Sharkskin texturing instabilities in the flow of polymer melts

Joel D. Shore\textsuperscript{a}, David Ronis\textsuperscript{b}, Luc Pich\textsuperscript{c}, Martin Grant\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Department of Physics and Centre for the Physics of Materials, McGill University, 3600 University St., Montréal, Québec, Canada H3A 2T8
\textsuperscript{b} Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montréal, Québec, Canada H3A 2K6
\textsuperscript{c} Industrial Materials Institute, National Research Council of Canada, 75 De Mortagne Boulevard, Boucherville, Québec, Canada J4B 6Y4

Abstract

The capillary flow of molten polymers has received much attention because at high flow rates the extrusion of the polymer melt is commonly accompanied by instabilities. These manifest themselves as surface distortions, called melt fracture, in the final plastic product. We have modeled this flow, incorporating a stick-slip boundary condition at the capillary wall. The boundary condition is enforced by a model for the local state of the polymer, which undergoes a phase transition controlled by the local shear. We numerically solve the model, coupled to the hydrodynamic flow and to a Maxwell model for viscoelasticity. In various regimes, the model exhibits steady flow, periodic oscillations, and more complicated spatiotemporal structures, which explain the sharkskin texturing observed in melt fracture.

Instabilities occur when a polymer melt is extruded through a capillary. The characterization and control of these instabilities, called melt fracture, is a longstanding problem in the plastics and chemical engineering communities. The problem can be best described by reference to the sketch of the flow curve [1,2] presented in Fig. 1. The horizontal axis specifies the shear rate of the polymer melt at the wall of the capillary while the vertical axis specifies the shear stress at the wall. The inset in Fig. 1 shows a typical experimental setup: a piston or screw feeds the polymer melt into a reservoir and eventually through the die and out the other end, where it cools and solidifies. Typically, as the flow rate is increased, the extrudate first develops a fine-scaled saw-tooth texturing on its surface called sharkskin; next, for experiments performed at a constant flow rate into the reservoir (as opposed to constant pressure),

* Corresponding author.

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Fig. 1. Sketch of a typical flow curve seen in experiments on extrusion of polymer melts. Shown is the shear stress at the wall, $\tau_{\text{wall}}$, as a function of the shear rate, $\dot{\gamma}_{\text{wall}}$, at the wall. Also shown are the approximate flow regimes where different imperfections are seen on the extrudate. The inset shows a typical experimental setup where the melt is pushed by a piston from a large reservoir through the capillary and out the other end where it solidifies.

there are relatively long time scale regular undulations during what is called spurt flow; finally, a very disordered lumpy structure called gross melt fracture is observed at the highest flow rates.

It has been controversial whether these effects are due to processes inside the die or are instead effects occurring at the entrance or exit of the die. An impetus for our work is recent ultrasonic measurements [3] which show that anomalous time-dependent behavior in the polymer flow occurs within the die, far from both the entrance and exit, suggesting that instabilities occur inside the die itself. In these experiments, the melt was forced through a slit die of length 15.0 cm, width 4.0 cm, and breadth 3.0 mm, at a temperature $T = 200^\circ$C, by a screw operating at 0–80 rpm. At midstream, two identical ultrasonic probes were attached flush to the walls of the capillary, facing each other: one generated ultrasound pulses, while the other sensed those pulses after they propagated across the melt. For a homogeneous system, the amplitude $A$ of successive echoes $n$ decays as $A(n + 1) = A(n)R^2 \exp(-2aL)$, where $R$ is the reflection coefficient, $a$ the attenuation, and $L$ is the distance separating the probes. In the experiment, longitudinal sound bursts with a duration of 0.5 $\mu$s and center frequency at 5.0 MHz were used. The signal was detected with a broadband amplifier and then digitized. The sampling rate was 30 MHz and the repetition rate near 100 Hz. In Fig. 2, we show the amplitude of successive echoes for a screw speed of 40 rpm (where no melt fracture was evident), and 60 rpm (where gross melt fracture was evident on extrusion), after time averaging over bins of 0.85 s. Successive echoes do not fit the standard form for amplitude decay.
Fig. 2. Amplitude of five successive echoes of ultrasound versus time, from top to bottom. Dashed curves are for flow driven by a screw at a rate of 40 rpm (no melt fracture); solid curves for 60 rpm (gross melt fracture evident). Data time averaged over 0.85 s.

of a homogeneous system, mentioned above, indicating inhomogeneities in the flow. Furthermore, note that when gross melt fracture occurs, sharp attenuation peaks are present, which are magnified with each echo, indicating incoherent scattering of the ultrasound signal. For our present purposes, this experiment implies that melt fracture may be addressed by a model which considers primarily effects inside the die.

