Unsteady circular tube flow of compressible polymeric liquids subject to pressure-dependent wall slip

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Synopsis

A mathematical model is developed for the time-dependent circular tube flow of compressible polymeric liquids subject to pressure-dependent slip at the wall and applied to a poly (dimethyl siloxane) (PDMS). The parameters of pressure-dependent wall slip velocity and shear viscosity of the PDMS were determined using combinations of small-amplitude oscillatory shear, steady torsional and squeeze flows and were employed in the prediction of the time-dependent circular tube flow behavior of the PDMS. The numerical solutions suggest that a steady tube flow is generated when the flow boundary condition at the wall is stable, that is, either a contiguous stick (or weak slip) or a contiguous strong slip condition along the entire length of the wall. On the other hand, when the flow boundary condition changes from stick (or weak slip) to strong slip at any location along the length of the wall, undamped periodic oscillations in pressure and mean velocity are observed. The experimentally characterized and simulated tube flow curves of PDMS are similar and the simulation findings for flow stability are in general consistent with the experimentally observed flow instability behavior of PDMS. © 2008 The Society of Rheology.

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I. INTRODUCTION

Experimental data collected from simple shear flows of polymeric liquids suggest that there are intimate links between the flow boundary condition at the wall and the time-dependent formation of flow instabilities and extrudate distortions for polymeric liquids [Benbow and Lamb (1963); Ramamurthy (1986); Piau et al. (1995); Denn (2001); Larrazabal et al. (2006)]. Three distinct types of extrudate irregularities are considered to have different initiating mechanisms, i.e., the shark skin region arising from slip and the uniaxial stretching that occurs at the exit of the die [Hatzikiriakos and Migler (2005)], the slip stick associated with wall slip [Denn (2001); Georgiou (2003)] and the gross bulk extrudate distortions, linked to the dynamics of the converging flow at the entrance to the die [Kim and Dealy (2002)]. Although the wall slip is assumed to be principally responsible for slip-stick type flow instabilities it is anticipated that slip will also play significant role in the development of flow instabilities in converging flow [Joshi and Denn (2003)] and uniaxial stretching at the exit of the die. Empirical experimental evidence indicates that flow instabilities are not encountered during pressure-driven flows for polymeric

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liquids or polymeric liquids incorporated with various additives, which generate either a stable wall stick condition or a stable wall slip condition [Ramamurthy (1986); Kalyon and Gevgilili (2003); Fujiyama and Inata (2002)].

The slip-based theoretical treatment of the development of polymer flow instabilities in simple channels has generally relied on the considerations of the compressibility and various empirical non-monotonic wall slip velocity versus wall shear stress expressions [Hatzikiriakos and Dealy (1992a, 1992b); Den Doelder et al. (1998); Georgiou (2003)]. Furthermore, it is determined that wall slip of polymers occurs as a function of normal stress/pressure at the wall with wall slip velocities decreasing with increasing normal stress/pressure [Vinogradov and Ivanova (1967); Kalika and Denn (1987); Hatzikiriakos and Dealy (1992a, 1992b); Person and Denn (1997)]. If the wall slip behavior is considered to be a function of pressure then obtaining the parameters of the shear viscosity material function in the relatively high shear rate range using the conventional pressure-driven capillary and rectangular slit rheometers becomes a significant challenge. For example, Hatzikiriakos and Dealy (1992a) have demonstrated the difficulties encountered in the application of the Bagley correction procedures for capillary rheometry (due to a lack of linearity of the pressure drop versus capillary length over the diameter curves). Currently there are no general methodologies available for the determination of the parameters of pressure-dependent wall slip and the shear viscosity material functions (under conditions in which wall slip is significant) simultaneously.

In this study, a mathematical model is first provided for the time-dependent isothermal laminar flow of compressible generalized Newtonian fluids through long circular tubes subject to pressure-dependent wall slip. Second, experimental procedures for the determination of the parameters of pressure-dependent wall slip and shear viscosity material function of polymeric liquids (based principally on the inverse-problem solution methodologies) are presented. These procedures rely on the collection of small-amplitude oscillatory shear, steady torsional and squeeze flow data. Finally, capillary flow data of a poly (dimethyl siloxane), PDMS, collected with relatively long capillaries with systematically varied diameters at constant length/diameter ratio, are compared directly with the numerical simulation results of unsteady circular tube flow to probe the underlying mechanisms for the development of flow instabilities for polymeric liquids.

