On numerical Simulations of Polymer Extrusion Instabilities

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Abstract:
The objective of this study is mainly to review recent work concerning the numerical modeling of the stick-slip and gross melt fracture polymer extrusion instabilities. Three different mechanisms of instability are discussed: (a) combination of nonlinear slip with compressibility; (b) combination of nonlinear slip with elasticity; and (c) constitutive instabilities. Furthermore, preliminary numerical simulations of the time-dependent, compressible extrudate-swell flow of a Carreau fluid with slip at the wall, using a realistic macroscopic slip equation that is based on experimental data for a high-density polyethylene, are presented.

Zusammenfassung:
Das Ziel dieses Übersichtsartikels ist es die neueste Arbeiten der numerischen Modellierung des “stick-slip” und der Extrusionsinstabilitäten bei Polymeren, die durch Schmelzebruch verursacht werden, vorzustellen. Es werden drei verschiedene Instabilitätsmechanismen besprochen: (a) die Kombination von nichtlinearem Gleiten mit Kompressibilität; (b) die Kombination von nichtlinearem Gleiten mit Elastizität; und (c) konstitutive Instabilitäten. Im weiteren werden vorläufige numerische Simulationen von zeitabhängiger, kompressibler Strangaufweitung einer Carreau-Flüssigkeit mit Wandgleiten vorgestellt, wobei für HDPE eine auf experimentellen Daten beruhende makroskopische Gleit-Gleichung verwendet wird.

Résumé:
L’objectif de cette étude est principalement de passer en revue les travaux récents qui visent à modéliser numériquement les instabilités rencontrées lors de l’extrusion de fondus de polymères telles que le glissement-accrochage et le phénomène de fracture. Trois mécanismes différents d’instabilités sont discutés: (a) la combinaison d’un glissement non linéaire avec la compressibilité; (b) la combinaison d’un glissement non linéaire avec l’élasticité; et (c) les instabilités constitutives. De plus, des simulations numériques préliminaires sont présentées. Elles simulent l’écoulement d’extrusion compressible avec gonflement d’un fluide de type Carreau avec glissement aux parois. Ce dernier est modélisé à l’aide d’une équation macroscopique réaliste, basée sur des données expérimentales obtenues avec un polyéthylène haute densité.

Key Words: Extrusion instabilities, Melt fracture, Slip, Carreau model, Oldroyd-B model, Compressible flow, Constitutive instability, Viscoelastic flow

1 INTRODUCTION

Polymer extrusion instabilities appear frequently in industrial practice, limiting the production rates and influencing the appearance and quality of polymer extrudate products. They have thus received considerable attention in the past fifty years in numerous experimental, theoretical, and numerical studies. The main goal of all the above studies was to reveal the origins and the mechanisms of the various forms of extrudate distortion, in order to develop efficient techniques for suppressing or eliminating the instabilities. Reviews on extrusion instabilities include those by Petrie and Denn [1], Denn [2, 3], Larson [4], Leonov and Prokunin [5], Piau et al. [6], El Kissi and Piau [7], and Wang [8]. In most experimental studies on extrusion instabilities, capillary rheometers are used, under either constant flow rate (i.e., constant piston speed) or constant pressure drop operation [9]. This work focuses on instabilities observed at constant piston speed.

It is well known that during the extrusion of polymers from capillary or slit dies under fixed piston speed, a variety of extrudate distortions are observed when the volumetric flow rate (or, equivalently, the apparent shear rate) exceeds a critical value [10 - 16]. As the volumetric flow rate increases, the size and the severity of the extrudate distortions increase. For most linear polymer melts, the flow curve (i.e., the plot of the wall shear stress versus the apparent shear rate at the wall, or, equivalently, the plot of the pressure drop versus the volumetric flow rate) consists of two positive-slope branches separated by a zone where the pressure drop oscillates, although the flow rate is kept constant [13 - 17]. A typical flow curve for a linear polyethylene, routinely obtained using a capillary rheometer under constant speed operation, is shown in Fig. 1. Connecting the two branches with an imaginary line results in a non-monotonic flow curve with a maximum and a minimum which define the range of the pressure drop oscillations.

When the flow rate is controlled, four distinct flow regions are, in general, observed for linear, narrow molecular weight distributed polymers (e.g., LLDPE [11], HDPE [13, 18], and linear polydimethylsiloxane [12]). These flow regions are illustrated in Fig. 1. At small shear rates, the extrudate has a smooth, glossy surface finish. This *stable* regime persists up to a critical shear rate at which the extrudate starts losing gradually its glossiness, and small-amplitude, short-wavelength periodic distortions appear on its surface, even though the pressure remains constant. This surface defect is known as the *sharkskin instability* or *surface melt fracture* and is observed up to the endpoint of the left branch of the flow curve. Some researchers associate sharkskin with a small departure from the no-slip boundary condition [10, 11, 13, 18 - 20], which is sometimes accompanied by a sharp change in the slope of the flow curve. Some experiments indicate that increased adhesion between the fluid and the wall reduces the sharkskin instability [10], while others show that enhancing wall slip suppresses the instability [6, 21, 22]. However, slip is not always present in the sharkskin regime; the experiments of El Kissi and Piau [14], Wang [8], and El Kissi et al. [15] showed that slip is negligible.

Beyond the sharkskin regime and within a certain range of apparent shear rates separating the two branches of the flow curve, no steady-state solutions can be achieved. Although the flow rate is kept constant, sustained pressure and mass flow rate oscillations are observed, and the extrudate surface is characterized by alternating sharkskin and relatively smooth regions. This instability is known as the *stick-slip instability* or *spurt phenomenon* or *oscillating melt fracture*. As discussed below, the pressure drop oscillations are attributed, by some researchers, to the combined effects of the finite compressibility of the polymer and the periodic transitions from a weak to a strong slip at the capillary wall and vice versa. Piau et al. [6] have shown experimentally that the oscillations can be eliminated

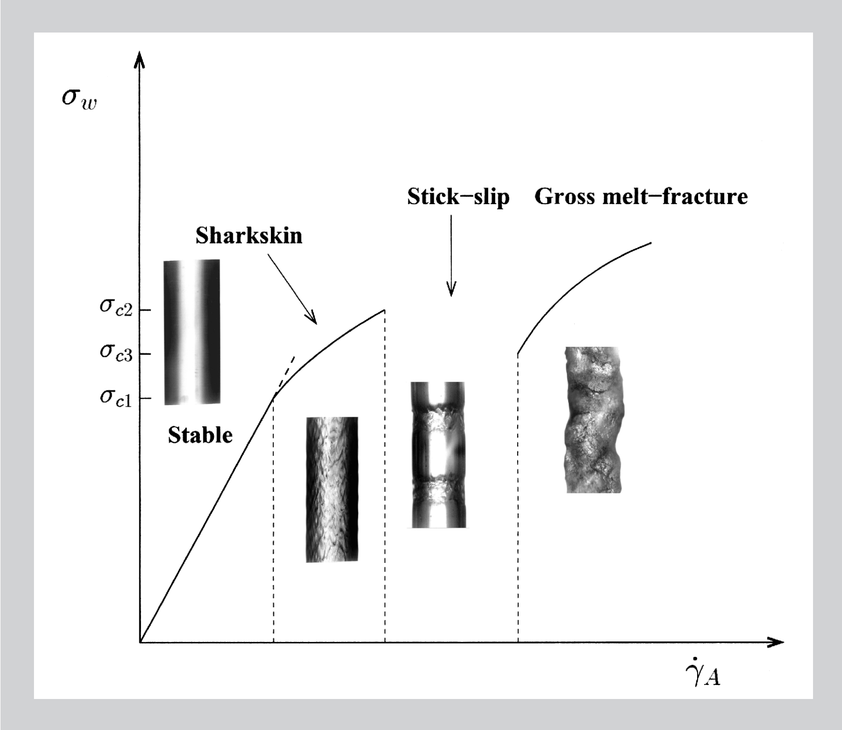

Figure 1: Typical flow curve for a linear polyethylene and regions of instability.

