“Development of Extrusion Instabilities and Surface Irregularities of Extrudates of Polymer Melts and Filled Polymers”

Dilhan M. Kalyon, Elvan Birinci and Halil Gevgilili

Highly Filled Materials Institute
Stevens Institute of Technology
Castle Point Station, Hoboken, NJ 07030

* dkalyon@stevens-tech.edu, 201 216 8225
Synopsis

This study is a continuation of an earlier study [Kalyon and Gevgilili (2003)] and aims at probing the effects of the flow boundary condition at the wall on the development of flow instabilities and extrudate surface irregularities upon the extrusion of polymer melts and polymeric suspensions. The wall slip and flow instability behavior of two polymers, i.e., a poly (dimethyl siloxane), PDMS and an oxetane based alternating block thermo plastic elastomer BAMO/AMMO-TPE were studied along with the wall slip and flow instability behavior of PDMS filled with 10, 20, 40% by volume of hollow glass spheres and 60% by volume of KCl Filled BAMO/AMMO- TPE. Steady torsional flow was used in conjunction with the straight-line marker technique to analyze wall slip in steady torsional flow. Thermal imaging and high-speed cinematography were used with capillary flow to characterize the surface features of extrudates emerging from capillary dies. The effects of the convergence angle from the reservoir into the capillary die were also investigated (15, 45 and 75°) for pure PDMS and 10% glass filled PDMS. The angle of convergence had no effect on the development of surface irregularities. The incorporation of the glass filler into the PDMS binder gave rise to a reduction of the shear rate range over which gross surface irregularities are observed. Furthermore, the extrudates of PDMS with 40% glass filler were largely free from surface irregularities. On the other hand, BAMO/AMMO elastomer melt, which exhibits stable stick over relatively high strains and shear rates in steady torsional flow does not exhibit surface irregularities in the same shear rate range in capillary flow [Kalyon and Gevgilili (2003)]. However, the incorporation of rigid particles into the BAMO/AMMO elastomer gives
rise to flow instabilities and surface irregularities during extrusion. These results suggest that the mechanisms for the development of surface irregularities of the extrudates of polymeric suspensions differ from those of the binder phase. Depending on the binder of the suspension and with the appropriate type and concentration of the rigid filler phase, the incorporation of the rigid fillers can prevent or induce the formation of surface irregularities in extrudates of polymeric suspensions.

**Key words:** flow instabilities, wall slip, extrudate, and surface irregularities
INTRODUCTION

The development of surface distortions in the extrudates of polymer melts emerging from extrusion dies (described as melt fracture, shark skin, gross surface irregularities) is an important industrial problem. The initiation on extrudate distortions presents an upper limit to the manufacturing rate in extrusion based processing of polymers and polymeric suspensions. Consistent with its industrial importance it has received significant academic and industrial attention [Benbow and Lamb (1963); Petrie and Denn (1976); Larson (1992); Denn (2001); Kalyon and Gevgilili (2003)].

Various polymer melts, especially linear polymers, exhibit wall slip [Awati et al. (2000); Hatzikiriakos and Dealy (1991); Gevgilili and Kalyon (2001); Rielly and Price (1961); Kalika and Denn (1987); Ramamurthy (1986); Chen et al. (1993); Migler et al. (1993); Münstedt et al. (2000)] and wall slip is considered to be one of the major factors which can affect the formation of extrudate distortions. Kissi and Piau (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 shear stress range. Benbow and Lamb (1963) used a similar experimental technique and determined a critical shear stress of 0.07 MPa for the onset of wall slip for PDMS.

The data presented in the literature indicate that there may be multiple mechanisms for the wall slip of polymers to allow the differentiation of two regimes in the wall slip velocity versus the shear stress (or shear rate) behavior. For example, with PDMS Migler
et al (1993) have determined a sharp transition between a regime of weak slip and one of strong slip as the shear rate is increased during simple shear in which the velocity distribution is directly measured within the 100 nm of the wall. 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 (Leger, Hervet and Massey, 1997). Here in this paper wall slip is taken to be synonymous with slip which can be detected with macroscopic means, i.e., through the dependence of the flow curves on the surface to volume ratio of the rheometer (Mooney method) [Mooney (1931); Yilmazer and Kalyon (1989); Kalyon et al. (1999)] or through the detection of mm-scale discontinuities at the free surface of the melt and the edges of the fixtures used in steady torsional flow upon following a marker line [Kalyon et al. (1993); Aral and Kalyon (1994)].