II. WALL SLIP BEHAVIOR OF POLYMERIC LIQUIDS

Various polymer melts, especially linear polymers, exhibit wall slip [Ramamurthy (1986); Kalika and Denn (1987); Hatzikiriakos and Dealy (1991, 1992a); Migler et al. (1993); Chen et al. (1993); Awati et al. (2000); Münstedt et al. (2000); Gevgilili and Kalyon (2001)]. Wall slip is considered to be one of the major factors that can affect the formation of extrudate distortions [Benbow and Lamb (1963); Kissi and Piau (1990)]. The literature suggests that there may be multiple mechanisms for the wall slip of polymer melts. For example, with PDMS Migler et al. (1993) have measured the velocity distribution directly within a distance of 100 nm of the wall and have observed a sharp transition between a regime of weak slip and one of strong slip. The transition from weak to strong slip in simple shear is considered to occur at a material-dependent wall shear stress, value of which depends on the surface density of surface-anchored chains and the molecular weight of the polymer melt [Brochard and de Gennes (1992); Léger et al. (1997)]. Low molecular weight polymer fractions, as well as various processing additives with relatively low shear viscosity, are generally present in commercial polymers. Such species can also generate wall slip on the basis of an apparent slip [Kalyon (2005)] mechanism.
Ramamurthy (1986) reported a critical wall shear stress of 0.14 MPa for the onset of wall slip for linear low density polyethylene. Hatzikiriakos and Dealy (1991) reported a critical wall shear stress of 0.09 MPa for the onset of wall slip for high density polyethylene (HDPE) using a sliding plate rheometer. In their study of high-density polyethylenes, Wang and Drda (1997) determined a critical stress of about 0.3 MPa (based on the discontinuity of the flow curve) for high density polyethylene at 180 °C. Kissi and Piet (1990) carried out flow visualization experiments with PDMS using transparent dies with tracer particles and were able to document wall slip in the 0.05–0.07 MPa wall shear stress range. On the other hand, Benbow and Lamb (1963) determined a critical shear stress of 0.07 MPa for the onset of wall slip for PDMS. Chen et al. (1993) used Mooney’s method for capillary flow and determined that wall slip of linear-low density polyethylene, prior to the onset of extrudate distortions upon flow through a capillary die, is related to the materials of construction and the roughness of the surface of the capillary.

Kalyon and Gevgilili (2003) have focused on the wall slip and flow instability behavior of three polymers during extrusion through capillary dies. Two of these polymers, i.e., a poly (dimethyl siloxane) and HDPE, exhibited easily detectable strong wall slip in simple shear flow with critical wall shear stress values of 0.07 and 0.2 MPa. On the other hand, the third material of their study, i.e., an oxetane-based alternating block copolymer, BAMO/AMMO, with hard blocks consisting of [3, 3-bis (azidomethyl) oxetane, BAMO] and with soft blocks of (3-azidomethyl-3-methyloxetane, AMMO) did not exhibit strong slip in steady torsional flow [Kalyon and Gevgilili (2003)] over a very wide range of strains and strain rates. The extrudates of the HDPE and the PDMS emerging from capillary flow were distortion free at wall shear stresses, which were lower than their respective critical shear stress values. On the other hand, the BAMO/AMMO thermoplastic elastomer of their study, which did not exhibit strong slip over a broad range of shear rates in simple shear flow, did not exhibit extrudate distortions during capillary flow over the same range of shear rates. This observation again emphasized the importance of wall slip in affecting the development of flow instabilities and extrudate distortions.

The relationship between the onset of strong wall slip of HDPE and its processability was further investigated by using a continuous shear roll extruder [Kalyon et al. (2004)]. The continuous shear roll extrusion is a continuous processing method that is based solely on the use of two parallel and grooved rolls. Since there is no barrel to enclose the rolls, the conveying of the melt takes place upon its sticking to one roll and its slipping at the surface of the second roll. Thus, the shear roll extruder can be considered to be a differential slip tester for polymer liquids (the stick or slip can be immediately observed and affected by changes in roll speeds, temperatures, and surface roughnesses). These experiments have revealed that the complete detachment of a HDPE melt from both roll surfaces occurs when the shear stress in the nip region between the two rolls surpasses the critical shear stress, $\tau_c$, at which strong wall slip is onset, providing a direct link between onset of strong wall slip and processability.

The weak to strong transition in slip velocity, $u_s$, at the critical wall shear stress, $\tau_c$, can be described in conjunction with a hyperbolic tangent dependence [Tang and Kalyon (2004a)]:

$$u_s = \beta \tau_w^{s_1}[0.5 + 0.5 \tanh(\alpha(\tau_w - \tau_c))].$$

(1)

Here, $\tau_w$ is the shear stress at the wall, $\beta$ and $s_1$ are the Navier’s slip coefficient and slip exponent, respectively, for the polymers and $\alpha$ is a positive constant describing the sharpness of the weak-to-strong slip transition in the slip velocity of the polymer at the critical wall shear stress, $\tau_c$. The power law dependence of the slip velocity on wall shear stress arises directly in the apparent slip mechanism when the fluid constituting the
apparent slip layer is non-Newtonian [Kalyon (2005)]. This power law dependence was assumed to hold also for the wall slip of the polymer melt. The hyperbolic tangent function allows the incorporation of the concept of the critical wall shear (at which the transition from weak to strong slip at the wall occurs) to describe the wall slip behavior of the polymer melt.

Hatzikiriakos and Dealy (1992a) have indicated that for viscoelastic polymeric liquids the slip velocity should be a function of the pressure and the first and second normal stress differences at the wall but only the pressure effect is considered here, following Person and Denn (1997). Kalyon et al. (1995) have investigated the pressure-driven flow of a concentrated suspension through a slit die, using high-speed cinematography and a microscope attached to a transparent die surface (at a location which is close to the exit of the die). The high-speed cinematography has revealed for the first time that the die surface is covered in a time-dependent fashion with air films. The bubbles of air were observed to approach the die surface, attach and flatten, and then slide, roll and detach upon contact with the wall for 30 ± 10 ms under the experimental conditions applied. The ramifications of the lubrication of the die wall by the vapor phase have been discussed in conjunction with the processing behavior of concentrated suspensions [Aral and Kalyon (1995)]. Imaging experiments with various other fluids have also revealed the formation of a vapor layer (some as nanobubbles) at the wall [Tyrrell and Attard (2001)].

