MELT FRACTURE BEHAVIOUR OF MOLTEN POLYPROPYLENES

by

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EXPERIMENTS were carried out in both sliding plate and capillary rheometers with two polypropylene resins to determine the conditions for the onset of slip, surface and gross melt fracture. It was found that there was no distinction between surface and gross melt fracture, which is commonly observed in the case of polyethylenes. Furthermore, the flow curves determined by using capillaries having various diameters are diameter independent, implying the absence of slip. However, performing experiments with slit dies having rough surfaces suggested the presence of wall slip. Further analysis has shown that the effect of viscous heating masks the detection of slip from the diameter dependency of the flow curves. The effect of presence of a thin layer of fluoropolymer (Teflon® PA and Viton®, DuPont) on the critical shear stress for the onset of wall slip and melt fracture as well as on the relationship between the wall slip and the shear stress were also examined. It was found that the presence of such layers increases the slip velocity while decreases the critical shear stress for the onset of slip. Surprisingly, this reduction in the wall shear stress had no effect on the critical shear rate for the onset of melt fracture.
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1. INTRODUCTION

The increasing role of synthetic polymers as materials of construction has prompted the study of their processing properties. It is known that the rate of production in such processes as extrusion, film blowing and moulding is limited by the onset of flow instabilities, which results in the deterioration of the surface appearance and lead to commercially unacceptable products. Most of the previous studies on melt fracture (surface and gross distortions) of polymers have essentially examined the behaviour of various types of polyethylenes (high density polyethylene, low density polyethylene and linear low density polyethylene), but very little is known about this phenomenon in the processing of polypropylene resins.

In the extrusion of polymer melts, below certain shear rates the emerging extrudates have smooth surface. As the rate increases, small amplitude periodic distortions appear on the surface (sharkskin melt fracture). As the rate increases further, the extrudate becomes severely distorted (gross melt fracture). In capillary flow of certain polymers (e.g. high density polyethylene [Hatzikiriakos and Dealy (1992b)], linear low density polyethylene [Ramamurthy (1986)] and fluorinated polyethylene/polypropylene [Rosenbaum et al. (1994)]) under constant piston speed, the pressure drop has been found to be a double-valued function of apparent shear rate over a limited range of apparent shear rates. As the extrusion rate is increased, a point is reached at which the pressure jumps between lower and higher critical values, while the extrudate appearance changes from smooth to alternating distorted and smooth portions due to these pressure oscillations. Thus, a hysteretic loop is obtained over a certain range of apparent shear rates. This finding is usually interpreted in terms of "slip", i.e., it is implied that the velocity of the fluid at the boundary is not zero as normally assumed.

For Newtonian fluids the assumption of zero velocity at the fluid-wall interface leads to a very good agreement with experimental observations. However, in the case of many
polymer melts this assumption ceases to be valid. For example, in the flow of linear polymers through cylindrical dies, the flow curve (shear stress versus apparent shear rate) has been found to depend on the diameter of the die once the wall shear stress rises above a critical value. This is consistent with the assumption of slip and, if it is assumed that slip occurs at the interface, the data can be superposed. Mooney (1931) derived explicit relations for the slip velocity that can be used to calculate the slip velocity as a function of wall shear stress.

Melt fracture has been the subject of many investigations over the past decades. Numerous experimental, theoretical and computational studies have been reported, aimed at determining the origin and nature of flow instabilities in polymer melts and solutions. Some workers attributed the onset of melt fracture to pressure fluctuations resulting from the flow irregularities in the entrance region of the capillary due to the contraction flow [Weill (1980), Bergem (1976)], while others related it to slip at the wall [Kraynik and Schowalter (1981), Kalika and Denn (1987)]. Many terms have been used in the literature to describe this phenomenon: "melt fracture", "sharkskin", "waviness", "ripple", "bamboo effect", "sausage link", etc. For polyethylene, the distinction is usually made between surface melt fracture (or "sharkskin"), when the distortions are relatively small and affect only a thin layer on the surface, and gross melt fracture, with the extrudate appearance ranging from helical screw thread to severe irregular distortions. If the shear rate is increased further, some materials (e.g. linear polyethylene, tetrafluoroethylene-hexafluoropropylene copolymer) exhibit a second stable flow regime in which the extrudate is again smooth [Tordella (1969)]. Polymers such as branched polyethylene, polypropylene and polystyrene do not appear to have a second stable regime.

Polypropylene is a material of great industrial importance, as it has found many applications, e.g. in fibre production, injection moulding, and film extrusion industry. The processing implications of this polymer have not been investigated to the same extent as those of polyethylenes. In this work, the melt fracture behaviour of two molten
polypropylenes is studied. Wall slip, which is believed to be related to the melt fracture, was also examined. Finally, Teflon\textsuperscript{®} PA and Viton\textsuperscript{®} were used to study the effect of interfacial conditions on wall slip and melt fracture of these resins.
2. LITERATURE REVIEW

Pressure driven flow through tubes, slits and other types of channels is of central importance in experimental rheology and in polymer processing. This flow is used as the basis for the most popular type of melt rheometer, and it is a flow that occurs often in melt processing, for example in an extrusion die or in the runner feeding of an injection mould. In this chapter the basic equations for flow in tubes and slits are presented, and it is shown how these can be used to interpret rheometer data. In addition, the melt fracture and wall slip phenomena are described and some previous knowledge on these phenomena for polypropylenes are reviewed.

2.1 Chemical structure of polypropylene and its applications

Polypropylene (PP) has the following structure:

\[
\begin{array}{c}
\text{CH}_2 - \text{CH} \\
\text{CH}_3
\end{array}
\]

The monomer for PP is propylene. This material is predominately produced by low-pressure processes based on Ziegler-Natta catalysts. The vast majority (over 90 percent) of the polymer is in the isotactic form (Fig. 2-1). Isotactic polypropylene crystallizes in a helical form whereby there are three monomer units per turn of the helix.