by using slippery surfaces. Slip can be promoted either by using dies constructed with appropriate materials, such as brass [22], or by means of polymer processing additives, such as fluoropolymers or Boron nitride [23 - 25]. It should be noted that in pressure-controlled experiments, an abrupt jump in the flow rate is observed in the spurt flow regime. Finally, at even higher wall shear rates corresponding to the right positive-slope branch of the flow curve, steady state can again be achieved, although the distortion of the extrudate is more severe, with its surface being rough and wavy. This instability is known as *wavy* or *gross melt fracture*. In this last regime, the velocity profile in the capillary is nearly plug [26, 27], which implies the occurrence of strong slip.

Melt fracture is a special phenomenon not exhibited by Newtonian fluids or by dilute to moderately concentrated polymer solutions. The various instabilities mentioned above may not all appear as the volumetric flow rate is increased, depending on the polymer used. Sharkskin is not always present in experiments [3, 28]. On the other hand, in certain cases before the appearance of sharkskin, *superficial scratching* (or *matting*) may appear in the form of stripes laid longitudinally along the axis and usually spaced equally around the free surface of the extrudate [7, 12, 29]. The stick-slip instability is found only with linear polymers, such as high-density or linear low-density polyethylenes [2, 27]. It has never been observed with long-branched polyethylenes [3, 27]. In some cases, a second distinct stick-slip region has been reported at higher shear rates [6, 7, 30]. The experiments of Robert et al. [31] with linear high-density polyethylene also showed that this secondary stick-slip region may occur at flow rates just above, or within, the primary stick-slip region. Another striking phenomenon reported recently by Fernández et al. [32], who carried out flow rate-controlled capillary extrusion experiments with copolymers of ethene and propylene, is the split of the extrudate into two severely sharkskinned branches above a critical flow rate.

As for the sharkskin instability, there is a general agreement that it is initiated at or near the die exit and is due to the relaxation of strains [4], rupture of the polymer at the exit [33], or local stick-slip at the exit due to polymer disentanglement [8]. Several reported causes of sharkskin are reviewed by Wang [8], Denn [3] and Barone and Wang [34]. The experiments of Piau et al. [6, 7, 12] indicate that melt fracture is initiated in the die entry region where unstable vortices appear and symmetry is lost. Unstable upstream vortices have also been observed by Pérez-González et al. [35]. More recently, Piau et al. [36] have shown experimentally that using porous media at the entrance of an extrusion die delays the occurrence of melt fracture. Migler et al. [37] using high-speed optical velocimetry and video microscopy have demonstrated that two distinct material failures during each sharkskin cycle take place. These failures resemble the rupture mechanism proposed by Cogswell [33].

The mechanisms of extrusion instability have long been the subject of controversy [2, 4, 28, 38, 39]. The proposed theories on the sharkskin instability (see the book of Leonov and Prokunin [5] and the recent reviews by Inn et al. [21], Wang [8], Graham [40], Venet and Vergnes [41], Rutgers and Mackley [42], and Denn [3]) are beyond the scope of the present work, since they involve microscopic phenomena near the die wall and/or the die exit which are not easily incorporated into the numerical dynamic simulations of the macroscopic extrusion problem. Numerical simulations for the sharkskin instability are restricted to steady-state calculations aiming at correlating the magnitudes of the stress concentration at the exit of the die to the experimental data on the onset of instability (see [44] and references therein). The main objective of this paper is to review numerical simulations based on two basic mechanisms proposed for the stick-slip and the gross fracture instabilities. These are [2, 3, 4]:

(i) slip (or adhesive failure) at the die wall, and
(ii) constitutive or material (or bulk failure) instabilities.

Both mechanisms require a non-monotonic law which leads to a nonmonotonic flow curve, i.e., a flow curve with a maximum and a minimum. The first is based on the non-monotonicity of the slip equation which relates the wall shear stress to the slip velocity, while the second is based on the non-monotonicity of the constitutive equation, i.e., on the non-monotonicity of the shear stress/shear rate curve in simple shear and Poiseuille flows.

The rest of the paper is organized as follows: Section 2 reviews experimental observations associating extrusion instabilities with wall slip and discusses theories of slip. Numerical simulations of extrusion instabilities based on the combination of slip with compressibility are reviewed in Section 3. Section 4 presents new numerical calculations for the time-dependent, compressible extrudate-swell flow of a shear-thinning fluid with slip at the wall. These have been obtained using the Carreau model and a realistic non-monotonic slip law which is based on the slip equations proposed by Hatzikiriakos and Dealy for a high-density polyethylene [13, 18]. Section 5 reviews numerical simulations based on the combination of slip with elasticity. Section 6 is devoted on the constitutive instability mechanism and relevant numerical simulations. Finally, the limitations of the three mechanisms and the related numerical simulations are discussed in Section 7.

2 SLIP AT THE WALL: EXPERIMENTS AND THEORY

Unlike Newtonian fluids, for which the no-slip boundary condition is practically valid regardless of the fluid and the material composition of the boundary, polymer melts and solutions slip over solid surfaces when the wall shear stress exceeds a critical value, which ranges from 0.1-1 MPa in melts, but it can be significantly lower in polymer solutions [43 - 45]. An extensive compilation of references concerning experimental observations on wall slip in polymer solutions, theoretical analyses on slip for polymer solutions and melts, and experimental observations of wall slip in extrusion of polymer melts is provided by Joshi et al. [46]. Recent reviews of slip and its relation to polymer processing are those by Piau et al. [6] and Denn [3]. The latter author points out that apparent slip is observed with some highly entangled linear polymers, but not with branched polymers or linear polymers with a sufficient number of entanglements per chain.

Many groups have reported indirect measurements of slip velocities, based on the macroscopic characterization of flow curves in capillary [10, 12, 18, 47 - 50], sliding-plate [43, 51 - 54], and torsional rheometers [55]. The experimental fluids in these studies included melts of low- and high-density polyethylenes, of silicones, of polyisobutylene and polystyrene, as well as concentrated polystyrene solutions.