The formation of such an apparent slip layer, entraining some of the vapor phase at the wall, would be affected by the bulk pressure. Thus, the slip velocity at the wall should diminish with increasing pressure. This provides an important mechanism to explain the experimentally observed pressure dependence of wall slip of polymer melts [Vinogradov and Ivanova (1967); Kalika and Denn (1987); Hatzikiriakos and Dealy (1992a, 1992b); Person and Denn (1997)]. Here, considering that the presence of a gas phase at the wall is the important factor to give rise to the observed pressure dependence of wall slip on pressure, the Navier’s slip coefficient for the polymer, \( \beta \), is assumed to vary inversely with pressure, akin to the experimentally observed wall slip behavior of compressible gases during flow through simple conduits [Knudsen (1950):]

\[ \beta = \beta_0 \left( \frac{p_a}{p} \right)^\kappa, \]

where \( p \) is the local pressure, \( p_a \) is the atmospheric pressure, and \( \beta_0 \) is the slip coefficient of the polymer at atmospheric pressure. The exponent \( \kappa \) is experimentally observed to be equal to one for slip flow of gases [Knudsen (1950)]. It is an empirical factor that needs to be determined experimentally for polymeric liquids.

III. UNSTEADY LAMINAR FLOW OF COMPRESSIBLE GENERALIZED NEWTONIAN FLUIDS THROUGH LONG CIRCULAR TUBES SUBJECT TO PRESSURE-DEPENDENT WALL SLIP

The unsteady isothermal laminar flow of a compressible fluid contained in a long circular tube of length \( L \) and radius \( R \) resulting from the sudden imposition of a flow condition at one end of the tube is considered. Consistent with the earlier literature investigating the dynamics of the flow of polymeric liquids in circular tubes, the compressible fluid is assumed to be purely viscous, i.e., generalized Newtonian fluid [Hatzikiriakos and Dealy (1992a); Den Doelder et al. (1998); Georgiou (2003)]. It is assumed that Ostwald-de Waele or “power law” behavior represents the shear viscosity, \( \tau = -m|dV_z/dr|^n(dV_z/dr), \) where \( m \) and \( n \) are the consistency index and the power law index parameters of the power law equation and \( V_z(r) \) is the velocity component in the
flow direction, \( z \). The inertial and gravitational effects are assumed to be negligible. The integrations of the governing equations of the continuity and momentum equations over the cross-sectional area, \( A \), provide

\[
\frac{\partial p}{\partial t} + \frac{\partial}{\partial z} \left[ \left( p - p_a + \frac{\rho_a}{\xi} \right) V \right] = 0,
\]

(3)

\[
\frac{\partial V}{\partial t} + \frac{1}{2} \frac{\partial \chi V^2}{\partial z} + \frac{2 \tau_w}{\xi(p - p_a) + \rho_a R} + \frac{1}{2} \frac{\partial p}{\partial z} = 0,
\]

(4)

where \( t \) is the time, \( V \) is the cross-section-averaged \( z \) velocity, the density is given by

\[\rho = \xi(p - p_a) + \rho_a,\]

i.e., \( \rho \) and \( p_a \) are the density values of the melt at pressures \( p \) and \( p_a \), respectively, \( \xi \) is the compressibility coefficient, and \( \chi = \frac{1}{2} \int_A \frac{\partial V^2}{\partial x} \, dA \). \( \frac{\partial V^2}{\partial x} \) was assumed to be negligible for creeping flow conditions. Under steady conditions the wall stress, \( \tau_w \), can be determined from the prevailing steady local pressure gradient, \( -\frac{\partial p}{\partial z} \), i.e.,

\[
\tau_w = -\frac{R}{2} \left( \frac{\partial p}{\partial z} \right),
\]

(5)

and the local averaged velocity, \( V \), can be obtained as

\[
V = \frac{R^{(1+1/n)}}{(2m)^{1/n}(3 + 1/n)} \left( -\frac{\partial p}{\partial z} \right)^{1/n} + u_s.
\]

(6)

The boundary conditions at the entry and exit planes of the tube are

\[
V = V_o \quad \text{at} \quad z = 0,
\]

(7)

\[
p = p_a \quad \text{at} \quad z = L.
\]

(8)

The details of numerical methods used for the solution of these equations are discussed in Appendix.

### IV. DETERMINATION OF THE PARAMETERS OF SHEAR VISCOSITY AND PRESSURE-DEPENDENT WALL SLIP VELOCITY

#### A. Materials

A poly (dimethyl siloxane), PDMS, manufactured by GE Silicones (SE-30) was used in the experimental studies. It has a density of 958 kg/m\(^3\) under ambient pressure (Table I). This PDMS was used in our earlier experimental investigations focusing on the flow instabilities of polymeric liquids on one hand and as the binder of concentrated suspensions used in studies concerned with the development of flow instabilities during capillary and rectangular slit die flows [Kalyon and Gevgilili (2003); Birinci and Kalyon (2006)].

#### B. Experimental apparatus and procedures

An Advanced Rheometric Expansion System rheometer, originally from Rheometric Scientific, Inc., Piscataway, NJ (currently TA Instruments), was utilized in conjunction with steady torsional flow, and small-amplitude oscillatory shear flows using cone-and-plate and parallel-disk configurations. The environmental chamber was equipped with an imaging window and auxiliary optics for continuous monitoring of the free surface of the specimen [Aral and Kalyon (1994); Gevgilili and Kalyon (2001)]. A high-speed camera,
capable of recording at filming speeds as high as 2000 frames per second, was a part of the setup to allow the monitoring of the free surface of the specimen. During steady torsional flow a straight-line marker was placed on the edges of the cone/plate and the free surface of the polymer melt. The discontinuities in the marker line that develop between the surface of the plates of the rheometer and the polymeric liquid suggest the initiation of strong wall slip, from which the critical shear stress for the onset of strong wall slip could be determined. The torque data of the steady torsional flow of the PDMS at various nominal shear rates were used for the determination of the slip parameters upon the solution of the inverse problem.