Polypropylene has a wide range of applications, ranging from fiber and filaments to films and extrusion coatings. PP fibers are manufactured by an oriented extrusion process. Two important advantages of polypropylene are its inertness to water and microorganisms and it is a low cost polymer.
(around $0.66 per kg). Typical applications include carpet backing, upholstery fabrics, carpet yarn, and interior trim for automobiles.

### 2.2 Viscometric flows

Simple shear flow is generated by the rectilinear motion of one flat plate relative to another, where the two plates are parallel and the gap between them is constant with time. Steady simple shear is a simple shear flow that has been carried out at a constant shear rate for a sufficient length of time that the stresses in the material are functions only of the shear rate.

Steady simple shear is a uniform deformation, i.e., each fluid element undergoes exactly the same deformation, and the stresses are independent of position in space. There are also nonuniform flows for which the three material functions, viscosity and normal stress differences, govern the behaviour of the fluid. Such deformations are called "viscometric flows." While different fluid elements in the field of flow may be subject to different shear rates, the shear rate experienced by any particular fluid element is constant with time. Three types of viscometric flows that were used in this work, viz., steady tube flow, steady slit flow, and steady simple shear flow, are discussed below.

#### 2.2.1 Flow in a circular channel

Capillary flow is an example of a partially controllable flow. Far from the entrance where the flow is fully developed, the streamlines are parallel to the channel axis, but the velocity profile depends on the rheological nature of the fluid. Unless a specific constitutive equation is known to be valid for the fluid, as in the case of a Newtonian fluid or a power-law fluid, special computational techniques are required to calculate shear stress, shear rate and viscosity.

For the steady flow of an incompressible fluid in a tube of radius $R$, the absolute value of the shear stress at the wall $\sigma_w$ is:
where $\Delta P$ is the pressure drop over a length of tube, $L$.

For a Newtonian fluid, the velocity distribution is parabolic and the shear rate at the wall is given by:

$$\gamma_w = \frac{du}{dr}igg|_{r=R} = \frac{4Q}{\pi R^3}$$  \hspace{1cm} (2-2)

For non-Newtonian fluids, if a specific constitutive equation is assumed, one can derive equations analogous to those valid for Newtonian fluids. For example, if the power law given by

$$\sigma_w = K\gamma^n$$  \hspace{1cm} (2-3)

it can be shown that the wall shear rate is given by:

$$\dot{\gamma}_w = \frac{3n + 1}{4n} \left( \frac{4Q}{\pi R^3} \right)$$  \hspace{1cm} (2-4)

The quantity in brackets, which is equal to the wall shear rate in the case of a Newtonian fluid, no longer has this significance when the fluid is non-Newtonian. It is, however, referred to as the "apparent shear rate", $\dot{\gamma}_A$.

Using Eq. 2-2, 2-3, and 2-4, it can be shown that

$$\sigma_w = K \left( \frac{3n + 1}{4n} \right)^n \left( \frac{4Q}{\pi R^3} \right)^n = K \left( \frac{3n + 1}{4n} \right)^n \dot{\gamma}_A^n$$  \hspace{1cm} (2-5)

Therefore, a plot of $\log(\sigma_w)$ versus $\log(\dot{\gamma}_A)$ will be a straight line for a power-law fluid, and the constants $K$ and $n$ can be determined from the slope and the intercept. However, even if there is no constitutive equation relating the shear stress to the shear rate, a special technique can be used to determine the true wall shear rate and the viscosity for any non-Newtonian fluid. This technique requires pressure drop data for a number of flow rates. It
can be shown that these data should fall on a single curve when a plot of \( \log(\sigma_w) \) versus \( \log(\dot{\gamma}_w) \) is made. The shear rate at the wall is given by

\[
\dot{\gamma}_w = \frac{3 + b}{4} \left( \frac{4Q}{\pi R^3} \right) = \frac{3 + b}{4} \dot{\gamma}_A
\]

(2-6)

where \( b \) is the Rabinowitsch correction given by

\[
b = \frac{d \log \dot{\gamma}_A}{d \log \sigma_w}
\]

(2-7)

This correction term is a measure of the deviation of a polymeric fluid from Newtonian behaviour. It equals unity for a Newtonian fluid and \( 1/n \) for a power-law fluid.

In a capillary rheometer there is a large pressure drop associated with the flow in the entrance region, and this must be taken into account if the reservoir pressure is the quantity measured to determine the wall shear stress. Moreover, it has been proposed that the excess pressure drop at the entrance to a capillary is itself a useful quantity that can be used to characterize polymers. There also appears to be a small residual pressure at the exit of the capillary. Wall pressures measured at various axial locations in a reservoir and capillary have been reported by Han (1976) for molten polymers. A typical result is shown in Fig. 2-2. The total pressure drop for flow from a reservoir, through a capillary and out to the ambient pressure can be thought to consist of three components:

\[
-\Delta P = \Delta P_{\text{entrance}} + \Delta P_{\text{cap}} + \Delta P_{\text{exit}} = \Delta P_{\text{end}} + \Delta P_{\text{cap}}
\]

(2-8)
The end correction, $\Delta P_{\text{end}}$, can be determined by using a technique outlined by Bagley (1931). He measured the driving pressure, $P_d$, for various values of the flow rate using a variety of capillaries having different lengths. For each value of $\dot{\gamma}_A$ the driving pressure is plotted versus $L/D$ and a straight line is drawn through the points. Extrapolating the lines corresponding to various values of $\dot{\gamma}_A$ to $L/D=0$, an end correction is obtained, which is often called "Bagley correction" (Fig. 2-3). Thus, the true wall shear stress which is obtained over most of the length of the capillary (except in the entrance) can be calculated as follows:

$$\sigma_w = \frac{(P_d - P_{\text{end}})}{(4L/D)} \quad (2-9)$$

In general, one should expect some curvature of the Bagley plot, which may indicate dependence of viscosity on pressure, slip at the wall [Hatzikiriakos and Dealy (1992a)] or viscous heating.