Direct measurements of nonzero fluid velocities at stationary solid surfaces have been reported by many researchers. Migler et al. [56] and Durliat et al. [57] used an evanescent wave fluorescence technique to measure velocities of a polydimethylsiloxane melt in plane Couette flow in a zone within 0.1 μm from the wall. Similarly, Archer and co-workers [45, 58] visualized the motions of micron-sized tracer particles in plane Couette flow of entangled polystyrene solutions using an optical microscope. Finally, direct velocity measurements in extrusion experiments through capillary and slit dies have been taken by Legrand et al. [59], Münstedt et al. [27], and Migler et al. [24] (also see references therein). Legrand et al. [59] used a fluorescence technique, together with a theoretical model that accounts for diffusion effects, to determine the velocity fields at a microscopic scale close to the wall, during extrusion of a high molecular weight polydimethylsiloxane through a rough slit die. Münstedt et al. [27] investigated the flow behavior of linear low- and high-density polyethylene melts in a slit die using a laser-Doppler velocimeter of high spatial and temporal resolution. They did not detect any indications of measurable wall slip for long-chain branched polyethylene. For linear high-density polyethylene, however, they reported pronounced slip velocities at low apparent shear rates before the appearance of pressure oscillations. In the stick-slip regime, they measured velocity fluctuations of the same frequency as that of the pressure oscillations but with different shapes of amplitude. Beyond this regime, the observed velocity profiles are nearly plug, which is an indication for strong slip at the wall. Migler et al. [24] used depth-resolved stroboscopic optical microscopy to measure the velocity profiles of a linear low-density polyethylene with and without a fluoropolymer additive in a transparent tube located at the exit of a twin-screw extruder. In the absence of the additive, they found that no slippage occurs and sharkskin is observed. Their measurements indicated that the additive migrates to the capillary wall where it sticks and induces slippage between itself and the polymer, which results in the elimination of sharkskin.

It should be noted that, in the capillary experiments of Piau and co-workers [6, 12], extrudate distortions accompanied with pressure oscillations are observed in the absence of slip, indicating that upstream instabilities in the die entrance region are, indeed, important. Similar observations have been made by Pérez-González et al. [35], in their capillary extrusion experiments with branched polyethylenes; they attribute the instability to the effect of compressibility on the upstream vortices. The recent experiments of Piau et al. [36] showed that the occurrence of melt fracture is delayed when porous media are placed at the the die entrance. As already mentioned, earlier experiments of Piau et al. [6] showed that oscillating flow regimes can also be eliminated using slippery surfaces, while upstream instabilities are still observed.

For a given die (i.e., material of construction), the slip velocity of linear polymers is a function of temperature, pressure, shear stress history, and molecular parameters [19, 60]. At the molecular level, de Gennes [61, 62] developed a widely accepted slip model for the case of a passive interface (no interaction between the polymer and the solid interface) by introducing the notion of the extrapolation length. Together with Brochard and co-workers [63 - 65], he extended the theory to distinguish a passive interface (no polymer absorption) from an absorbing one. The extended theory predicts the transition from a weak to a strong slip, in agreement with experimental observations [10, 48, 56, 66]. Weak slip occurs at shear rates sufficiently low so that bulk-wall entanglements are maintained, while strong slip occurs at higher shear rates when the bulk and wall chains are effectively disentangled. This and two other slip theories, based on the assumption that slip is the result of adhesive failure of the polymer chains at the solid surface or on the existence of a lubricated layer at the wall, are discussed by Denn [3].

Most macroscopic slip equations proposed in the literature predict a power-law relation between the shear stress at the wall and the slip velocity (at constant temperature) [13, 58, 67 - 69]. As mentioned above, of particular interest are equations which exhibit maxima and minima, such as the equations proposed by El Kissi and Piau [70] and Leonov [71]. The non-monotone slip equation derived by Leonov [71], from a simple stochastic model of interface molecular dynamics for cross-linked elastomers, has recently been modified for polymer melts by Adewale and Leonov [9]. Hatzikiriakos and Dealy [13] give two different slip equations corresponding to the two positive-slope branches of their experimental flow curve, with which the slip velocity is again multi-valued for some range of the wall shear stress.

Multivalued microstructural slip models have more recently been proposed by Mhetar and Archer [45], Yarin and Graham [72], and Wang and co-workers [8, 73], who developed theories similar to that of Brochard and de Gennes, and by Hill [74], who developed a continuum slip model based on adhesive failure. Slip models in which the slip velocity depends not only on the shear stress but also on the pressure or the normal stress have also been proposed [13, 17, 18, 69, 74 - 77].

Linear stability analyses of simple shear and/or Poiseuille flows with slip along the wall show that steady-state solutions corresponding to the negative-slope part of the slip equation are linearly unstable [78 - 84]. As discussed in subsequent sections, the combination of the nonmonotonicity of the slip equation with either compressibility or elasticity leads to oscillatory solutions at fixed volumetric flow rate, provided that the latter is in the negative slope regime of the flow curve.

3 COMPRESSIBILITY COMBINED WITH NONLINEAR SLIP

Based on the linear stability analysis of incompressible Newtonian Poiseuille flow with slip at the wall, Pearson [85] pointed out that the combination of a nonmonotonic slip equation with melt compressibility can lead to self-sustained oscillations of the pressure drop and of the mass flow rate, similar to those observed experimentally with the stick-slip instability. Georgiou and Crochet [86, 87] verified numerically the ideas of Pearson [85], by solving the time-dependent compressible Newtonian Poiseuille and extrudate-swell flows with slip along the wall. Their calculations showed that steady-state solutions corresponding to the negative-slope regime of the slip equation are unstable in agreement with the linear stability analysis of Pearson and Petrie [78]. Compressibility acts as the storage of elastic energy that sustains the oscillations of the pressure drop and the mass flow rate and generates waves on the extrudate surface, in the case of the extrudate-swell problem. These oscillations are similar to those observed with the stick-slip instability. The amplitude and the wavelength of the free-surface waves increase with compressibility. By means of finite-element calculations, Georgiou [88] demonstrated that imposing periodic volumetric flow rate at the inlet of the die leads to more involved periodic responses and to free surface oscillations similar to those observed experimentally with the stick-slip instability.

The combination of compressibility and non-linear slip represents the underlying mechanism in various one-dimensional phenomenological relaxation/oscillation models describing the oscillations of the pressure and the volumetric flow rate in the stick-slip instability regime (see Refs. [89] and [90] and references therein). These models, include the reservoir region and take into account the compressibility of the fluid. However, they require the calculation of certain parameters from experimental data and are based on the assumption that the time-dependent solution follows the hysteresis loop resulting from the nonmonotonic steady-state flow curve. One-dimensional phenomenological models cannot predict the onset of instability and the wall slip. Moreover, they do not include the extrudate region, and, therefore, they cannot relate the distortions of the extrudate to the pressure oscillations. Kumar and Graham [91] used a one-dimensional relaxation model and modified the slip equation used by Georgiou and Crochet [86], in order to include the pressure dependence of the slip velocity. They considered both generalized Newtonian and viscoelastic fluids. An interesting consequence of the dependence of slip velocity on pressure, which may be used for explaining the sharkskin instability, is that the flow curve might not be multivalued even if the slip model is.