A further specific motivation for the model we will introduce is recent work which implies that polymeric fluids might not always obey "stick" boundary conditions on mesoscopic length scales. In particular, de Gennes and co-workers [4] have suggested that polymer melts can slip at walls and, moreover, that a sharp transition between slip and stick should be observed as the shear rate at the walls is increased. Indeed, there is an experimental evidence for the existence of slip in polymer melts. While much of this evidence has been rather indirect [1,2,5], a recent experiment by Migler et al. [6] measured the velocity of a polymeric fluid within 100 nm of the wall and found a sharp transition between small and large slip velocities as the shear rate was increased. Here, we generalize these ideas by introducing a hydrodynamic model to describe the flow of a viscoelastic fluid in which the conformation of polymers near the surface of the die undergoes a first-order transition as a function of the shear stress at the wall [7]. This conformational change leads to a change in the frictional force between the wall and the polymer in the bulk, producing stick-slip behavior and leading, in a natural way, to a multivalued flow curve (Fig. 3(a)). In addition, we find that the elastic nature of the fluid can give rise to periodic oscillations, chaotic behavior, and large-scale spatial
structures in the die, which we conjecture is responsible for sharkskin. In this paper, we shall only discuss our model’s relationship to sharkskin texturing [7].

The slipping length, \( \ell \psi(x,t) \), is commonly defined by a relation between the velocity component parallel to the wall, \( v_\parallel \), and its normal derivative \([1,4-6]\); i.e.,

\[
v_\parallel = \ell \psi \hat{\mathbf{n}} \cdot \nabla v_\parallel,
\]

with \( \hat{\mathbf{n}} \) the inward unit normal. Here, \( \ell \) is a constant and \( \psi \) is a dimensionless quantity defined locally at each point \( x \) along the walls at time \( t \); \( \psi = 0 \) gives stick, while \( \psi \to \infty \) gives total slip. Experiments show that the slipping length jumps sharply at a critical value of the shear \([5,6]\), while hysteresis is observed on the multivalued flow curves seen in extrusion \([1,2]\). Together, these two features suggest the change in slipping length is the nonequilibrium analogue of a first-order phase transition, presumably the result of a transition in the local conformational state of the polymer at the wall. We describe this using a Ginzburg–Landau phase-field model for \( \psi(x,t) \), as is standard in the theory of phase transitions \([8,9]\). The microscopic picture of de Gennes and coworkers \([4]\) suggests associating larger \( \psi \) with the stretching and uncoiling of some polymers attached to the wall although other mechanisms, such as absorption–desorption, have also been proposed as the cause of the stick-slip transition in some systems \([5]\). The first-order transition is determined by the free energy functional

\[
F = \int_{\text{walls}} d\mathbf{x} \left[ (\xi_0^2/2)(\partial \psi/\partial \mathbf{x})^2 + f(\psi) \right],
\]
where the local free energy density is \( f(\psi) \equiv (c/4)\psi^4 + (b/3)\psi^3 + (a/2)\psi^2 - H|\sigma_y|/\psi \), \( \sigma_y \) is the local shear stress at the wall, and \( a, b, c, H \), and the bare correlation length \( \xi_0 \) are positive constants. The time dependence of the process obeys \[ \frac{\partial \psi}{\partial t} = -\frac{\delta F}{\delta \psi}, \] (3)

where \( \tau \) is a kinetic coefficient related to the time scale for polymer reorientation.

The equilibrium value of \( \psi \) is zero for \( \sigma_y = 0 \) but as the stress increases, for appropriately chosen values of the parameters, there can be a first-order transition to a large value of \( \psi \) (Fig. 3(b)). Since there is a range of values of \(|\sigma_y|\) where the local free energy density \( f(\psi) \) has a double-well structure, this gives rise to hysteresis associated with the spinodal part of the van der Waals loop in \( \partial f/\partial \psi \), where the local susceptibility \( \chi \equiv (\partial^2 f/\partial \psi^2)^{-1} \) is negative, while retaining consistency with a sharp first-order phase transition in the thermodynamic limit. This hysteresis has been seen experimentally, and much recent theoretical work has incorporated it [1,2,10].