2.2.2 Flow in a rectangular channel

When a fluid flows through a rectangular channel in which the width, $W$, is much larger than the thickness, $H$, the edges make a negligible contribution to the pressure drop and this geometry can effectively be used for rheological measurements. The basic equations and entrance correction procedures are similar to those for capillary flow, but the difference in geometry has certain experimental advantages: flush-mounted wall pressure transducers can obviate the need for end corrections; two dimensional flow field facilitates the observation of flow.
For the steady flow of an incompressible fluid in such a channel, the absolute value of the shear stress at the wall, $\sigma_w$, is given by:

$$\sigma_w = -\Delta P \cdot \frac{H}{2L} \quad (2-10)$$

where $\Delta P$ is the pressure drop over a length of channel, $L$.

The apparent shear rate in a slit, which is the true wall shear rate for a Newtonian fluid is given by:

$$\dot{\gamma}_A = \frac{6Q}{H^2W} \quad (2-11)$$

For non-Newtonian fluids the wall shear rate is given by:

$$\dot{\gamma}_w = \frac{2 + b}{3} \left( \frac{6Q}{H^2W} \right) \quad (2-12)$$

where $b$ is the Rabinowitsch correction given by

$$b = \frac{d \log \dot{\gamma}_A}{d \log \sigma_w} \quad (2-13)$$

As in the case of circular channels, a plot of $\log(\sigma_w)$ versus $\log(\dot{\gamma}_A)$ reveals the behaviour of the fluid. If all the data fall on a straight line with a slope of one, then Newtonian behaviour is obtained. If they fall on a straight line but the slope is not equal to one, then power-law behaviour is exhibited, with $n = 1/b$. Curvature indicates general non-Newtonian behaviour.

For a power-law fluid the wall shear stress is as follows:

$$\sigma_w = K \left[ \frac{2n + 1}{3n} \right]^n \dot{\gamma}_A^n \quad (2-14)$$

The procedure for determination of the end effects is analogous to the one used for circular channels.
2.2.3 Flow in a sliding plate rheometer

The laboratory procedure that most closely approximates simple shear is to place a thin layer of fluid between two flat plates, clamp one of the plates in place, and translate the second plate at a constant velocity, as shown in Fig. 2-4. Under no-slip conditions the actual shear rate, $\dot{\gamma}$, is equal to the nominal shear rate, $\dot{\gamma}_n$.

The wall shear stress can be determined by measuring the force required to drive the motion of the moving plate and dividing it by the wetted area of the plates. When slip is present, the true shear rate is less than the nominal shear rate, as illustrated in Fig. 2-5.

The advantages of the sliding plate geometry over the other two geometries discussed above are that there are no effects of pressure on measurements, and that the edge effects can be eliminated by measuring the shear stress locally (using flush-mounted shear stress transducer). If a sliding plate rheometer is used to study viscous Newtonian liquid, the fluid itself serves to maintain the plate spacing. However, if the first normal stress
difference $N_1 = \sigma_{11} - \sigma_{22}$ is positive, which seems to be the case for molten polymers, then the shearing deformation will result in a force tending to separate the plates, and some way must be found to maintain the gap without introducing a significant frictional force.

For this work a sliding plate rheometer with a flush-mounted shear stress transducer was used [Giacomin et al. (1989)]. The basic features of the transducer are shown in Fig. 2-6. An end plate is acted on by the shear stress generated by the fluid and transmits the resulting moment to the cantilever beam. To avoid the melt penetration into the gap around the end plate, the deflection of the latter must be limited to very small levels. That is why a capacitance system was used, where a capacitor is formed by the probe acting as one of the plates, and the beam as the second plate.

There are many advantages associated with the direct measurement of the shear stress:

- Uncontrolled flow at the edges of the sample does not affect the determination of the shear stress, allowing tests with large and rapid deformation to be carried out;
- Degradation occurring as a result of contact between the exposed edges of the sample and the environment does not affect the measurement;
- The exact size and shape of the sample need not to be known, and this greatly simplifies sample loading;
- Tests can be carried out with only a few grams of sample;
- Bearing friction has no effect on the measured shear stress, as long as it does not introduce mechanical noise.
2.3 Wall slip and slip velocity measurements

For wall shear stresses greater than a critical value, $\sigma_w$, it has been observed that the melt loses its adhesion at the wall (or cohesion near the wall) and that the no-slip boundary condition is no longer valid.

The question of slip was first addressed by Mooney and Black (1952), who used capillaries of different radii to determine the flow curve of raw rubbers. They found that the flow curves depended on the radius of the capillary, once the stress exceeded a critical value. Mooney (1931) derived an explicit relation for determining the slip velocity as a function of wall shear stress by assuming that the wall shear stress, slip velocity and pressure gradient are all constant along the entire length of the capillary. This expression for the case of circular channels is as follows:

$$ \dot{\gamma}_A = \dot{\gamma}_{A,s} + \frac{8 u_s}{D} $$

(2-15)

where $\dot{\gamma}_A$ is the apparent shear rate, $\dot{\gamma}_{A,s}$ is the apparent shear rate corrected for slip, $u_s$ is the slip velocity, and $D$ is the diameter of the capillary. For a constant wall shear stress, and thus a constant $\dot{\gamma}_{A,s}$, a plot of $\dot{\gamma}_A$ versus $1/D$ should result in a straight line with a slope equal to $8u_s$, if the slip velocity is solely a function of the wall shear stress. To apply this technique one requires $\sigma_w$ versus $\dot{\gamma}_A$ data from at least three capillaries of various diameters.