Recently, Kalyon and Gevgilili (2003) have focused on the wall slip and flow instability behavior of three polymers, two of which exhibit easily detectable wall slip in simple shear flow and one that does not. The polymers included a high density polyethylene (Exxon-Mobil HAD 601, a PDMS (GE Silicones-SE-30) and 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-metylloxytane, AMMO) from ATK Thiokol of Promontory, Utah. The same PDMS and the BAMO/AMMO are used in this study also. However, in this study these polymers were filled with rigid fillers to allow the investigation of the effect of the incorporation of rigid filler particles to the development of extrudate surface irregularities. For PDMS the filler
consisted of spherical hollow glass particles with a specific gravity of 1.09 and an arithmetic mean particle diameter of 12 μm (Potters Industry). For BAMO/AMMO a KCl filler with approximately cubical particle shape was used.

**Experimental Apparatus and Procedures**

An Advanced Rheometric Expansion System (ARES) rheometer, from Rheometric Scientific, Inc., Piscataway, NJ, was utilized in conjunction with steady torsional flow 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 2,000 frames per second, was part of the set-up shown in Figure 1.

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 to enable the characterization of the wall slip velocity and the true deformation rate [Kalyon et al. (1993), Aral and Kalyon (1994); Gevgilili and Kalyon (2001)]. The discontinuities that develop between the surface of the plates of the rheometer and the bulk of the melt suggest the initiation of wall slip (Figure 2). The steady wall slip velocity values determined using the straight-line marker technique agree well with the steady wall slip velocity values determined upon the analysis of the dependence of the shear stress on the surface to volume ratio of the rheometer, i.e., the conventional Mooney technique [Kalyon et al. (1993)]. The steady torsional flow behavior of the three resins was characterized at various shear rates and
temperatures to determine the conditions under which the catastrophic failure of the no-slip condition became apparent.

An Instron capillary rheometer was employed to collect additional shear viscosity data and to study the development of extrudate distortions upon exit from the die. The diameters, length over the diameter ratios and the converging angle of the taper connecting the reservoir of the barrel of the rheometer to the straight land section of the capillary die (Figure 3) were changed systematically. The shapes of the extruded samples, immediately upon extrusion from the die, were captured using a high-speed camera (Figure 4) to allow the immediate characterization of the surfaces of the extrudates (Figure 5). The temperature distributions of the extrudates emerging from the die were also monitored using a ThermaCam thermal imaging camera. A typical image showing the temperature distribution on an extrudate upon emerging from the die is shown in Figure 4 to reflect the temperature of the material at the die wall. The temperature of the material immediately upon exit provided data on the effect of viscous energy dissipation and allowed the determination of the true temperature of the melt (Figure 6).

RESULTS AND DISCUSSION

Unfilled polymers:

The steady torsional flow behavior of poly(dimethylsiloxane) (PDMS) was characterized at 10, 30 and 50°C. Fig. 7 shows the results of shear stress growth experiments performed at various shear rates at 30°C using the cone-and-plate fixtures. At relatively small shear rates, i.e., less than 1 s⁻¹, the shear stress grows monotonically as a function of time until
steady state values are reached. In this relatively small shear rate range the shear stress
curves are approximately parallel to each other and do not exhibit overshoots. The typical
results of the straight-line marker technique corresponding to this set of experiments are
shown in Fig. 7. At relatively small shear rates the straight-line marker remains
continuous and connects the moving and stationary walls. On the other hand, at the
higher shear rates, for example, at 40 s⁻¹ the continuity of the straight-line marker is lost
during steady torsional flow. The formation of the mm-scale discontinuity at the wall is
indicative of the loss of the wall stick condition at the wall “macroscopic wall slip”. On
the other hand, at greater shear rates the occurrence of wall slip and the eventual ejection
of the specimen from the gap force the shear stress to decrease upon reaching maxima.
For PDMS the shear stress maximum at which wall slip is initiated occurs around 0.07
MPa at 30°C at a shear rate of 40 s⁻¹. This critical shear stress value was determined to be
the same at 10 and 50 °C also [Kalyon and Gevgilili (2003)].