An Instron Floor Tester was employed in conjunction with a capillary rheometer to study the development of extrudate distortions of PDMS upon exit from capillaries with differing diameters at constant capillary length over diameter ratio. The shapes of the extruded samples were captured immediately upon exit from the capillary using a high-speed camera. The temperature distributions of the extrudates emerging from the die were also monitored using a ThermaCam thermal imaging camera. Typically, the surface temperature of the PDMS extrude upon exit from the capillary die is observed to increase up to 4 °C rise in the 2–40 s⁻¹ range (over relatively long runs and with capillary length/diameter ratio of 60). The viscous energy dissipation effect is thus important in affecting the flow curve but was ignored in our current isothermal analysis.

An Instron capillary rheometer was used in conjunction with a plug to seal the reservoir kept under isothermal conditions for the pressure-volume-temperature experiments. The compressibility coefficient, \( \varsigma \), of the PDMS, was determined to be \( 1.4 \times 10^{-6} \) kg/m³. The table below shows the parameters of PDMS associated with density, wall slip and K-BKZ equation:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at ambient, ( \rho_0 )</td>
<td>958 kg/m³</td>
</tr>
<tr>
<td>Compressibility, ( \varsigma )</td>
<td>( 1.4 \times 10^{-6} ) s²/m²</td>
</tr>
<tr>
<td>Critical shear stress, ( \tau_c )</td>
<td>70,000 Pa</td>
</tr>
<tr>
<td>Pressure coefficient of slip, ( \kappa )</td>
<td>0.7</td>
</tr>
<tr>
<td>Navier’s slip coefficient, ( \beta_0 )</td>
<td>( 5 \times 10^{-16} ) m/(s-Pa)</td>
</tr>
<tr>
<td>Slip exponent, ( s_1 )</td>
<td>3.1</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>20</td>
</tr>
<tr>
<td>Damping function parameters: ( f )</td>
<td>1.0</td>
</tr>
<tr>
<td>( n_1 )</td>
<td>0.283</td>
</tr>
<tr>
<td>( n_2 )</td>
<td>-</td>
</tr>
<tr>
<td>Relaxation time, ( \lambda_i ), s:</td>
<td>Relaxation strength, ( G_i ), Pa</td>
</tr>
<tr>
<td>0.0003</td>
<td>61,040</td>
</tr>
<tr>
<td>0.006</td>
<td>47,140</td>
</tr>
<tr>
<td>0.034</td>
<td>40,730</td>
</tr>
<tr>
<td>0.16</td>
<td>29,210</td>
</tr>
<tr>
<td>0.72</td>
<td>11,970</td>
</tr>
<tr>
<td>3.27</td>
<td>2,435</td>
</tr>
<tr>
<td>21.1</td>
<td>290</td>
</tr>
<tr>
<td>80</td>
<td>38</td>
</tr>
<tr>
<td>Power law parameters: ( \dot{\gamma} \leq 40 ) s⁻¹:</td>
<td>( m=19,000 ) Pa sⁿ and ( n=0.37 )</td>
</tr>
<tr>
<td>( \dot{\gamma} &gt; 40 ) s⁻¹:</td>
<td>( m=31,000 ) Pa sⁿ and ( n=0.21 )</td>
</tr>
</tbody>
</table>
(s²/m²), which agreed with the available pressure-volume-temperature data of PDMS fitted with the Sanchez and Lacombe Lattice Fluid Model [Brandrup et al. (1999)].

C. Characterization of the shear viscosity of the PDMS

The pressure dependence of the slip velocity suggests that the shear viscosity of the PDMS cannot be characterized in the relevant high shear rate range using conventional pressure-driven viscometers. This was also recognized in the investigation of Smillo and Dealy (2006), in which the magnitude of complex viscosity values was utilized to represent slip-free shear viscosity values on the basis of the Cox–Merz rule. Here the shear viscosity of the PDMS at the relevant high shear rate range was predicted using a factorized K-BKZ integral constitutive equation in conjunction with an exponential type damping function [Bernstein et al. (1963); Wagner (1976); Gevgilili (2003)]

\[
\tau(t) = \int_{-\infty}^{t} M(t-t')h(I_1,I_2)B(t')dt',
\]

where \(h(I_1,I_2)\) is the damping function and \(I_1\) and \(I_2\) are the first and second invariants of the relative Finger strain tensor, \(B\). \(M(t-t')\) is the rubberlike-liquid memory function, which can be determined from linear viscoelastic data. The determination of the parameters of the memory function and the damping function needs to be undertaken using simple shear flow conditions at which the wall slip of the PDMS is negligible (i.e., under conditions for which the shear stress is less than the critical shear stress, \(\tau_c\), at which the weak to strong slip transition takes place). Thus, for example, the relaxation modulus versus time and strain data obtained upon the step strain experiment could not be used due to the significant slip observed during the step strain experiment [Gevgilili and Kalyon (2001)]. The parameters of the constitutive equation were determined upon the best fit of the relaxation spectra from the dynamic properties, collected using small-amplitude oscillatory shear, and the shear stress growth and shear stress relaxation upon cessation of steady shear material functions collected at the relatively low shear rates at which wall slip of the PDMS was negligible.