If it is known that a material follows power-law behaviour, then the slip velocity can be calculated from a single apparent flow curve. For a power-law fluid $\dot{\gamma}_A$ can be replaced by $\dot{\gamma}_{A,s}$ in Eq. 2-5, and by solving for the slip velocity the following equation can be obtained:

$$ 8 \frac{u_s}{D} = \dot{\gamma}_A - \frac{4n}{3n + 1} \left[ \frac{\sigma_w}{K} \right]^\frac{1}{n} $$

(2-16)
Thus, if the power-law constants have been determined in experiments in which slip did not occur (e.g. at low shear rates), they can be used to calculate the slip velocity from a measured value of $\sigma_w$ for any given value of $\dot{\gamma}_A$.

Making the same assumptions as for the capillaries and neglecting the edge effects, Eq. 2-15 can be written for a slit as follows:

$$\dot{\gamma}_A = \dot{\gamma}_{A,s} + 6 \frac{u_s}{H} \tag{2-17}$$

Thus, if the slip velocity is solely a function of wall shear stress, a plot of $\dot{\gamma}_A$ versus $1/H$ for constant $\sigma_w$ will give a straight line with a slope equal to $6u_s$.

For a sliding plate rheometer under slip conditions it can be easily shown that

$$\dot{\gamma}_n = \dot{\gamma} + 2 \frac{u_s}{h} \tag{2-18}$$

with the assumption of equal slip velocities on both plates. Figure 2-7 illustrates the use of the Mooney technique for the case of sliding plate rheometer. At low shear rates the flow curves (wall shear stress versus nominal shear rate) for different gap spacings, $h_1$ to $h_3$, superpose, which indicates that there is no slip. However, for higher shear rates the flow curves start to diverge above a certain value of the wall shear stress. From Equation 2-18 it follows that the slip has a greater effect on the flow curve obtained with the smallest gap spacing. The slip velocity as a function of the shear stress can be calculated by taking two points for different $h$ at a constant shear stress and solving Equation 2-18 for $u_s$. 

![Fig. 2-7. Flow curves under slip conditions (schematic)]
2.4 Melt fracture

A principal problem in the extrusion of polyolefins is the phenomenon of extrudate distortion commonly known as melt fracture. This usually appears when the wall shear stress exceeds a critical value [Ramamurthy (1986)]. The flow instabilities are reflected in the apparent flow curve (a plot of $\sigma_w$ versus $\dot{\gamma}_A$). A typical apparent flow curve for a linear polymer such as a high density polyethylene (HDPE) or a linear low density polyethylene (LLDPE) is shown in figure 2-8, where six distinct flow regions can be identified. At extremely low shear rates (below 1 s$^{-1}$) the wall shear stress is proportional to the shear rate, and the fluid behaves as a Newtonian fluid. In this region the viscosity of the fluid is constant, and the apparent shear rate, $\dot{\gamma}_A$, is equal to the true wall shear rate, $\dot{\gamma}_w$. The second region is the transition from Newtonian behaviour to power-law behaviour. In the power-law region ($#3$) the viscosity decreases with shear rate, and the $\sigma_w - \dot{\gamma}_w$ relationship is given by Eq. 2-3. All these flow regions are stable, the extrudates are smooth (sample A), and the no-slip boundary condition is consistent with experimental observations.

However, when the wall shear stress is greater than a critical value $\sigma_{c1}$, the extrudate

![Fig. 2-8. A typical apparent flow curve for a linear polyethylene and extrudate distortions.](image-url)
loses its glossiness, which is accompanied by a noticeable change in the slope of the apparent flow curve. This region (4) is known as the sharkskin flow region due to the fact that small amplitude periodic distortions appear on the surface of the extrudate (sample B). In addition, the apparent flow curve is diameter-dependent — an observation that is consistent with the assumption of a slip boundary condition.

At shear rates greater than a second critical value \( \sigma_c \), and within a certain range of apparent shear rates, the flow ceases to be stable (region 5). The pressure drop oscillates between two extreme values, and this fact causes a discontinuity in the apparent flow curve. The periodic variations of the pressure and apparent shear rate define a hysteresis loop that connects the two branches of the apparent flow curve. The extrudate appearance (sample C) follows the oscillations, with the smooth portion associated with the descending part of the flow curve and the fractured portion associated with the ascending one. If the rate is increased further, the gross fracture flow regime (6) starts where the extrudate is initially smooth with some kinks (sample D), then it becomes grossly distorted (sample E). In this flow regime the extrudate appearance depends on the type of polymer used and the design details of the die.

2.5 Melt fracture in polypropylene extrusion

While different flow regimes and types of distortion obtained in polyethylene extrusion have been studied extensively and are essentially well documented, very little information can be found for polypropylene (PP) on these phenomena. In this section some of the previous work related to the melt fracture of PP is reviewed.

Bartos (1964) studied the melt fracture behaviour of a series of polypropylenes to examine the critical conditions for the onset of extrudate distortions. He found that melt fracture occurs at a critical value of a "melt fracture" number, \( N_{MF} = 8.5 \text{ MPa} \), which is
defined as $N_{MF} = \eta_0 \dot{\gamma} / I$, where $\eta_0$ is the zero-shear viscosity, $\dot{\gamma}$ is the critical shear rate for the onset of melt fracture, and $I$ is the polydispersity. Kamide et al. (1966) found a critical value of 10.9 MPa while Barnett (1967) a critical value of 10.4 MPa for other series of polypropylenes. It would be desirable to have this information in terms of a critical shear stress, which unfortunately is lacking in these papers.

Middleman (1977) has noted that linear polypropylene did not show the flow discontinuity when exhibiting melt fracture, and the severity of the melt fracture of linear polymers increased as the die was lengthened. He argued that the criteria for determining the onset of melt fracture was the recoverable shear defined as $S_R = (\tau_{11} - \tau_{22}) / 2\tau_{12}$, where $\tau_{11}$ and $\tau_{22}$ are the normal stresses, and $\tau_{12}$ is the shear stress. The critical value of $S_R$ was found to be about 2.6.