4 COMPRESSIBLE EXTRUDATE-SWELL FLOW OF A CARREAU FLUID WITH SLIP

Two simplifications in the simulations of Georgiou and Crochet [86, 87] were the use of a simple, arbitrary nonmonotonic slip equation and the employment of the Newtonian constitutive equation. To overcome these limitations, we consider the time-dependent, compressible axisymmetric extrudate-swell flow of a Carreau (i.e. shear thinning) fluid using a realistic slip equation based on the experimental data of Hatzikiriakos and Dealy [13, 18], and present preliminary finite-element calculations in the unstable flow regime.

We employ the non-monotonic slip law shown in Fig. 2. This is a multi-valued slip model given by

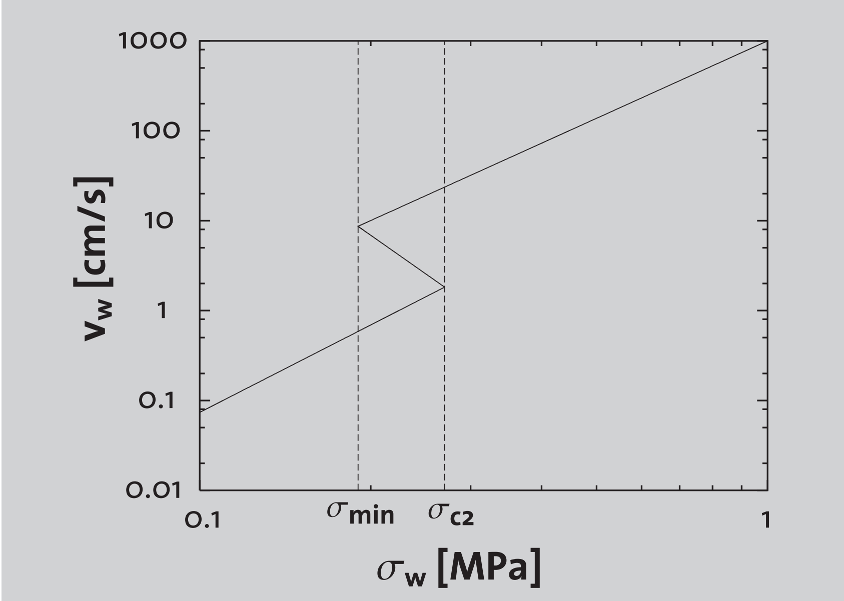

Figure 2: The nonmonotonic slip law based on the experimental data of Hatzikiriakos and Dealy with a high-density polyethylene at 180°C [13, 18]

$$v_w = \begin{cases} a_1\sigma_w^{m_1}, & 0 \le v_w \le v_{c2} \\ a_3\sigma_w^{m_3}, & v_{c2} \le v_w \le v_{\min} \\ a_2\sigma_w^{m_2}, & v_w \ge v_{\min} \end{cases} \tag{1}$$

where v_w is the relative velocity of the fluid with respect to the wall, σ_w is the shear stress on the wall, v_{c2} is the maximum slip velocity at σ_{c2}, v_{min} is the minimum slip velocity at σ_{min}, and m_1, m_2, and m_3, are power-law parameters. The third branch is the power-law slip equation suggested by Hatzikiriakos and Dealy [13] for the right branch of their flow curve. The first branch results from the slip equation they propose for the left branch of their slope curve after substituting all parameters for resin A at 180°C and taking the normal stress as infinite. The intermediate, negative-slope branch, which corresponds to the unstable region of the flow curve, is simply the line connecting the other two branches. The values of all the slip equation parameters are given in Tab. 1.

Parameter	Value
a_1, $(MPa)^{-m_1}$ cm/s	125.09
m_1	3.23
a_2, $(MPa)^{-m_1}$ cm/s	1000
m_2	2.86
a_3, $(MPa)^{-m_1}$ cm/s	$5.484*10^{-3}$
m_3	-4.434
σ_{c2}, (MPa)	0.27
σ_{min}, (MPa)	0.19
v_{c2}, cm/s	1.82
v_{min}, cm/s	8.65

Table 1: Values of the slip model parameters.

Hatzikiriakos and Dealy [13] measured the power-law parameters and the isothermal compressibility, β, of the experimental polymer melt (HDPE), assuming that the density varies linearly with pressure. Here we use the Carreau model with zero infinite-shear-viscosity which generalizes the power-law model as follows:

$$\eta = \eta_0\left[1+\lambda^2(2II_d)^2\right]^{(n-1)/2} \tag{2}$$

where η is the viscosity, η_0 = 0.03 MPas is the zero-shear-rate viscosity, λ is a time constant, n = 0.44 is the power-law constant, and $II_\mathbf{d}$ is the second invariant of the rate-of-deformation tensor **d**. The latter is defined as:

$$\mathbf{d} = \frac{1}{2}\left[(\nabla\mathbf{v}) + (\nabla\mathbf{v})^T\right] \tag{3}$$

where **v** is the velocity vector, and the superscipt T denotes the transpose.

To non-dimensionalize the governing equations, we scale the lengths by the radius R, the velocity by the mean velocity V in the capillary, the pressure, p, and the stress tensor, $\boldsymbol{\sigma}$, by $\eta_0\ \lambda^{n-1}\ V^n\ /\ R^n$, the density, ρ, by the density at atmospheric pressure ρ_0, and the time by R/V. With this scaling, the continuity and momentum equations for time-dependent, compressible, isothermal flow become

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\rho\mathbf{v} = 0 \tag{4}$$

and

$$Re\rho\left(\frac{\partial\mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = \nabla\cdot\boldsymbol{\sigma} \tag{5}$$

where all variables are now dimensionless, and Re is the Reynolds number defined as

$$\mathrm{Re} \equiv \frac{\rho_0 R^n V^{2-n}\lambda^{1-n}}{\eta_0} \tag{6}$$

The dimensionless stress tensor for the Carreau fluid is

$$\boldsymbol{\sigma} = -p\mathbf{I} + \left[1+\Lambda^2(2II_d)^2\right]^{(n-1)/2}\left(2\boldsymbol{d} - \frac{2}{3}\boldsymbol{I}\nabla\cdot\mathbf{v}\right) \tag{7}$$

where **I** is the unit tensor, and

$$\Lambda \equiv \frac{\lambda V}{R} \tag{8}$$

Another dimensionless number is the compressibility number,

$$B \equiv \frac{\beta\eta_0 V^n}{\lambda^{1-n}R^n} \tag{9}$$

which appears in the equation of state,

$$\rho = 1 + Bp \tag{10}$$

The dimensionless form of the slip equation is

$$v_w = \begin{cases} A_1\sigma_w^{m_1}, & 0 \le v_w \le v_{c2} \\ A_3\sigma_w^{m_3}, & v_{c2} \le v_w \le v_{\min} \\ A_2\sigma_w^{m_2}, & v_w \ge v_{\min} \end{cases} \tag{11}$$

where

$$A \equiv \frac{a_i\eta_0^{m_i}V^{m_i n-1}}{\lambda^{m_i(1-n)}R^{m_i n}} \qquad i = 1,2,3 \tag{12}$$

The volumetric flow rate is scaled by $\pi R^2 V$.

