of possible high-throughput processing; there is an historical review in Leonov & Prokunin (1994). Extrudate distortions in this flow regime are frequently attributed to the propagation of disturbances generated at the die inlet, and the early literature often distinguishes between "inlet" and "die land" fracture. The experiments of Bergem (1976), which include a microtome image demonstrating the propagation of recirculating regions, illustrate the presence of a complex flow throughout the die region. Slip is thus unlikely to cause the instabilities, but it is likely that the presence of slip enhances the propagation of the disturbances. [The calculations of Brasseur and coworkers (1998) are of some interest in this regard. They show that a secondary flow forms and propagates throughout the die when a simple viscoelastic constitutive equation is combined with a wall slip law that causes a discontinuity in the flow curve.] It is significant that similar disturbances are observed on extrudates of branched polymers and linear polymers with a small number of entanglements per chain. These polymers do not undergo a discontinuity in the flow curve; hence they are unlikely to experience massive slip, probably because the molecular architecture precludes the disentanglement mechanism for strong slip.

There is extensive literature on extrusion instability mechanisms that result from non-monotonicity in the flow curve, which causes a sudden transition characteristic of the slip-stick instability in a rate-controlled experiment and a region of oscillations between the upper and lower branches of the flow curve (e.g. Denn 1990); the work of Aarts & van de Ven (1999) is a recent example. This concept, which is more than 40 years old, has been stimulated by the fact that most molecular models of melt flow predict a multivalued flow curve. Shear bands (discontinuities in the velocity gradient) will exist in the flow field above the transition, and these could be indistinguishable from slip in a macroscopic experiment; indeed, shear banding is a possible mechanism for the formation of a lubricated low-viscosity region adjacent to the wall. A recent contribution by Olmsted and coworkers (2000) illustrates the phenomenon and contains references to other relevant work during the past decade. Shear banding in polymer melts has never been observed, but shear banding has been established in a wormlike micellar solution using nuclear magnetic resonance velocimetry (Britton & Callaghan 1997, Britton et al 1999). Pomar and coworkers (1994) studied transitions in LLDPE diluted with octadecane to vary the modulus; the slip-stick transition occurred at a constant stress from the pure melt to 30% diluent, after which the transition vanished. Independence of the modulus is inconsistent with theories based on a non-monotonic flow curve, whereas earlier experiments by Vinogradov and coworkers (1973) on solutions of narrow-distribution polybutadiene are consistent with such theories. Adewale & Leonov (1997) have argued that the transition to the upper branch of the flow curve corresponds to a rubberlike “hardening” of the material in the wall region that is incorporated into their continuum theory by a strain-dependent relaxation time, and they implement a wall-slip model at the point of transition. Their simulations are in good agreement with some of Vinogradov’s polyisoprene data for a variety of flow fields, including the slip-stick regime. What distinguishes their results from other analyses using multivalued flow curves is the ability to fit Vinogradov’s extensional flow data for the same polymer with the same set of parameters, but the inclusion of wall slip as well as shear banding decouples the oscillations and the upper branch of the flow curve from the fit to the extensional data.

EXIT REGION FLOW

The flow at the exit of a die requires a rearrangement of the velocity field from a fully developed shear flow (with or without wall slip) to a uniform plug flow. The large extrudate swell observed in polymer melts and concentrated solutions is one manifestation of this flow rearrangement; the possible mechanism for the development of sharkskin due to the extensional flow near the free surface in the region of reorganization is another. The rearrangement occurs in a small region near the die exit, and the mechanicsfor polymeric liquids are not well understood. The large effect of the small reorganization region within the die on the pressure gradient in the exit region and on extrudate swell was analyzed by Boger & Denn (1980), who were addressing the use of exit effects for rheological measurement; a similar analysis was used by Bulters & Meijer (1990) with filament-spinning experiments to analyze the detachment of concentrated polymer solutions from the interior die wall and the recession of the contact line into the die. These studies used macroscopic momentum balances and could not address the details of the flow field. Joseph (1990) has used macroscopic momentum balances to study extrudate swell, and his work contains excellent photographs of extrudate swell in polymer solutions, including many that demonstrate a delay in the initiation of swell. The most recent experimental study of extrudate swell in polymer melts seems to be that of Yang and coworkers (1998), who showed, among other results, that swell is decreased by coating the exit region of the die with a fluoropolymer, which presumably induces slip. This result is consistent with correlations and theories of extrudate swell (e.g. Pearson 1985) that relate the magnitude of the swell to the level of elastic stress, sometimes denoted as "recoverable shear."

Simulation of the flow in the die exit region for viscoelastic liquids has not been successful, although there have been some continuum calculations of extrudate flow; typical results, with references to earlier studies, can be found in Normandin et al (1999). Jay et al (1998) numerically explored the effect of wall slip on extrudate swell with an inelastic fluid model, following earlier studies cited therein. Attempts to quantify the stress state near the exit by numerical simulation (Tremblay 1991, Mackley et al 1998) are unreliable, because it has been impossible to establish convergence of numerical algorithms in the region where the melt separates from the die. [See Keunings (2000) for a recent review of numerical simulation of viscoelastic flow.] The reason for the failure to establish convergence is the unknown nature of the stress singularity, which is probably much stronger than the corresponding singularity for a Newtonian fluid. The singularity at a reentrant corner for a viscoelastic fluid has attracted more attention than the exit singularity and also remains unknown; attacks on the singularity problem may be found in Davies & Devlin (1993), Hinch (1993), Renardy (1997), and Tanner & Huang (1993), but the problem remains unsolved and is the major barrier to employing computational analysis in the interpretation of exit phenomena.

CONCLUDING REMARKS

Further progress in elucidating the nature of wall slip and the molecular-scale mechanisms that produce extrusion instabilities in polymer melts is unlikely to occur without two needed major advances. The first is the development of a suitable experimental tool to study polymer chain behavior within one radius of gyration of the wall; current experimental probes are either unable to achieve sufficient spatial resolution to avoid model-based deconvolution or require averaging over timescales that are long relative to the important physical processes. Macroscopic experiments, including flow visualization at the micrometer scale, cannot provide mechanistic information. The second is the development of a computational technique for which convergence can be demonstrated in the neighborhood of the singularity where the melt separates from the die, possibly through identification of the strength of the singularity; attempts to use computed solutions to deduce or discriminate between physical mechanisms in the absence of a demonstration of convergence will remain unconvincing.

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