Ui et al. (1964) have also studied the melt fracture behaviour of a number of different polymers at various temperatures, including polypropylene. The flow curves obtained were smooth without any discontinuity. Discontinuities are commonly observed in the flow curves of high density and linear low density polyethylenes [Ramamurthy (1986), Kalika and Denn (1987), Hatzikiriakos and Dealy (1992a)]. The type of melt fracture obtained was fairly regular with a sharp transition from a smooth to a gross fracture appearance. Thus, small amplitude periodic distortions which are obtained in the extrusion of linear low density polyethylenes were not obtained. Finally, they found that melt fracture occurs at a critical value of the wall shear stress in the range of 0.1-0.13 MPa, independently of temperature (in the range of 180-260°C).

Athey et al. (1986) and Rudin et al. (1985) studied the melt fracture of a molten polypropylene and used a small amount of fluoropolymer additive to the resin to suppress this phenomenon. They found that this additive provided some benefits in the extrusion process, such as reduction in power and die pressure. Other references addressing the melt fracture of PP include Akay (1983) and Fujiyama and Kawasaki (1991). They have reported critical shear stresses for the onset of melt fracture ranging from 0.13 to 0.2 MPa.
All the existing studies of polypropylene resins can be summarized as follows:

- There is no sharkskin region. As the shear rate increases, the extrudate appearance suddenly changes from smooth to gross melt fracture;
- Melt fracture occurs at a critical value of the wall shear stress of about 0.15 MPa;
- No previous work has examined wall slip.

2.6 Pressure effects

Large pressure gradients are typical in the processing of molten polymers. The compressibility of these materials in a molten state is quite high, and the effect of pressure on the viscosity cannot be neglected. It is known from experiments [Rauwendaal and Fernandez (1985), Kalika and Denn (1987)] that the apparent flow curves do not superpose for capillaries of different L/D ratios. Instead, the apparent flow curves shift to higher values of the wall shear stress with increase of the L/D ratio and therefore, pressure. The pressure dependence of viscosity is typically represented by an exponential function (first order approximation) which for a given temperature can be written as

$$\eta = \eta^0 \exp(\alpha P)$$  \hspace{1cm} (2-19)

where $\eta^0$ is the viscosity at ambient pressure, $\alpha$ is the pressure coefficient of viscosity and $P$ is the absolute pressure.

It has been proven that pressure has also an effect on the slip velocity. Hatzikiriakos and Dealy (1992a) studied the slip behaviour of several high density polyethylene blends at various pressures and temperatures. They have found that the slip velocity decreases with increase in pressure and this effect saturates at very high pressures. Therefore, as the pressure drops along the capillary, the slip velocity increases and the fluid accelerates near the exit of the capillary. This gives rise to a high extensional rate which may be the primary cause of the surface melt fracture (sharkskin) [Hatzikiriakos (1994)].
Another effect of pressure is that the viscosity increases with pressure, which results in the formation of a "prestress zone" at the die entrance [Mounihan (1990)]. Therefore, it can be argued that the melt fracture occurs in the entrance region where a material passes through a maximum in the wall shear stress.

2.7 Temperature effects – time-temperature superposition

Rheological properties are usually highly temperature dependent. This means that to obtain a complete picture of the behaviour, experiments must be carried out at several temperatures. It is often found that data taken at several temperatures can be brought together on a single master curve by means of "time-temperature superposition." This greatly simplifies the description of the effect of temperature. Furthermore, it makes possible the display on a single curve of material behaviour covering a much broader range of time or frequency than can ever be measured at a single temperature. Materials whose behaviour can be displayed in this way are said to be "thermorheologically simple" [Dealy and Wissbrun (1990)].

It was found that data for different temperatures can often be superposed by introducing a shift factor, $\alpha_T$, determined empirically. Thus, if one makes a plot of a rheological property versus time, $\alpha_T$ is obtained from the horizontal shift necessary to bring the data for any temperature $T$ onto the same curve as data for temperature $T_0$. For example, flow curves (shear stress vs. shear rate) will be plotted as shear stress versus $\gamma a_T$. Note that no shift factor is required for quantities not containing units of time. This implies that a plot of one such quantity versus another will be temperature independent.

The shift factor is a function of temperature, and the WLF equation has been found useful [Tanner (1985)]:

$$\log(\alpha_T) = -\frac{C_1(T - T_0)}{C_2 + (T - T_0)}$$  \hspace{1cm} (2-20)
where $C_1^0$ and $C_2^0$ are constants determined at $T_0$ for each material.

### 2.8 Viscous heating

In high speed processing operations, such as extrusion, viscous heating is inevitable because of the high viscosity of the polymeric liquids and because of the large velocity gradients. Moreover, because of the low thermal conductivity of polymers, temperature increases due to the viscous heating can be considerable and very non-uniform. A reliable estimation of viscous heating effects and local temperatures is of particular interest in polymer flow problems because of their strong influence on the properties of polymers, such as viscosity and rate of chemical degradation.

Cox and Macosco (1974) observed large temperature rises in capillary extrusion of acrylonitrile butadiene styrene (ABS) which can be as high as 70 K for apparent shear rates of the order of $10^4$ s$^{-1}$. Shidara and Denn (1993) have discussed the effect of viscous heating for a molten polystyrene in slit extrusion. To explain their result they assessed this effect to be significant. They also pointed out that a numerical solution of the full field in capillary/slit flow incorporating pressure and temperature effects is needed. One normally expects that the effect of viscous heating is less significant for high density polyethylene, and increases in significance for linear low density polyethylene, polypropylene and polystyrene respectively. This can be determined by examining the values of the temperature-dependency coefficient of viscosity [Ui et al. (1964), Van Krevelen (1990)].