The geometry and the boundary conditions of the time-dependent, compressible, axisymmetric extrudate-swell flow are shown in Fig. 3. Along the axis of symmetry we have the usual symmetry conditions. Along the wall, the radial velocity vanishes whereas the axial velocity satisfies the slip Eq. 11. At the inlet plane, we assume that the radial velocity component, v_r, vanishes, and that v_z is given by

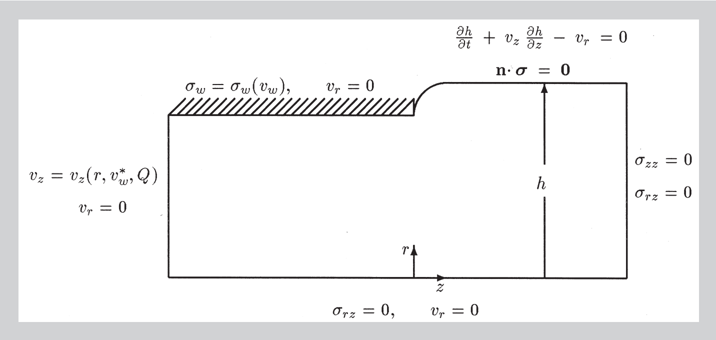

Figure 3 (left): Geometry and boundary conditions for the compressible extrudate-swell flow of a Carreau fluid with slip at the wall.

$$v_z = v_z(r, v_w^*, Q) = \frac{1}{n+1}\left[(3n+1)r^{\frac{1}{n}+1} - 2n\right]v_w^* + \frac{3n+1}{n+1}\left(1 - r^{\frac{1}{n}+1}\right)Q \tag{13}$$

where Q is the volumetric flow rate, and v^*_w is the slip velocity calculated by means of the slip equation. At the outlet plane, we assume that σ_{rz} and the total normal stress, σ_{zz}, are zero. Finally, on the free surface, we assume that surface tension is zero and impose vanishing normal and tangential stresses. The unknown position $h(z, t)$ of the free surface satisfies the kinematic condition.

The steady-state solution of the stick-slip flow (i.e. for flat free surface) is taken as the initial condition, and the free surface is released at t = 0. The governing equations along with the above boundary conditions are solved using standard finite elements in space and the standard fully-implicit scheme in time [87].

In Fig. 4, preliminary calculations in the unstable negative-slope regime of the flow curve are given for Q = 1.5, Re = 0.01, $B = 1.541 \ast 10^{-4}$, Λ = 349.2, A_1 = 0.0583, A_2 = 0.929 and A_3 = 4.04. All the above dimensionless numbers correspond to experimental conditions, the only exception being the Reynolds number which is rather high. Fig. 4a depicts the evolution and the development of self-sustained oscillations of the pressure gradient, $-\nabla P$, at constant volumetric flow rate. In Fig. 4b, the evolution of the solution on the flow curve plane is illustrated ($\dot{M}_O$ is the mass flow rate at the outlet plane). The solid curve is the non-monotonic, steady-state flow curve; after the initial oscillations, a limit cycle is eventually reached. Finally, in Fig. 4c, a representative free surface profile is illustrated. Small-amplitude, high frequency waves are obtained, which stresses the need for adequately refined finite-element mesh and sufficiently small time step. The numerical simulations are thus very demanding in CPU time. As indicated by the numerical simulations, both the amplitude and the wavelength of the free surface waves are reduced and the time-dependent flow problem becomes stiffer, as Re is decreased. Therefore, extremely refined meshes and very small time steps must be employed in order to simulate the experiments in which Re is about 10^{-5}. This work is currently under progress.

5 ELASTICITY COMBINED WITH NONLINEAR SLIP

In some recent papers [26, 79, 80, 81], Georgiou and co-workers demonstrated that viscoelastic-

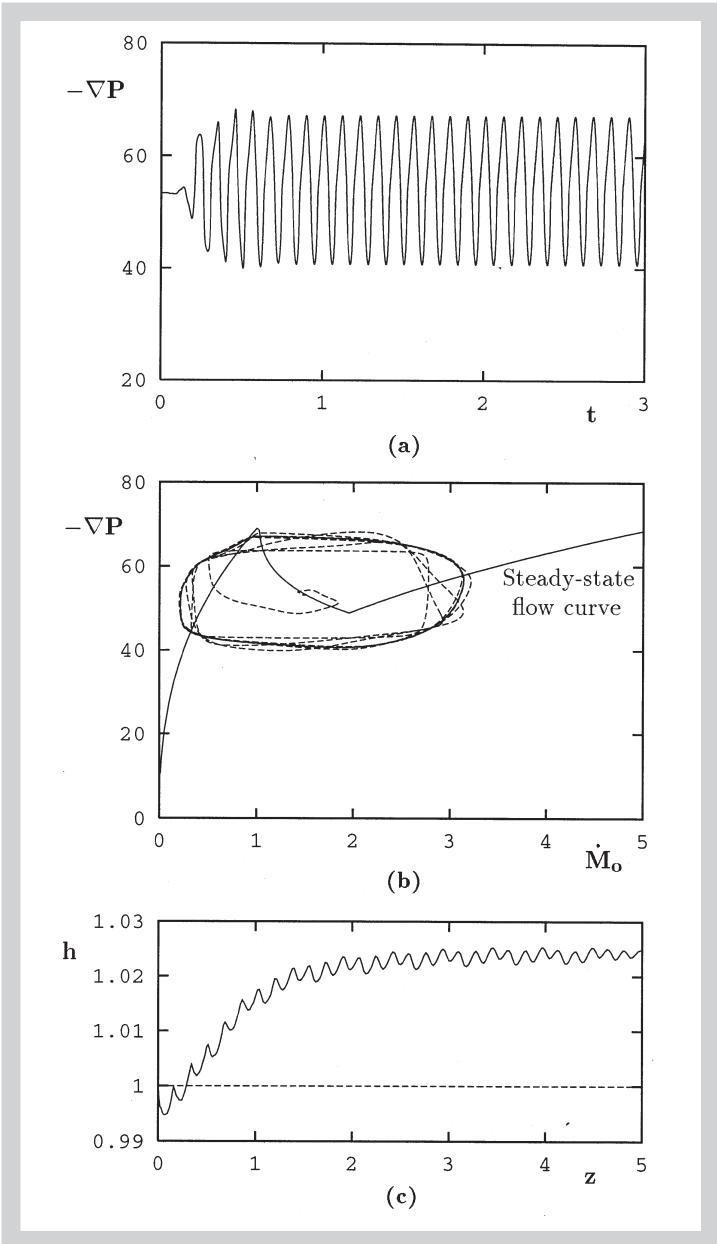

Figure 4 (right): Transient extrudate-swell flow of a Carreau fluid with n = 0.44, Re = 0.01, $B = 1.541 \ast 10^{-4}$ and Q =1.5: (a) Evolution of the pressure drop; (b) Trajectory of the solution on the flow curve plane; (c) Oscillations of the free surface.