The capillary flow curve of PDMS at 30°C is shown in Figure 8. At apparent shear rates
of 19 s⁻¹ and lower, the extrudates of PDMS did not exhibit any type of surface or bulk
distortions. As the shear rate is increased to 25 s⁻¹, distortions of the extrudate surface in
the form of fine sharkskin were observed (Fig. 8). At 38 s⁻¹, thread-like sharkskin forms
at a wall shear stress of 0.067 MPa. At 50 s⁻¹ and the corresponding wall shear stress of
0.08 MPa, the sharkskin loses its uniformly repeating thread-like structure and becomes
more non-uniform. Thus, one observes a dramatic change in the surface topology of the
extrudate in approximately the same mean wall shear stress range at which wall slip
becomes apparent in steady torsional flow. Is this behavior dependent on the surface to
volume ratio of the capillary die? Data collected at three different capillary die diameters are shown in Figure 9. The flow curves and the surface topologies of the extrudates are found not to be affected by the surface to volume ratio of the die. Thus, regardless of the diameter of the die, the wall shear stress at which the transition to the unstable region (at which the extrudate surface is no longer smooth) coincides with the critical shear stress range at which wall slip is onset under steady torsional flow.

Is the flow instability behavior of the polymer melt affected by the convergence angle of the capillary die entrance? The effect of the convergence angle for PDMS is shown in Figure 10. This typical behavior indicates that the flow curves and the development of the surface irregularities are not affected by the convergence angle.

The steady torsional flow behavior of the TPE (over a very broad range of shear rates up to 200 s\(^{-1}\)) was very different than PDMS. Even at the highest shear rates investigated the samples of TPE stayed intact within the gap, without any sign of wall slip, edge distortion and outward ejection for strains as high as 50. For TPE the straight-line marker was observed to retain its continuity even after one whole revolution of the moving surface [Kalyon and Gevgilili (2003)]. The thermoplastic elastomer thus appears to exhibit little affinity to slip at the wall and behaves very differently than PDMS. This significant difference can possibly be attributed to the strong electrostatic interaction between the azido groups of the thermoplastic elastomer and the metal surface as revealed using force-field calculations (U. Olgun, private communication, 2002). During capillary flow
the extrudates of the TPE were relatively smooth and exhibited only non-periodic minor surface blemishes regardless of the shear rate.

The general trend in the development of flow instabilities during extrusion of polymer melts involves the absence of extrudate surface distortions at relatively low shear rate/stress values (at which presumably the wall slip velocity is negligible) on one hand and at relatively very high shear rate/stress values at which correspondingly high (and presumably stable) wall slip velocities exist. This suggests that extrudate distortions are less likely to occur under conditions in which a stable flow boundary condition exists at the wall; whether it is either a stable wall stick or stable wall slip condition.

Filled Polymers:

PDMS and TPE were compounded with glass spheres and KCl, respectively. From earlier studies it is known that in the presence of the particles an apparent slip layer (the Vand layer) forms at the wall during both steady torsional and capillary flows [Yilmazer and Kalyon (1989); Kalyon et al. (1993)]. The formation of the apparent slip layer is the dominant mechanism for wall slip of suspensions with rigid particles [Aral and Kalyon (1994)].

The incorporation of the KCl particles into BAMO/AMMO TPE gives rise to the development of flow instabilities at shear stress values, which surpass 0.3 Mpa (Figure 11). This is an interesting finding and suggests that the presence of particles can render the flow unstable for a polymeric binder, which only exhibits stable flow over the same
apparent shear rate range. Since the BAMA/AMMO TPE is energetic it was not possible to make additional supporting measurements, so our attention was turned to PDMS compounded with differing concentrations of spherical glass particles. How will the behavior of PDMS be affected by the presence of rigid particles in the 10 to 40% by volume range?

The typical flow curves of PDMS incorporated with 10% by volume glass collected with three capillaries with the same length over diameter ratio of 40 but with differing diameters are shown in Figure 12. The images pertain to extrudates extruded at approximately the same apparent shear rate of about 30 to 50 s\(^{-1}\). Thus, at the same apparent shear rate all of the extrudates extruded with capillary dies with differing diameters exhibit a similar type of surface irregularities.