A review of approximate analytical solutions to the flow of power-law fluids in circular channels with viscous heating is given by Bird et al. (1987). These are series solutions that exist for certain values of the power-law constant (Eq. 2-3) and constant values of thermophysical properties. To make the calculations in order to assess viscous heating effects, it is necessary to make an assumption for boundary conditions at the wall of the capillary, and two limiting cases are usually considered. In the isothermal case, the
wall is assumed to be at a uniform temperature, and in the adiabatic case, it is assumed that there is no heat transfer at the wall. In the first case, the temperature profile asymptotically reaches a fully developed profile, while in the second case a continuous, infinite temperature rise is predicted. The real conditions in the extrusion of polymer melts are somewhere between these limiting cases. It is also important to note that, according to these solutions, the temperature rise is higher for longer capillaries having a larger diameter. Thus, length and diameter of capillaries or length and height of slits are important parameters which should be taken into account.
3. OBJECTIVES

The primary objective of this work is to study the origins of extrudate distortion in the extrusion of polypropylene resins. Due to the fact that extrudate distortion of polyethylenes (high density and linear low density polyethylene) is accompanied by wall slip, a comprehensive study of slip is also needed. Moreover, it is not known whether these two phenomena, melt fracture and wall slip, are linked together for polypropylenes.

It is known that a thin layer of fluoropolymers, acting as a slip promoter, suppresses the surface melt fracture of polyethylenes and allows to decrease the wall shear stress and consequently the driving pressure required to extrude the material. Therefore, it is necessary to check if the slip promoters have a similar effect on the processing behaviour of polypropylenes.

The objectives can be summarized as follows:

1. To determine the critical wall shear stresses for the onset of wall slip and melt fracture as functions of:
   - Temperature
   - Pressure
   - Interface conditions

2. To study the effect of interface conditions on slip velocity and extrudate distortion by application of processing aids (mainly fluoropolymers) to the solid walls.
4. WALL SLIP AND MELT FRACTURE OF MOLTEN POLYPROPYLENES:
CAPILLARY RHEOMETER STUDIES

In this chapter the behaviour of two polypropylene resins is examined in capillary extrusion to determine the critical conditions for the occurrence of wall slip and melt fracture. To determine the flow curves from capillary data, the entrance effects are first assessed by using orifice dies and consequently the Rabinowitsch correction is used to determine the viscosity. To determine the wall slip, viscous heating should be taken into account and a critical discussion for its effects is presented. Finally, effects of processing aids on melt fracture and wall slip of polypropylene are examined.

4.1 Experimental

The experiments were carried out on Instron Model 1123 constant-speed piston-driven capillary rheometer. Circular dies of various diameters, \( D \), and length to diameter ratios \( (L/D) \) were used to examine possible effects of pressure on viscosity and slip velocity. To determine the Bagley correction with accuracy, capillary dies having a length-to-diameter ratio of zero were also used for each series of dies. All the circular dies had a 90° entrance angle. The dimensions of all capillary dies used in this work are listed in Table 4-1.

Slit dies (having a rectangular cross-section) were also used in order to examine the effect of surface coating on extrudate distortion and wall slip. These slit dies were constructed of two pieces so that the inside surface could be exposed, and the wall coating

<table>
<thead>
<tr>
<th>Diameter, mm</th>
<th>( L/D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.508 (0.02&quot;)</td>
<td>0, 40, 100</td>
</tr>
<tr>
<td>0.762 (0.03&quot;)</td>
<td>0, 10, 20, 40, 70, 100</td>
</tr>
<tr>
<td>1.27 (0.05&quot;)</td>
<td>0, 40, 70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Height, mm</th>
<th>( L/H )</th>
<th>( W/H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.254</td>
<td>100</td>
<td>10.1</td>
</tr>
<tr>
<td>0.508</td>
<td>60</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Table 4-1. Circular dies used.
Table 4-2. Slit dies used.
could be applied on the surface. The dimensions of all slits used are listed in Table 4-2 (height, \(H\); width, \(W\); and length, \(L\)). More details on the method of applying the coating onto the slits and their schematic diagram are given below.

As previously discussed, the resins used in this work were two polypropylenes (PPs). The experiments for the first PP were carried out at three temperatures: 200, 230 and 260 °C, while those for the other resin (PP Profax) were done at 200 °C only. The average molecular weights, \(M_w\), of the resins were 510,000 and 550,000 kg/kmol. These were determined from zero-shear viscosity (\(\eta_0\)) data, making use of a correlation between \(M_w\) and \(\eta_0\) for other linear polypropylenes [Hingmann and Marczinke (1994)].

Teflon® PA in the form of solution, provided by DuPont, was used to coat the surface of slits. Some additional experiments using Viton® as a processing aid were also carried out to determine its effects on wall slip and extrudate distortion of polypropylene. Viton® is available in the form of pellets and a 2% acetone solution was prepared. A certain amount of the solution was applied on the surface and enough time was allowed for the solvent to evaporate, which resulted in a uniform coating on the surface.