ity may replace compressibility and, when combined with nonlinear slip, can act as a storage of elastic energy generating oscillations of the pressure drop similar to those observed experimentally in extrusion instabilities. They employed the Oldroyd-B constitutive model which exhibits a monotonic steady-shear response in the absence of slip. Therefore, their approach is fundamentally different from the constitutive instability mechanism in which the constitutive models exhibit a nonmonotonic (i.e. double-valued) steady shear response (see Section 6). They first studied the time-dependent one-dimensional shear flow and Poiseuille flow of an Oldroyd-B fluid assuming that slip occurs along the fixed wall, following an arbitrary nonmonotonic slip equation which relates the shear stress to the velocity at the wall. The stability of the steady-state solutions has been investigated by means of a one-dimensional linear stability analysis and time-dependent calculations, which revealed the existence of unstable solutions in the negative-slope regime of the flow curve, even though the volumetric flow rate, Q, is kept constant. Figure 5a shows the neutral stability curves for different values of the dimensionless Newtonian viscosity η_2 on the plane of the elasticity number ϵ and the derivative F' of the slip function $F(\sigma_w) = -F(v_w)$. The elasticity number is defined as

$$\epsilon = \frac{We}{Re} \tag{14}$$

where $We = \lambda V/R$ and $Re = \rho VR/(\eta_1 + \eta_2)$ are the Weissenberg and Reynolds numbers, respectively, λ, η_1 and η_2 are the usual material parameters of the Oldroyd-B model [81], and $\eta_1 + \eta_2$ is the zero shear-rate viscosity. The slip function F is the arbitrary non-monotonic function employed by Georgiou and Crochet [86, 87]. This is subject to the constraint $F'(\bar{v}_w) > -4$, which ensures that the volumetric flow rate for fully-developed round Poiseuille flow is a monotonic function of the steady-state slip velocity $\bar{v}_w$. If $F'(\bar{v}_w) > 0$, the solution is stable independent of the elasticity number ϵ. If $F'(\bar{v}_w) < 0$, the solution is unstable for values above the corresponding marginal stability curve. Hence, the Newtonian solutions are stable everywhere, and the interval of instability grows as one moves from the Newtonian to the upper-convected Maxwell model. When an unstable steady-state is perturbed, periodic solutions are obtained, while the volumetric flow rate is kept fixed (as in the experiments). The amplitude and the period of the oscillations are increasing functions of the elasticity [79, 80].

In [81], the numerical calculations have been extended to the time-dependent one- and two-dimensional axisymmetric Poiseuille and extrudate-swell flows using the elastic-viscous split stress (EVSS) method for the integration of the constitutive equation. The two-dimensional calculations showed that the pressure oscillations obtained in the unstable regime are of smaller amplitude and period than in the one-dimensional flow (Fig. 5b). They also revealed the existence of a second mode of periodicity in space, i.e. in the axial direction (Fig. 6a). The oscillations in the die result in small-amplitude oscillations of the extrudate surface, as shown in Fig. 6b.

More recently, Shore and co-workers [82 - 84] presented a phenomenological hydrodynamic model describing the Poiseuille flow of

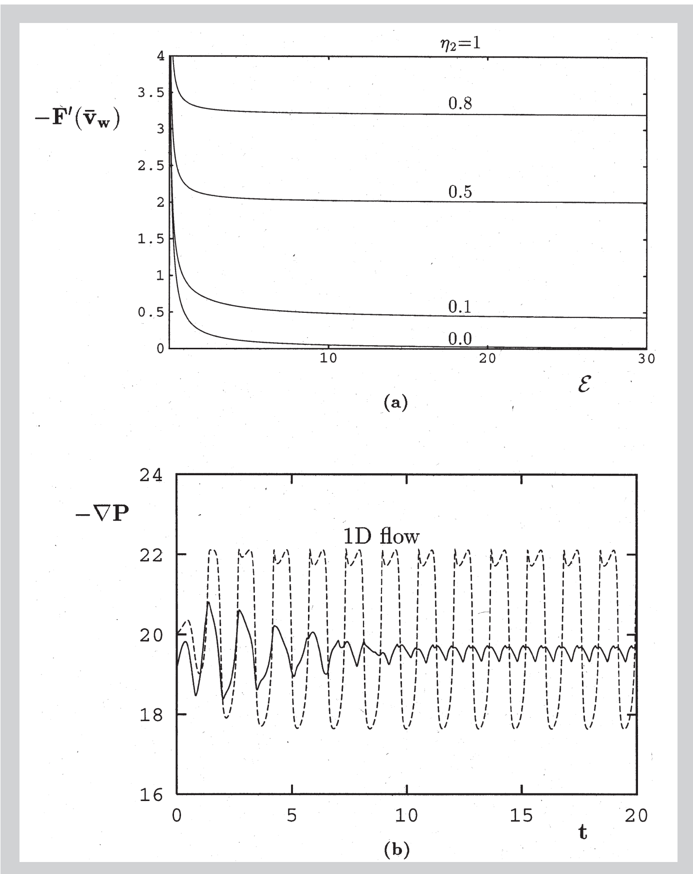

Figure 5: (a) Linear stability diagram for the Poiseuille flow of an Oldroyd-B fluid with slip at the wall and constant volumetric flow rate; solutions above the corresponding marginal stability curve up to $-F'(\bar{v}_w) = 4$ are unstable; (b) Pressure-drop oscillations in two-dimensional Poiseuille flow and comparisons with the one-dimensional calculations (broken line); $Q = 0.45$, $Re = 1$, $We = 1$, and $\eta_2 = 0.1$.

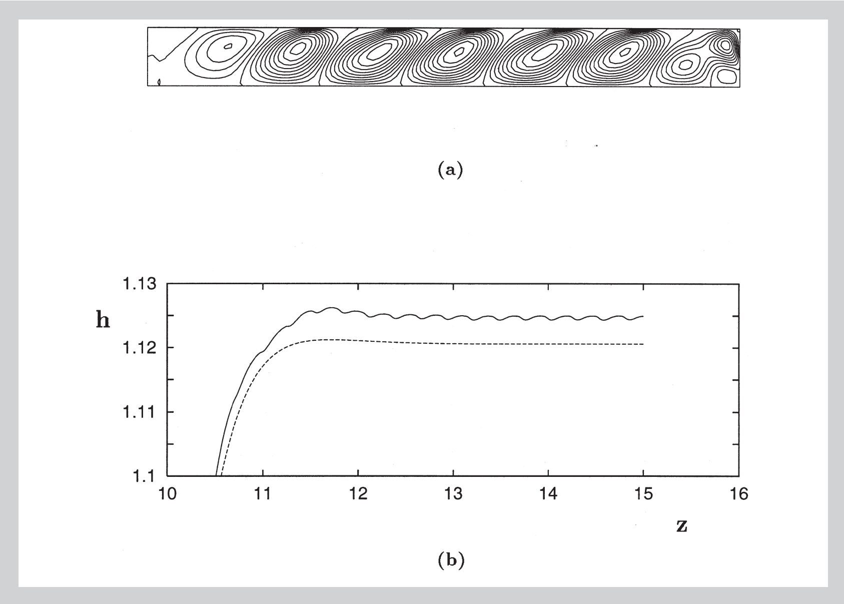

Figure 6: (a) Cells of radial velocity contours in Poiseuille flow of an Oldroyd-B fluid with slip at the wall; (b) Detail of the free-surface oscillations in extrudate-swell flow for Q = 0.45, Re = 1, We = 1, and η_2 = 0.1 (the broken line corresponds to the steady-state position of the free surface).