The dynamic properties of the PDMS are shown in Fig. 1. The collected storage modulus, \(G'\), and loss modulus, \(G''\), data as a function of frequency, \(\omega\), were employed to determine the relaxation strength, \(G_i\), versus the relaxation time, \(\lambda_i\), as follows:

\[
G'(\omega) = \sum_i \frac{G_i\lambda_i^2\omega^2}{1 + \lambda_i^2\omega^2}, \quad G''(\omega) = \sum_i \frac{G_i\lambda_i\omega}{1 + \lambda_i^2\omega^2}.
\]
The characterization of the discrete relaxation spectra, i.e., the relaxation strength, \( G_i \), versus the relaxation time, \( \lambda_i \), values was carried out in conjunction with the Generalized Reduced Gradient type of nonlinear optimization by using a pattern search method.

The determination of the parameters of the shear damping function \( h_s(\gamma) \), as a function of shear strain, \( \gamma \), i.e., \( f, n_1 \) and \( n_2 \) [Osaki (1976); Laun (1978)]

\[
\begin{align*}
\frac{h_s(\gamma)}{\eta(\dot{\gamma})} &= f \exp(-n_1 \gamma) + (1 - f) \exp(-n_2 \gamma)
\end{align*}
\]

required the use of two additional material functions, i.e., the shear stress growth upon the inception of simple shear flow, \( \eta^p(t, \dot{\gamma}) \), and the relaxation of the shearing stress upon the cessation of steady shear flow, \( \eta^r(t, \dot{\gamma}) \), data at shear rates under which wall slip is negligible for PDMS [Kalyon and Gevgilili (2003)]. The shear stress growth and relaxation material functions predicted on the basis of the double exponential damping function in conjunction with the Wagner postulate of the K-BKZ equation were available from [Kalyon et al. (1988)]. The parameters \( f, n_1 \) and \( n_2 \) of the damping function for shear were sought upon the solution of the inverse problem to minimize the objective functions evaluated by the forward difference method.

The inverse problem solution procedure suggested that two parameters are sufficient to represent the shear stress growth and relaxation behavior and provided \( f \) and \( n_1 \) values of 1 and 0.283, respectively. The typical comparisons between the time-dependent shear stress growth upon the inception of steady torsional flow and shear stress relaxation upon the cessation of steady shear data and the fit of the inverse problem solutions are shown in Fig. 2. The agreement is acceptable.

The set of parameters \( G_i, \lambda_i, f \) and \( n_1 \), determined using conditions under which wall slip is negligible, allowed the determination of the shear viscosity material function, \( \eta(\dot{\gamma}) \) which was further fitted with two sets of power law parameters for computational convenience (Table I). The accuracy of the parameters representing the shear viscosity material function of PDMS are obviously limited by the capability of the Wagner postulate of the K-BKZ equation to predict the shear viscosity over a broad range of shear rates. There may be other methods to determine the shear viscosity of the polymer melt without using pressure-driven flows, for example, from the extrapolation of the shear viscosity data collected in the low apparent shear rate range (determined at wall shear stress values smaller than the critical wall shear stress at which slip effects are negligible) to the high

**FIG. 2.** Shear stress growth upon the inception of flow and shear stress relaxation upon the cessation of steady shear data of PDMS and the best fit of the shear damping function parameters.
apparent shear rate range but such procedures would not have been more accurate than the use of the K-BKZ equation to determine the shear viscosity behavior over a broad range of deformation rates.

D. Characterization of the wall slip behavior of the PDMS

The steady torsional flow experiments of PDMS, carried out in conjunction with the straight-line marker method and image analysis [Kalyon and Gevgilili (2003)], were used directly for the determination of the critical wall shear stress, $\tau_c$ (at which strong slip is onset). The additional slip parameters of the PDMS melt, $\beta_0$ and $s_1$, were determined from the inverse problem solution using the steady torque, $T$, data collected at different apparent shear rates in torsional flow

$$T = 2\pi \int_0^R r^2 \tau_w dr,$$

$$\tau_w = m \left( \frac{rW - 2u_s}{H} \right)^n,$$

where $H$ is the gap, $R$ is the disk radius, $W$ is the angular velocity, $u_s$ is the slip velocity of the PDMS given from Eq. (1). The best fit of the slip parameters, $\beta_0$ and $s_1$, from the inverse problem solution generated the values given in Table I.

The pressure coefficient for wall slip, $\kappa$, of the PDMS melt [Eq. (2)] was determined from the squeeze flow experiments. The squeeze flow offers a combination of drag and pressure-driven flow and conveniently covers a broad range of deformation rates. Our finite element method based source codes developed for the analysis of the squeeze flow of viscoplastic fluids subject to wall slip [Lawal and Kalyon (2000); Kalyon and Tang (2007)] were modified to allow the imposition of the pressure dependence of wall slip [Eqs. (1) and (2)] and the determination of the slip coefficient, $\kappa$, upon the imposition of the inverse problem solution methodologies [Tang and Kalyon (2004b)]. The agreement between the normal force, $F$, versus time data collected with squeeze flow and those that were numerically predicted using the $\kappa$ value of 0.7 (obtained from the inverse problem solution) are shown in Fig. 3. All of the determined parameters of PDMS are listed in Table I and the resulting behavior of wall slip velocity versus pressure and wall shear stress is shown in Fig. 4.