Figure 13 shows all of the points on the flow curves at which extrudate surface irregularities were observed (as indicated by the presence of arrows here.) Thus, the points marked with arrows indicate that surface irregularities occur at those points of the flow curves and the absence of an arrow for a point indicates that there were no extrudate surface irregularities evident at that shear rate.

The data indicate that extrudates free of surface or bulk distortions could be obtained either at the low apparent shear rates (less than 10 s\(^{-1}\)) or at the relatively high shear rates (over 1000 s\(^{-1}\)). In the wall shear stress range of 0.07 to 0.1 MPa the extrudates exhibited surface irregularities. In the relatively high shear rate regime, smaller shear stress values
are generated for the capillaries with smaller diameters at constant length over the
diameter ratio, suggesting that the suspension is slipping strongly. The flattening of the
flow curves at the highest apparent shear rates at which wall slip is clearly observed is
also interesting. Such flattening is generally associated with plug flow of the suspension
[Kalyon et al. (1993); Yaras et al. (1994)].

The wall slip behavior of the suspensions of PDMS with 10, 20 and 40% by volume glass
particles were investigated using steady torsional flow. Generally, there was widespread
wall slip of the suspension samples. Earlier experimental evidence suggests that the flow
instabilities and extrudate distortions occur under conditions in which the stability of the
flow boundary condition at the wall is perturbed [Atwood and Schowalter (1989)].
Distortion-free extrudates are obtained when a stable wall slip condition, for example
through the generation of an apparent slip layer at the wall by coating of the wall surfaces
with fluoroelastomers, is introduced [Kissi and Piau (1997) and Wang and Drda (1997)].
One can surmise that an apparent wall slip mechanism is also introduced upon the
incorporation of the rigid particles into PDMS, to be superimposed on the wall slip of the
PDMS itself. The incorporation of the particles broadens the shear rate range over which
flow stabilities occur but at the same time generates smooth extrudates at the highest
apparent shear rates.

The effect of the convergence angle of the entry region of the flow geometry to the
development of the surface irregularities of the extrudates of suspensions of PDMS with
10% rigid glass filler particles is shown in Figure 14. Similar to the behavior of pure
PDMS the angle of convergence values between 15 to 75° do not affect the development of the extrudate distortions, suggesting that the source of the observed flow instabilities for both the pure PDMS and filled PDMS is not likely to be related to the dynamics of the entry flow.

The flow curves obtained for the suspension of PDMS with 20% by volume glass are shown in Figure 15. The arrows are used again to indicate that distorted extrudates are extruded under that particular condition and the absence of an arrow over a given point suggests that the extrudate was smooth and free of distortions. In comparison to 10% suspension the range of shear rates over which flow instabilities are observed is considerably reduced at 20% by volume glass (between 100 to 1000 s⁻¹) with no extrudate distortions observed below an apparent shear rate of 100 s⁻¹, regardless of the diameter of the capillary die.

The flow curves of the 40% by volume glass spheres incorporated PDMS are shown in Figure 16. Except for one flow condition involving an apparent shear rate of 72 s⁻¹ collected at the highest capillary diameter of 0.1378” (3.5 mm), all of the extrudates were smooth and were free of distortions. The elimination of the surface irregularities over the same apparent shear rate upon increasing the concentration of the particles from 20 to 40 is counter to conventional thinking. The incorporation of the particles increases the apparent shear viscosity of the material thus increasing the shear stress at the wall and hence is expected to give rise to conditions at which extrudate distortions would occur more readily. However, the opposite occurs here with the extent of extrudate distortions
decreasing or being eliminated completely with increasing concentration of rigid particles.

The occurrence of wall slip is clearly surmised by comparing the data collected at different diameters (at constant length over the diameter ratio). As the diameter increases (hence a decrease of the surface to volume ratio) the wall shear stress increases suggesting that there is significant wall slip, with the slip velocity increasing with increasing wall shear stress. This is consistent with our findings from steady torsional flow that suggest that wall slip prevails over a broader range of shear rates as the particle concentration increases. Again the flattening of the flow curves is a precursor of plug flow, which renders the application of Mooney's approach for the determination of the wall slip velocities irrelevant [Mooney (1939); Yaras et al. (1994); Kalyon (2003)].