4.2 Raw data

Figure 4-1 shows some typical responses obtained in the capillary rheometer. It can be seen that the time required to reach a steady state depends on the shear rate and geometric characteristics of the capillary. The curve levels off slower for longer capillaries and lower shear rates. At small rates the materials behave as viscous fluids (no overshoot), however, as the shear rate increases the response becomes more elastic and thus overshoots appear in the shear stress response. This behaviour is due to the viscoelastic nature of the material.
4.3 Entrance effects

To determine the pressure drop associated with changes in the velocity distribution near the entrance and exit of the capillary, a technique outlined by Bagley (1957) was employed. Figure 4-2 plots the driving pressure, $P_d$, as a function of the $L/D$ ratio for several values of the apparent shear rate, $\dot{\gamma}_A = 4Q / \pi R^3$, where $Q$ is the volumetric flow rate and $R$ is the capillary radius. The Bagley correction, $P_{end}$, can be found by extrapolating the data to zero $L/D$. It can be seen from Fig. 4-2 that the data do not fall on straight lines even for the smaller values of the apparent shear rate. This implies that the viscosity is a function of pressure. To extrapolate to zero $L/D$, a quadratic function was fitted to the data, a technique previously used by Laun (1983) and Hatzikiriakos and Dealy (1992a).
Another method of determining the Bagley correction is to make use of orifice capillaries ($L/D = 0$). The Bagley corrections obtained with such capillaries and those determined by extrapolation from the Bagley plot are compared in Fig. 4-3. Most of the data points fall approximately on the same line. A degree of scatter exhibited by the data particularly at the smaller values of wall shear stress can be attributed to the experimental error. The same agreement for the Bagley corrections determined independently using two different methods can be observed for another type of polypropylene (Fig. 4-4), designated here as "PP Profax". This good agreement indicates that the obtained Bagley corrections are accurate enough to allow for an accurate determination of the flow curves.
Fig. 4-3. Bagley corrections determined by using various capillaries for polypropylene at 200 °C.

Fig. 4-4. Bagley corrections determined by using various capillaries for Profax polypropylene at 200 °C.
Fig. 4-5. Bagley corrections for three different temperatures (200, 230 and 260 °C).

It is interesting to note that the dependence of the Bagley correction on the wall shear stress does not seem to be affected by temperature. Figure 4-5 compares the Bagley corrections versus wall shear stress, obtained at three different temperatures. The data essentially defines a single line on a log-log plot. It is noted that no trends are observed as far as the dependency of the Bagley correction on temperature is concerned.
4.4 Flow curves

Using the Bagley corrections determined in the previous section, one may determine the apparent flow curves (wall shear stress vs. apparent shear rate) for various values of capillary diameter and $L/D$ ratios. The wall shear stress, $\sigma_w$, is assumed to be uniform along the capillary and is defined as:

$$\sigma_w = \frac{(P_d - P_{end})}{(4L/D)}$$  \hspace{1cm} (4-1)
Figure 4-6 shows apparent flow curves obtained with dies having a constant diameter and various $L/D$ ratios at 200 °C. It can be seen that the data does not fall on a single curve. Instead, the apparent flow curves shift to higher values of the wall shear stress with increase of the $L/D$ ratio, thus pressure. This implies that the viscosity of polypropylene is a function of pressure. This was also concluded from the Bagley plot (Fig. 4-2) as discussed in the previous section. Similar effects were obtained at the other two temperatures, i.e. at 230 and 260 °C. As seen in Fig. 4-7 and 4-8, the data does not fall on a single curve indicating an effect of pressure on the viscosity of the melt.

![Graph showing apparent flow curves for polypropylene at 230 °C](image)

Fig. 4-7. Apparent flow curves for polypropylene at 230 °C determined by using capillary dies having various $L/D$ ratios.
The pressure dependence of viscosity is typically represented by an exponential function, Eq. 2-19. The value of the pressure coefficient of viscosity, $\alpha$, required to superpose the data reasonably well was found to be in the range $5.9 \times 10^9$ to $10^8$ Pa$^{-1}$, increasing with temperature. The free volume increases with temperature, and thus pressure has a higher effect on the viscosity at a higher temperature. The values of $\alpha$ determined in this work are higher than those reported in the literature for polyethylenes: e.g., Kalika and Denn (1987) reported the pressure coefficient of viscosity for a LLDPE to be $5 \times 10^9$ Pa$^{-1}$, while for HDPE $\alpha$ is believed to be less than $0.52 \times 10^9$ Pa$^{-1}$.
[Rauwendaal and Fernandez (1985)]. Using Eq. 2-19 a pressure correction can be applied to the flow curve. The resulting pressure-corrected flow curves are shown on Fig. 4-9, 4-10 and 4-11 for the three temperatures. A reasonable superposition of the data for wall shear stresses less than about 0.18 MPa is obtained. Note that a semi-log plot was used to show clearly the superposition of the data.

![Pressure-corrected apparent flow curves](image)

**Fig. 4-9.** The pressure-corrected apparent flow curves of Fig. 4-5.
Fig. 4-10. The pressure-corrected apparent flow curves of Fig. 4-6.

Fig. 4-11. The pressure-corrected apparent flow curves of Fig. 4-7.
A similar approach was used to apply the pressure correction to the apparent flow curves obtained for Profax polypropylene (Fig. 4-12). The shaded area corresponds to the range of shear stresses where the onset of melt fracture was observed. Again, the apparent flow curves shift to higher values of the wall shear stress with increase of the $L/D$ ratio. The value of the pressure coefficient of viscosity was found to be about $1.0 \times 10^8$ Pa$^{-1}$, which is close to that for the other polypropylene used in this study. The resulting pressure-corrected flow curves are shown in Fig. 4-13.

![Figure 4-12](image-url)  
Fig. 4-12. Apparent flow curves for PP Profax at 200 °C determined by using capillary dies having various $L/D$ ratios.
Fig. 4-13. The pressure-corrected apparent flow curves of Fig. 4-11.

4.5 Wall slip

To calculate the slip velocity as a function of wall shear stress one may use the Mooney (1931) technique. According to this technique the flow curves determined with a series of capillaries having different diameters diverge at the critical shear stress for the onset of slip. In addition, to eliminate the effects of pressure on viscosity and slip velocity one should keep the $L/D$ ratio constant. This technique was used in the past for a series of HDPE's and it was found that these polymers slip at critical shear stresses in the range of 0.1-0.18 MPa depending on the molecular weight and polydispersity of the resin
[Hatzikiriakos and Dealy (1992a)]. Ramamurthy (1986) also determined critical shear stresses in the same range for LLDPE's.