Both the pressure and the wall shear stress play significant roles in affecting the development of the wall slip behavior of PDMS (Fig. 4). The wall slip velocity values are negligible at wall shear stress values smaller than the critical wall shear stress, $\tau_c$, of
70 kPa. Wall slip velocity values decrease with increasing pressure with the pressure effect becoming more pronounced at the relatively higher wall shear stress values. The wall slip behavior observed in Fig. 4 suggests that significant distributions in the flow boundary condition could occur in circular tube flow as governed by the prevailing density, pressure and wall shear stress conditions.

V. NUMERICAL SIMULATION AND EXPERIMENTAL RESULTS

The governing Eqs. (1)–(6) were numerically solved to analyze the time-dependent tube flow of PDMS for circular tubes with diameters of 0.83, 1.5, and 2.5 mm at a constant tube L/D ratio of 40. These dimensions are the same as those of the straight land sections of the capillaries that were used to generate the flow curves as well as the experimental data related to the development of extrudate shape distortions and flow instabilities of the same PDMS and its suspensions with rigid spherical particles [Birinci and Kalyon 2006].

The numerical simulation results for the solution of the time-dependent flow behavior of the PDMS in a tube with a diameter of 1.5 mm at an apparent shear rate of 10 s⁻¹ are shown in Figs. 5 and 6 (determined at \( I = 21 \), \( CFL = 0.25 \), and \( Von = 0.25 \) where \( I \) is the number of mesh nodes, \( CFL \) is the Courant-Friedrichs-Levy number, and \( Von \) is the von Neumann number—see Appendix for details). Figure 5 shows the pressure, mean velocity, slip velocity, and shear stress as a function of time at a specific location next to the exit (\( z = 0.9 \) L) and Fig. 6 shows the distributions of pressure, mean velocity, slip velocity, and shear stress over the entire length of the tube at \( t = 0.9 \) s. These numerical results indicate that a steady state in flow could be reached at this apparent shear rate (Fig. 5). Under the steady state conditions the wall shear stress increases from 52 to 52.2 kPa in the axial, i.e., the \( z \) direction over the length of the tube (Fig. 6) and the mean velocity increases only slightly with increasing axial distance due to the compressibility of the polymer. The wall slip velocity is negligible over the entire length of the tube (Fig. 6).

The numerical solution was determined to be independent of the grid spacing and time interval upon systematically varying the values of mesh density and CFL and von Neumann numbers. Overall, the simulation results revealed no fluctuations in pressure, shear

![FIG. 4. Wall slip velocity versus pressure and wall shear stress behavior of PDMS.](image-url)
stress, mean velocity and slip velocity and indicated that steady flow could be achieved upon the imposition of the flow condition on the PDMS initially at rest, when the imposed apparent shear rates are smaller than about 20 s⁻¹.

On the other hand, when the apparent shear rate is increased further (>20 s⁻¹ but <1200 s⁻¹) the pressure, mean velocity and the wall slip velocity were determined to oscillate without dampening. Over the apparent shear rate range of 20 s⁻¹ < \dot{\gamma} < 1200 s⁻¹ the mean velocity, and the wall slip velocity exhibit time-dependent oscillations (varying periodically in between the stick to strong slip conditions) that did not dampen to a steady state regardless of the conditions of the simulation, i.e., time and mesh parameters over a broad range of CFL and von Neumann numbers. The typical results for an apparent shear rate of 266 s⁻¹ are shown in Figs. 7 and 8. Here with increasing time no damping is observed and the flow remains oscillatory at any location in the circular tube indefinitely (Fig. 7). Figure 8 shows the typical distributions of the pressure, shear stress, mean and wall slip velocities as a function of location at fixed time. At all locations the wall slip velocity approaches the mean velocity. Over this apparent shear rate range, a transition between the weak and strong slip condition occurs revealing the source of the instabilities shown in Fig. 7.

The steady flow behavior was again achieved at apparent shear rates higher than 1200 s⁻¹ with typical results shown in Figs. 9 and 10 for the apparent shear rate of

![FIG. 5. Time dependent behavior of PDMS (pressure, p, wall shear stress, \( \tau_w \), mean velocity, \( V \), and slip velocity, \( u_s \)) at an apparent shear rate of 10 s⁻¹ (tube diameter of 1.5 mm).](image)

![FIG. 6. Distributions of pressure, p, wall shear stress, \( \tau_w \), mean velocity, \( V \), and slip velocity, \( u_s \), at an apparent shear rate of 10 s⁻¹ (tube diameter of 1.5 mm).](image)
1333 s$^{-1}$ using I=21, CFL=0.1, and Von=0.1. Again, numerical tests were made to ensure that the numerical solution was mesh and time step independent over a broad range of I, CFL and Von values. The flow reaches a steady state solution within a short duration of time ($<0.1$ s) and remains steady indefinitely (Fig. 9). The steady distributions of the mean velocity, wall slip velocity, pressure and wall shear stress as a function of axial location, $z$, along the length of the tube are shown in Fig. 10. Under such high apparent shear rate conditions the shear stress values at the wall are all greater than the critical wall shear stress at which the transition from the weak to the strong slip condition occurs. The wall shear stress decreases monotonically with distance in the 140–75 kPa range and the mean velocity decreases slightly.