To complete the description of the fluid, the boundary condition (1) must be coupled to the bulk fluid flow. We simply use the linearized Navier–Stokes equation for an incompressible fluid, with Maxwell’s constitutive relation for the viscous stress of a viscoelastic fluid [11]. Namely, the velocity field \( \mathbf{v}(r,t) \) at position \( r \) satisfies, \( \rho \partial \mathbf{v}(r,t)/\partial t = -\nabla p(r,t) + \nabla \cdot \mathbf{\sigma}(r,t) \). Here, \( \rho \) is the density of the melt, assumed incompressible \( [\nabla \cdot \mathbf{v}(r,t) = 0] \), and \( p \) is pressure. The viscous stress tensor \( \mathbf{\sigma} \) satisfies [11] the Maxwell model \( \tau_m \partial \mathbf{\sigma}(r,t)/\partial t = -[\mathbf{\sigma}(r,t) - \eta \mathbf{e}(r,t)] \), where the rate of strain tensor components are \( e_{ij} \equiv \partial v_i/\partial x_j + \partial v_j/\partial x_i \). Depending on the Maxwell relaxation time \( \tau_m \), this interpolates between a viscous fluid \( (\tau_m \rightarrow 0) \) with viscosity \( \eta \) and an elastic solid \( (\tau_m, \eta \rightarrow \infty) \). This constitutes a minimal model necessary to demonstrate our results.

Hereafter, we shall consider a two-dimensional slit of size \( L_x \times L_y \) with periodic boundary conditions in the x (flow) direction and impermeable walls at \( y = 0 \) and \( L_y \) in the direction normal to the flow. It is convenient to separate the pressure into a uniform pressure gradient and an excess part, as \( p(r,t) = g(t)x + \overline{\delta p}(r,t) \). The excess part \( \overline{\delta p}(r,t) \) is periodic in \( x \), while the uniform gradient satisfies \( g(t) = (\bar{\sigma}_{xy}(L_y,t) - \bar{\sigma}_{xy}(0,t))/L_y \), where \( \bar{\sigma}_{xy}(y,t) \) is the average of the shear stress over the flow direction \( x \). This enforces a constant flow rate through the die, which we find it to be necessary to produce sustained oscillations when the boundary conditions are uniform along the entire wall. (Relaxation of this condition in the nonuniform case is discussed in Ref. [7].)

We use material parameters typical of commodity polymers; \( \rho = 740 \text{ kg/m}^3 \) and \( \eta = 1.0 \times 10^4 \text{ Pa s} \). We choose a capillary size \( L_y = 4 \times 10^{-3} \text{ m} \). The parameters in the phase-field model are taken to be \( c = 10, b = 13, a = 5, H = 3.2 \times 10^{-6} \text{ Pa}^{-1} \), and \( \ell = 4 \times 10^{-2} \text{ m} \). These values are chosen so that steady-state solutions of the equations give a multivalued flow curve (Fig. 3), typical of ones seen experimentally [1,2]. The three branches of the curve in a range of \(|\sigma_y|\) correspond directly to the two minima and one maxima in \( f(\psi) \). The range of \( \bar{v}_x \) for which oscillations occur can be determined from an exact linear stability analysis about the steady-state value \( \psi = \bar{\psi} \) [7]. To a
Fig. 4. Behavior of the slipping length $\psi$ at the two walls for $\xi_0 \geq L_x$. Shown are power spectra of $\psi(t)$ for regular oscillations (top) and chaos (bottom); insets show time traces. Walls at $y = 0$ and $L_y$ are indicated by solid and dashed lines, respectively. Parameters used are $\tau_m = 10^{-3}$ s, $\tau = 10^{-4}$ s; the exact values of $\xi_0$ and $L_x$ are not relevant.