a viscoelastic Maxwell fluid. They assumed that the polymer near the surface undergoes a first-order transition in conformation as the wall shear stress increases, which produces stick-slip behavior and leads to a multivalued shear stress/slip velocity curve. Using linear stability analysis and carrying out numerical calculations of the linearized, incompressible, two-dimensional momentum equations under the assumption of periodic conditions in the direction of the flow, they demonstrated the existence of self-sustained oscillations, and related the latter to the sharkskin instability [82 - 84]. Nevertheless, Denn [3] points out that the linearized stress-constitutive equation used by Shore and co-workers is not properly invariant.

Black and Graham [75 - 77] demonstrated that the combination of elasticity with a *monotonic* slip model that takes into account the dependence of the slip velocity on the normal stress leads to short wavelength shear flow instabilities at sufficiently high shear rates, which is qualitatively consistent with experimental observations of the sharkskin instability. (If the slip velocity depends only on shear stress, then the flow is always stable.) Black and Graham employed a simple phenomenological evolution equation for the slip process and carried out a linear stability analysis for the creeping, plane, incompressible Couette flow of the upper convected Maxwell and the Phan-Thien-Tanner fluids.

6 CONSTITUTIVE INSTABILITIES

While slip-induced instability is based on the nonmonotonicity of the slip equation, most of the proposed studies of constitutive instability are caused by the nonmonotonicity of the shear stress/shear rate curve. It should be pointed out that, in both mechanisms, the flow curves for Poiseuille flow have similar forms, i.e. they exhibit a maximum followed by a minimum. Nonmonotone constitutive models include the three-constant Oldroyd model [92], the Doi-Edwards model with a Rouse relaxation mode [93, 94], the Johnson-Segalman model with an added Newtonian (solvent) viscosity [95], the Giesekus model [95, 96], and the KBKZ model with an extra viscous term [97]. The nonmonotonicity of the constitutive equation is predicted by reptation theories for highly entangled polymer melts and can be viewed physically as the separation of flow into two dynamic regimes with histories at low and high deformation rates, away from or near to the solid boundary, respectively [93], which implies the existence of two characteristic times of the viscoelastic fluids. There is experimental evidence that wormlike surfactant solutions obey a nonmonotone constitutive law [98 - 100]. Moreover, Callaghan et al. [101] and Britton et al. [100] observed the spurt (stick-slip) instability in wormlike micelles using nuclear magnetic resonance velocimetry techniques.

A consequence of the nonmonotonicity of the constitutive models is that, in viscometric (one-dimensional) flows, such as the simple shear and Poiseuille flows, multiple steady-state solutions are allowed, within a certain range of shear stress. In addition to the standard steady-state solution, there exist uncountably infinite weak solutions which are characterized by an arbitrary number of shear rate discontinuities. In Poiseuille flow, these discontinuities are located over a very thin layer of the fluid close to the wall where the shear rate can be high. The thin high-shear-rate layer near the wall leads to an apparent slip, whereas the flow in the bulk is almost plug [95, 102, 103]. The apparent slip may practically be considered as wall slip, and, thus, another possible physical interpretation of the stick-slip instability is provided through constitutive instabilities. The appearance of zones of different shear rates, also referred to as *shear banding* [104], has been shown experimentally for wormlike surfactant semidilute solutions which exhibit a narrow spectrum of relaxation times [98, 99].

Linear stability and/or time-dependent numerical analyses of the shear and Poiseuille flows of three-constant Oldroyd [92], Doi-Edwards [93, 94], Johnson-Segalman and Giesekus [95] fluids show that steady-state solutions with segments corresponding to the decreasing portion of the shear stress/shear rate curve may be unstable and that a flow curve hysteresis is obtained between the two stable branches. Various investigators considered this inherent constitutive instability in order to explain the spurt effects observed during the pressure-controlled capillary extrusion of certain polymer melts. Kolkka et al. [95] solved the pressure gradient-controlled plane Poiseuille flow of a Johnson-Segalman fluid with an added Newtonian viscosity and showed that the time-dependent solution jumps to one of the two stable positive-slope branches of the steady shear stress/shear rate curve and thus the negative-slope branch is unattainable. Malkus et al. [105] obtained numerical time-dependent results for the startup of axisymmetric Poiseuille flow (i.e., at fixed volumetric flow rate) and found that the pressure drop becomes periodic for very small values of the Newtonian viscosity. The persistent oscillations arise as a Hopf bifurcation to periodic orbits as the volumetric flow rate is increased beyond a critical value. Similar results have been obtained more recently by Aarts and van de Ven [106]. Solutions of oscillatory character have also been reported by Yuan et al. [107] who solved the creeping two-dimensional plane Poiseuille flow of a Johnson-Segalman fluid using a Lagrangian/Eulerian simulation technique and periodic boundary conditions at the inlet and outlet planes of the flow domain. They did not mention, however, whether oscillations persist or decay.

Georgiou and co-workers [103, 108] solved numerically the one-dimensional time-dependent simple shear and plane Poiseuille flows of a Johnson-Segalman fluid with added Newtonian viscosity, and investigated the stability of the steady-state solutions focusing on the case where the steady-state shear stress/shear rate curve is not monotonic. Their numerical simulations showed that the steady-state solutions are unstable only if a part of the velocity profile corresponds to the negative-slope regime of the standard steady-state shear stress/shear rate curve, in agreement with linear stability analysis. Their time-dependent solutions are always bounded and converge to different stable steady states, depending on the initial perturbation. No regimes of self-sustained oscillations (similar to those observed in the stick-slip extrusion instability) have been found, for values of the dimensionless solvent viscosity as low as 0.01. Oscillatory solutions are observed in certain cases but the oscillations are always decaying, in contrast to the numerical findings of Malkus et al. [105, 109], and Aarts [106]. Similar results demonstrating that the selection of the final steady-state is history dependent have also been reported by Olmsted et al. [110]. The addition of a diffusion (nonlocal) term to the Johnson-Segalman model allows, under most conditions, for unique stress selection and history-independent banding profiles in the unstable regime [111, 112]. Note that, for very small values of the solvent viscosity, the negative slope regime of the constitutive equation becomes large and extends to very high shear rates, which is not expected physically, since short-relaxation time processes become important causing the stress to increase [104].