The behavior of wall slip velocity with distance along the length of the tube observed in this second steady zone, however, is very different than the steady behavior observed at the low apparent shear rate (compare Fig. 10 with Fig. 6). In this second steady zone, the wall slip velocities are significant. The slip velocity is about 40% of the mean velocity at the inlet plane of the tube. The ratio of the wall slip velocity, $u_s$, over the mean velocity, $V$, increases further with increasing axial distance and the ratio reaches one (plug flow) at the exit of the tube, that is, $V = u_s$. It is interesting to note that the generation
of pure plug flow at the exit plane removes the stress singularity, which is associated with
the transition of the velocity profile of the melt from the parabolic flow in the tube to a
plug flow upon exit from the tube.

Overall, the model results indicated that whenever the flow did not reach a steady
condition the critical wall shear stress and pressure combinations, at which weak to
strong wall slip transitions occur, or vice versa, were crossed. On the other hand, steady
flow was predicted when the pressure and wall shear stress values consistently stayed
above or below the critical conditions.

To explain the numerical observations that the flow becomes unsteady once it experi-
ences a slip velocity jump, let us consider the weak solutions of Eqs. (3) and (4), which
permit discontinuities. Suppose the tube flow reaches a steady state and exhibits a dis-
continuous wall slip velocity at a certain location \( z \). The Rankine–Hugoniot condition can
be derived from Eqs. (3) and (4) as (e.g., [Sod (1985)]):

\[
\left\{ p - p_a + \frac{p_a}{\varepsilon} \right\} V = 0,
\]

\[ \text{FIG. 9.} \] Time dependent behavior (pressure, \( p \), wall shear stress, \( \tau_w \), mean velocity, \( V \), and slip velocity, \( u_s \)) at an apparent shear rate of 1333 s\(^{-1}\) (tube diameter of 1.5 mm).

\[ \text{FIG. 10.} \] Distributions of pressure, \( p \), wall shear stress, \( \tau_w \), mean velocity, \( V \), and slip velocity, \( u_s \), at an apparent shear rate of 1333 s\(^{-1}\) (tube diameter of 1.5 mm).
\[ \{ \ln(\zeta(p - p_{in}) + \rho_f) \} = 0, \]  
(14)

where \( f \equiv f_l - f_r \), subscripts \( l \) and \( r \) standing, respectively, for the left and right sides of the location \( z \). From Eqs. (13) and (14), one obtains

\[ p_l = p_r, \]  
(15)

\[ V_l = V_r, \]  
(16)

which indicate that both velocity and pressure must be continuous across the location where slip velocity jumps.

In the case of a power law fluid, suppose \( \tau_{wl} < \tau_c < \tau_{wr} \), which is contradictory to Eq. (17). Therefore, it is concluded that the solution of the problem stated by Eqs. (3) and (4) cannot have two steady states separated by a discontinuity in slip velocity, as indeed observed in the numerical simulations.

For the PDMS the predicted flow curves (with the predicted stable and unstable regions delineated) are compared with the experimental capillary flow curve in Fig. 11. The numerical wall shear stress values are mean values determined upon integration with respect to time and distance. The reported experimental wall shear stress values are determined from the mean values of the pressure with time data obtained from capillary rheometry. As shown in Fig. 11, the experimentally characterized and numerically predicted values of the wall shear stress values agree with each other for the entire apparent shear rate range considered. Considering that the capillary flow data have not been used as part of the parameter estimation procedures for wall slip or shear viscosity small-amplitude, steady torsional and squeeze flows are used, the agreement is promising.
>20 s\(^{-1}\), the extrudate surfaces first become matt, followed by high frequency surface irregularities in turn followed by gross bulk extrudate distortions (Fig. 11). The numerical simulations also predict that the flow becomes unsteady in the same apparent shear rate range.

On the other hand, the experimental capillary flow data do not reveal steady behavior for apparent shear rates >1300 s\(^{-1}\). However, the experimental results for other polymeric liquids indicate that the flow curves of polymeric liquids typically show two steady zones, one in the low shear rate range and the second in the high shear rate range, with unstable behavior observed in between. Unfortunately, we were at the limits of our experimental capabilities and could not increase the apparent shear rates further without significant viscous energy dissipation. Thus, it is not clear if the predicted second steady range in the high apparent shear rate regime indeed exists or not. However, for other polymers it is known that three zones akin to what is predicted by the simulations exist (stable at the low and high apparent shear rate ranges and unstable in between) [Münstedt et al. (2000)]. Furthermore, the flow curves of the suspensions of the PDMS used in this study incorporated with rigid glass spheres (10–40% by vol.) exhibit the two steady zones, i.e., one in the low apparent shear rate and the second in the high apparent shear rate range [Birinci and Kalyon (2006)], suggesting that a second steady zone at the high apparent shear rates is present but was not accessible in our experimental study.

VI. CONCLUDING REMARKS

The important roles played by the compressibility and wall slip in the simple shear flow were elucidated in conjunction with a pressure-dependent wall slip coefficient and a mathematical model of the time-dependent laminar isothermal flow. The consideration of the pressure dependence of the slip coefficient mandated that new experimental methodologies be established to characterize the shear viscosity of the polymeric liquid over a broad range of shear rates and the determination of the pressure coefficients of the slip parameters without the use of pressure-driven flows. The study specifically focused on a PDMS for which experimental data were available and the experimental and numerically determined flow curves could be compared.
To enable the determination of the parameters of shear viscosity material function in the high shear rate region at which the behavior is generally subject to wall slip, the Wagner postulate of the K-BKZ equation was utilized, using data collected at sufficiently low apparent shear rates at which wall slip was negligible. The slip behavior of the polymer was characterized using steady torsional flow used together with the straight line marker method for the determination of the conditions under which strong slip is onset and squeeze flow, all used in conjunction with the inverse problem solution methods.