The comparisons of the behavior of the effects of incorporation of the rigid particles into the polymer matrix are more clearly seen in Figures 17-19, which show the flow curves of the 10, 20 and 40 % by volume particle incorporated suspensions at each capillary diameter. The arrows again indicate that extrudate distortions occur at that point. The data suggest that although the wall shear stress increases with increasing particle concentration the range of apparent shear rates, over which flow instabilities and extrudate distortions prevail, decrease with increasing particle concentration.

Conclusions: This study suggests that the flow instabilities observed with a polymeric binder can be eliminated upon the incorporation of particles (with the right concentration
and characteristics) into the binder phase. This is an important finding and can be exploited to our industrial advantage. Conversely, if the extrudates of the binder phase are smooth and distortion free, the incorporation of rigid particles can introduce extrudate distortions. This is another important finding and should be kept in mind especially when polymeric compounds are formulated to include various solid ingredients. These results attest to the intimate relationship between the wall slip of polymers and polymeric suspensions and the development of surface irregularities in their extrudates. Understanding of the factors that control the stability of the flow boundary condition at the wall can provide a better understanding to the underlying mechanisms of the development of extrudate distortions.

References


Environmental controller

Force Rebalance Transducer

Actuator Motor

Computer interface for rheometer and high speed Camera

High Speed Camera 500-2000 fps

Figure 1
A discontinuity in the straight-line marker indicates loss of no-slip boundary condition at the polymer melt-metal interface.

Figure 2
The angle of convergence was varied between 15, 45 and 75 degrees.
Thermal Imaging Camera

High Speed Camera

Figure 4
PDMS

45deg d=0.096 L/D=40 Crosshead Speed: 2in/min

Figure 5
Discharge of the die

Cross-Head speed = 0.5"/min, \( \gamma = 467.3 \text{ s}^{-1} \), \( T_{\text{max}} = 182.5°C \)

\[ T_{\text{barrel}} = 180°C \]

Diameter = 0.03" L/D = 66
Figure 7
Figure 8

PDMS in capillary flow, development of surface irregularities
Figure 9

PDMS: development of extrudate surface irregularities
As a function of capillary surface/volume ratio
Pure PDMS: Apparent Shear Stress vs. Apparent Shear Rate Behavior:
Comparison of Different Converging Entry Angles

Figure 10
KCl filled BAMO/AMMO TPE

Figure 11
Figure 12

PDMS + Hallow Sphere Glass Particles (10% by vol.) Mixture
Corrected Shear Stress vs. Apparent Shear Rate Behavior
Comparison of Different Diameters

PDMS + Glass Sphere (10% by vol.) Mixture
Corrected Shear Stress vs. Apparent Shear Rate Behavior
Comparison of Different Diameters

Figure 13
Apparent Shear Stress vs. Apparent Shear Rate Behavior
Comparison of Different Convergence Angles

Figure 14
Corrected Shear Stress vs. Apparent Shear Rate Behavior
Comparison of Different Diameters

PDMS + Glass Sphere (20% by vol.) Mixture
Corrected Shear Stress vs. Apparent Shear Rate Behavior
Comparison of Different Diameters

Figure 15
PDMS + Glass Sphere (40% by vol.) Mixture
Corrected Shear Stress vs. Apparent Shear Rate Behavior
Comparison of Different Diameters

Figure 16
Corrected Shear Stress vs. Apparent Shear Rate Behavior

Comparison of Different Loaded Material

PDMS + Glass Sphere Mixture

At 40% there is no irregularity

10% D=0.0328in
At 26, 53, 106, 265, 531 s⁻¹

At 20% D=0.0328in
At 265, 531, 1062 s⁻¹

Figure 17
At 40% there is no irregularity

Apparent Shear Rate, s⁻¹

PDMS + Glass Sphere Mixture

Apparent Shear Stress vs. Apparent Shear Rate Behavior
Comparison of Different Loaded Material

Figure 18
**Apparent Shear Stress vs. Apparent Shear Rate Behavior**

**PDMS + Glass Sphere Mixture**

**Apparent Shear Stress vs. Apparent Shear Rate Behavior**

Comparison of Different Loaded Material

Figure 19