A good approximation, the criterion for instability of the steady state is simply

$$\lambda^{-1} + \omega_0^2 k_x^2 < -\frac{\tau}{\tau_m},$$

where $\lambda^{-1} \equiv a - 2b\psi + 3c\psi^2$. We see that the most unstable mode has wave number $k_x = 0$. It can be shown that $\lambda^{-1}$ is negative precisely on that part of the flow curve between the maximum and the minimum, indicated by the dotted portion of the curve in Fig. 3. Thus, Eq. (4) will be satisfied for $k_x = 0$ over a range of $\psi_x$, provided that $\tau_m/\tau$ is sufficiently large. In this regime oscillations occur: At a critical stress the stick state becomes metastable, and at some stress beyond that the system jumps to the slip condition. However, once in the new slip state, the stress between the fluid and wall decreases, the slip state itself becomes metastable, and a transition to stick eventually ensues. Hence, the system can repeatedly cycle between stick and slip. However, unlike the normal spinodal instability for which $\lambda^{-1} < 0$, here the criterion for instability also depends on the relative magnitudes of the elastic time scale, $\tau_m$, and the time scale for relaxation of the conformation of the polymer at the surface, $\tau$, as shown in the inset to Fig. 3. If $\tau_m/\tau$ is too small, there is no instability. Thus, the elastic nature of the fluid (a large $\tau_m$) is an essential ingredient of the instability.

We have carried out further investigation of our model numerically, with a mixed finite-difference and spectral method [7]. We first consider the limit $\xi_0 \geq L_x$, where the system is uniform in the flow direction. The results from the linear stability analysis are
Fig. 5. (a) Typical random flow pattern in the channel for $\xi_0 \ll L_x$. Shown is the velocity relative to the mean flow velocity, $v(x, y) = \xi_i \tilde{z}$, with the magnitude indicated by the size of the arrow. (b) Space-time plot of the slipping length $\xi = \xi(x, t)$ along one of the channel walls. The value of $\xi$ is indicated by the brightness on this grey scale plot. The defect structures evident in (b) are associated with the rolls in the channel shown in (a). Parameters used are the same as in the bottom panel of Fig. 4, except here $\xi_0 = 0.1$ m and $L_x = 0.1$ m.

confirmed by the numerics; in particular, the stability criteria for $k_x = 0$ is in excellent agreement with where oscillating solutions first occur numerically. It is also found that the period of those oscillations is $O(\tau_m)$, as is evident in Fig. 4. An order-of-magnitude estimate of the $\tau_m$ appropriate for polymer melts yields an oscillation period which corresponds well, given the flow rate, to the wavelength of experimentally observed sharkskin [7]. For values of the average flow $\bar{\xi}_i$ which are close to the minimal and maximal ranges of the stick-slip regime, we find complex oscillatory behavior. This includes chaos, shown in Fig. 4, as well as oscillations with periodicities that are integer multiples of the fundamental oscillation period. The oscillations of $\psi$ at the two walls are most often out of phase, although oscillations still occur if mirror symmetry is enforced.

For smaller $\xi_0$, rolls spanning the capillary can appear, Fig. 5(a); these rolls are coupled to the out-of-phase oscillations at the walls. Indeed, experimentally, sharkskin in a cylindrical die often has a spiral pattern with opposite sides of the extrudate being out of phase. In our model, the roll structures in Fig. 5(a) lead to complicated spatiotemporal patterns at the walls (Fig. 5(b)). These, and analogous structures in the third dimension not included in our calculation, should manifest themselves as defects on the surface of the extrudate. Although no direct comparison can be made without including the third dimension, we are encouraged by recent experiments [3] showing
Fig. 6. The surface of linear low-density polyethylene extrudate at two different extrusion rates in the sharkskin regime from the experiment of Ref. [3]. Shown are gray scale plots of the height with white representing peaks and black representing valleys. The polymer melt was extruded in the upward direction, relative to the orientation of these images, which show a region of the surface approximately 1 cm across. Note that the patterns on the extrudate look qualitatively similar to the defect structures seen in Fig. 5(b).

defect patterns on the surface of the extrudate (Fig. 6) similar to the patterns seen here in the $x-t$ plane.

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References

[9] A full description of local polymer conformation would involve a complicated order parameter and would be applied throughout the fluid, with its local expectation value related to shear thinning; for related ideas, see M. Urbakh, L. Dalkhin and J. Klafter, J. Chem. Phys. 103 (1995) 10707 and references therein. However, here we consider only that aspect of the conformation which is relevant in determining the slipping length.