The numerical solutions applied to the PDMS indicated that steady solutions could be obtained only under conditions under which the weak to strong wall slip transition did not take place at any location along the length of the entire tube. When such transitions occurred no steady solution was possible. Furthermore, the detailed rheological characterization of the PDMS followed by numerical simulation of its tube flow behavior generated flow curves which agreed well with the experimental flow curves, including the ranges of apparent shear rates over which steady or unsteady flow could be obtained (except at the highest apparent shear rates).

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APPENDIX: NUMERICAL METHOD

The flow domain was covered by a uniform grid with nodes $i=1,2,3,\ldots,I$. The staggered mesh method, in which $V$ is defined at grid nodes $i$ and $p$, is assigned at half nodes $i+1/2$, is employed and the predictor-corrector scheme is used to discretize governing Eqs. (1)–(3), (5), and (6), that is:

1. PREDICTION

\[
\frac{\hat{p}_{i+1/2} - \hat{p}_{i+1/2}}{\Delta t} + \frac{(p_{i+3/2}^l + p_{i+1/2}^l)/2 - p_a + p_o/s) V_{i+1}^l - (p_{i+1/2}^l + p_{i-1/2}^l)/2 - p_a + p_o/s) V_i^l}{\Delta z} = 0, \quad (A1)
\]

\[
\hat{\tau}_{wi} = -\frac{R}{2} \left( \frac{\partial \hat{p}}{\partial z} \right)_i, \quad (A2)
\]

\[
\hat{u}_s = A' (\hat{p}_{i+1/2}, \hat{\tau}_{wi}), \quad (A3)
\]

\[
\hat{V}_{i}^l = B' \left( \frac{\partial \hat{p}}{\partial z} \right)_i \hat{u}_{si}, \quad (A4)
\]

where $\Delta t^l$ is the time step, $l$ being the time step index, $\Delta z$ is the grid spacing, and $A'$ and $B'$ are the functions defined as the right-hand side of Eq. (1) and (6), respectively. In calculating Eq. (A3), Eq. (1) is used.
2. CORRECTION

\[
\frac{p_{i+1/2}^l - p_{i+1/2}^l}{\Delta t} + \left((p_{i+3/2}^l + p_{i+1/2}^l)/2 - p_a + \rho_a/\rho_s\right) V_{i+1}^l - \left((p_{i+1/2}^l + p_{i-1/2}^l)/2 - p_a + \rho_a/\rho_s\right) V_i^l \\
= \frac{1}{2\Delta z} \left((\hat{p}_{i+3/2} + \hat{p}_{i+1/2}^l)/2 - p_a + \rho_a/\rho_s\right) \hat{V}_{i+1}^l - \left((\hat{p}_{i+1/2} + \hat{p}_{i-1/2}^l)/2 - p_a + \rho_a/\rho_s\right) \hat{V}_i^l
\]

\[
= 0,
\]

\[
V_i^{l+1} = B' \left[ \left( \frac{\partial p}{\partial z} \right)_{i}^{l+1}, u_{s_i}^{l+1} \right],
\]

\[
\hat{V}_i^{l+1} = B' \left[ \left( \frac{\partial \hat{p}}{\partial z} \right)_{i}^{l+1}, \hat{u}_{s_i}^{l+1} \right].
\]

In the above, pressure at the entry plane and velocity at the exit plane are obtained by extrapolation. The numerical solution was validated using analytical solutions related to steady-state solutions of the above equations.

In order to prevent numerical instability, the stability criteria for one-dimensional compressible flows and heat transfer flows is used to control the time step,

\[
\Delta t' \leq \min \left\{ \frac{\text{CFL} \cdot \Delta z}{c + |V_i| \cdot \frac{\Delta z^2}{\Omega}}, \quad i = 1, 2, 3, \ldots, I \right\},
\]

where CFL and Von are the Courant-Friedrichs-Levy number and von Neumann number, respectively, \( c \) is the velocity of sound, i.e., \( \sqrt{\partial p/\partial z} = \sqrt{1/s} \), and \( \Omega \) is a viscosity like number. For a Newtonian fluid with Navier’s wall slip under steady state:

\[
V = \left( \frac{R^2}{8m} + \frac{\beta_0 R}{2} \right) \left( -\frac{dp}{dz} \right).
\]

Plugging Eq. (A10) into Eq. (3) and, in view that \( p \ll \rho_a/\rho_s \), letting \( p + \rho_a/\rho_s = \rho_a/\rho_s \), leads to

\[
\frac{\partial p}{\partial t} \approx \left( \frac{R^2}{8m} + \frac{\beta_0 R}{2} \right) \frac{\rho_a \partial^2 p}{\partial z^2} \approx \left( \frac{R^2}{8m} + \frac{\beta_0 R}{2} \right) \frac{\rho_a \partial^2 \rho_a}{\partial z^2}.
\]

Therefore, one may use

\[
\Omega \approx \left( \frac{R^2}{8m} + \frac{\beta_0 R}{2} \right) \frac{\rho_a}{\rho_s} \approx \frac{\rho_a}{\rho_s} \frac{V_i}{(\partial p/\partial z)_i^l}.
\]

Besides, to suppress numerical oscillations, a small amount of artificial viscosity in form of \( e \partial^2 p / \partial z^2 \) was used for Eq. (3) in both prediction and correction steps. Here \( e \) is a small positive constant and values of \( e \) that were in the range of 0.001—0.1 were employed in the simulations.
References


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