We believe that the oscillations obtained with non-monotonic constitutive models are due to the inability of the numerical schemes to capture the shear rate discontinuity which tends towards the wall as the dimensionless solvent viscosity goes to zero. Malkus et al. [109] note that the oscillations might be an artifact of the numerical algorithm, i.e., a consequence of the system being slightly damped. Aarts [106] also admits that the oscillations of the velocity gradient and of the stress components have a larger amplitude and 'tend to become discontinuous' near the wall. Similarly, Malkus [105] reports that the velocity rises and falls nearly periodically at the thin layer near the boundary. Note also that neither Español et al. [113], who solved the creeping one- and two-dimensional plane shear flows of a Johnson-Segalman fluid with added Newtonian viscosity using a Lagrangian/Eulerian method, nor Greco and Ball [114], who solved the creeping circular Couette flow of a Johnson-Segalman fluid using a variational principle, have reported the appearance of self-sustained oscillations in the negative-slope regime of the flow curve. They have shown instead, that a steady-state solution is always reached according to a selection mechanism for the position of the discontinuity and for the total shear stress. Other works in which no periodic solutions have been found are those of Den Doelder et al. [89] and Ashrafi and Khayat [115]. Den Doelder et al. [89] adjusted the one-dimensional relaxation-oscillation model of Molenaar and Koopmans [116] for a Johnson-Segalman fluid with a no-slip boundary condition. Ashrafi and Khayat [115] examined the nonlinear stability of the one-dimensional plane Couette flow of a Johnson-Segalman fluid and obtained a six-dimensional dynamical system using the Galerkin projection method. They found that time-dependent solutions always converge to the corresponding steady states either monotonically or oscillatorily, at low or high Reynolds numbers, respectively. Thus, the fact that non-monotonic constitutive equations allow the existence of unstable steady states in some range of the shear rate cannot alone be used for explaining the stick-slip instability.

7 DISCUSSION

Recent work concerning the numerical modeling of the stick-slip and gross melt fracture instabilities in polymer melt extrusion has been reviewed. The following three mechanisms of instability have been considered:

(i) combination of nonlinear slip with compressibility;
(ii) combination of nonlinear slip with elasticity; and
(iii) constitutive instabilities.

It is clear that only the first two mechanisms, i.e. those involving slip, lead to periodic solutions in (time-dependent) Poiseuille and extrudate-swell flows. Both compressibility and elasticity, in combination with a nonmonotonic slip law, act as a storage of elastic energy generating self-sustained oscillations of the pressure-drop in Poiseuille flow and waves on the extrudate surface in extrudate-swell flow, similar to those observed in extrusion experiments. There is a general agreement that the compressibility-slip instability mechanism is present in the stick-slip and gross melt fracture regimes. The elasticity-slip mechanism may also be present and appears to generate small-amplitude high-frequency oscillations which are qualitatively consistent with the sharkskin instability [75 - 77], and are superimposed to the much larger oscillations caused by the combined effect of compressibility and slip.

We believe that the oscillations obtained with non-monotonic constitutive models are of numerical nature, caused by the inability of the numerical schemes to capture the shear rate discontinuities admitted by such models. This is not the only criticism to the constitutive-instability mechanism. Even though Larson [4] notes that gross fracture is most probably caused by constitutive instabilities and not by slip, since the onset of gross melt fracture is not significantly affected by changes in the die material, he points out that the main drawback of the constitutive instability approach is that it cannot account for the dependence of the oscillations on the capillary die effects [4, 117]. The flow curves obtained from a capillary rheometer are diameter-dependent in the sharkskin regime, which indicates the crucial role of slip [96]. Hence the constitutive instability mechanism may only be used for molten polymers exhibiting no-slip in the sharkskin regime, such as nearly monodisperse polybutadienes [16, 118]. The strong dependence of the upper branch of the apparent flow curve on the capillary radius and the importance of slip to the spurt instability are also noted by Adewale and Leonov [9]. The interfacial nature of the stick-slip transition, which depends on the surface roughness and the surface energy of the capillary die, is supported by the experiments of of Piau et al. [6] and Wang and Drda [50]. On the other hand, Aarts and Van de Ven [106] note that the critical volumetric flow rate for the Johnson-Segalman fluid does scale with the radius, and this is consistent with the experimental data of El Kissi and Piau [119].

Other criticisms on the use of the constitutive instability mechanism for explaining the spurt instability for polymer melts or solutions have also been reported. Denn [2] remarked that the oscillations obtained by Malkus et al. [109] are not of the type of the slip induced persistent oscillations between the two stable branches of the flow curve that are observed experimentally with polydisperse LLDPE in the stick-slip instability regime. Adewale and Leonov have shown that the Johnson-Segalman model is unable to match simultaneously the experimental data for narrow-distributed polyethylene in the critical regime of shear flow leading to the spurt phenomenon and in the critical regime of elongational flow [120], and underline the fact that non-monotone flow curves have been reported only for some materials with yield stress and not for common polymer melts or elastomers [9]. De Kee and Wissbrun [16] note that the constitutive instability theory does not account for the lack of spurt flow for most polymers. Finally, Wang et al. [117] note that the observed hysteresis in spurt flow cannot be attributed to the constitutive properties of the polymer that is being continuously extruded out and therefore does not re-visit itself during the experiment, and that stick-slip oscillations can be eliminated in the same stress range using an identical die with its wall chemically treated to weaken polymer adsorption.

In the numerical simulations of Section 4, some progress has been made with respect to our previous work on the compressibility-slip mechanism [86 - 88], by using the Carreau model and employing a macroscopic slip equation suggested by the experimental data of Hatzikiriakos and Dealy for a HDPE [13, 18]. It should be noted, however, that many other important factors must be taken into account in order to achieve meaningful macroscopic simulations of extrusion instabilities that will allow the prediction of the critical conditions for the onset of slip and/or unstable flow and will establish the relation of the extrudate characteristics, such as amplitude and wavelength of the surface waves, to the flow conditions. These factors include [31, 81]:

(i) The use of more sophisticated *dynamic* slip equations describing the polymer/wall adhesion physics and involving the dependence of slip on normal stress (pressure) and history. These equations can be tested by micro-macro or multiscale simulations describing accurately the entanglement dynamics and the conformational changes near the wall.

(ii) The use of appropriate viscoelastic constitutive equations for the polymer melts under study.

(iii) The inclusion of the reservoir region. In addition to the fact that the compressibility effect is more important in this region, the die-entry flow is crucial in the development (or the elimination) of melt fracture, as shown by Piau et al. [7, 12, 36] and Pérez-González et al. [35].

(iv) The development of special numerical methods that will overcome the convergence difficulties encountered in the neighborhood of the stress singularity at the exit of the die, as emphasized by Denn [3]. Such singular methods, however, require the knowledge of the strength and the angular dependence of the singularity [121], which are unknown for all viscoelastic constitutive equations of interest. Convergence difficulties also occur in the neighborhood of the re-entrant corner, when the reservoir region is included.

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