Fig. 4-14. Apparent flow curves for polypropylene at 200 °C with a constant L/D and various diameters to detect the presence of slip.

Figures 4-14, 4-15 and 4-16 show the apparent flow curves of PP determined with dies having different diameters but constant L/D ratio, for three different temperatures. Note that a semi-log plot is used to show clearly any divergence of the flow curves. It can be
Fig. 4-15. Apparent flow curves for polypropylene at 230 °C with a constant $L/D$ and various diameters to detect the presence of slip.

Fig. 4-16. Apparent flow curves for polypropylene at 260 °C with a constant $L/D$ and various diameters to detect the presence of slip.
seen that these flow curves show no divergence for wall shear stresses less than about 0.2 MPa, implying the absence of slip. One could conclude that the data for 260 °C diverge in the pre-fracture region (the points for a smaller diameter fall below others), but the difference is too small and too close to the experimental error to consider this as an indication of slip. These observations are in agreement with the data obtained by Hatzikiriakos (1991) for Profax 6631 polypropylene using both a sliding plate rheometer with various gap spacings and a capillary rheometer with capillaries of various diameters and L/D ratios. He found that Profax 6631 PP does not slip for wall shear stresses less than about 0.16 MPa in capillary flow.

However, in view of the experimental observations discussed below that this resin fractures at shear stresses greater than 0.12 MPa, and that there is a change of slope of the flow curves on a log-log plot (Fig. 4-18), one usually anticipates the presence of slip. This was investigated further by using the slit dies described above. A typical schematic of a slit die is shown in Fig. 4-17.

Experiments were initially carried out with smooth surfaces and subsequently the walls of the slit were roughened by sandblasting. To detect any changes of the slit height resulting from the roughening procedure, the walls were polished again and the experiments were repeated.
Fig. 4-18. Change of slope of the flow curves.

Fig. 4-19. The effect of the wall roughness on the flow curve in slit extrusion.
The results are plotted in Fig. 4-19. Three apparent flow curves appear labelled as: "clean surface" (cleaning the surface by using normal procedures; the presence of oxides which lower substantially the surface energy cannot be excluded [Fowkes (1964)]; "rough" surface using sandblasting; and "polished" (polishing the surface has possibly increased the surface energy compared to the normal "clean surface"). The experimental error has also been assessed, indicating reproducibility of the results over a long period of time. It can clearly be seen that the data for "rough surface" fall above the other two sets. These data suggest that slip is present and that the flow curves are affected by the surface roughness. White et al. (1991) used grooved and smooth surfaces to assess the slip behaviour of rubber. They found that the shear stresses obtained with grooved surfaces were higher than those with smooth surfaces, indicating that grooved surfaces decrease wall slip. The same was observed for PVC by Chauffoureaux et al. (1979).

As discussed above, the experiments were carried out at three different temperatures. A technique known as "time-temperature superposition" or "method of reduced variables" is often employed in rheological measurements to obtain values of a material function over a wide range of shear rates (see Chapter 2). It is based on the observation that temperature does not affect the functional dependence of that property. In case of viscosity, the temperature merely alters the zero-shear-rate viscosity and the shear rate at which the transition from constant viscosity to power-law behaviour occurs. In the absence of slip, application of the time-temperature superposition principle on the apparent flow curves for several temperatures should result in a reasonable superposition. This is done in Fig. 4-20 where it can be seen that the superposition is reasonable up to shear stresses of about 0.13 MPa. It is noted that for shear stresses greater than this critical value melt fracture occurs. It can also be seen that for shear stresses greater than 0.13 MPa the curves do not superpose well but rather diverge. It is believed that this is due to the effect of slip. In general, the slip velocity increases with temperature [Hatzikiriakos and Dealy (1992a)]. Thus, as the temperature increases, one expects that the part of the flow curve beyond the
critical stress would shift toward the lower values of shear stress, exactly as obtained in Fig. 4-20.

![Flow curves at various temperatures using the time-temperature superposition principle.](image)

**Fig. 4-20.** Flow curves at various temperatures using the time-temperature superposition principle. Note that the superposition is very poor at wall shear stresses in the melt fracture region.

### 4.6 Viscous heating

Based on the results discussed in the previous section, it is believed that slip is present. However, one should explain why a diameter dependence is not obtained for the flow curves in Figures 4-14, 4-15 and 4-16. It is believed that the effect of viscous heating masks the determination of slip velocity by using the Mooney method (diameter-dependency of flow curves determined with capillaries having a fixed $L/D$ ratio). The
effect of viscous heating on rheological measurements in capillary/slit flow was discussed by many workers in the past [Bird (1955), Cox and Macosko (1974)].

To calculate the temperature rise in a capillary or slit flow, it is necessary to make an assumption about the boundary conditions for the energy equation. There are two limiting cases which are usually considered. In the isothermal case, the wall is assumed to be at a uniform temperature, and in the adiabatic case, it is assumed that there is no heat transfer at the wall. Ybarra and Eckert (1980) obtained an approximate solution of the energy equation for the slit flow of a power-law fluid. Using their numerical results a case study for the slit flow of PP is presented here.

According to the series solution for the slit flow of a power-law fluid, the temperature rise is a function of thermophysical properties and power-law constants of the fluid and geometrical characteristics of the slit. This function is rather complex, but a simple relationship can be derived: for constant \( L/H \) in the isothermal case the temperature rise is proportional to \( H^n \), where \( H \) is the slit height, \( L \) is the slit length, and \( n \) varies from 0 to 2 for \( 0 < L < \infty \). It is clear that the effect of the slit height on the temperature rise may be quite strong, and this point is demonstrated on a numerical example for polypropylene.

The thermophysical properties and power-law constants of a typical PP were obtained from Van Krevelen (1990) and these are summarized in Table 4-3. Figure 4-21 plots the average temperature rise as a function of the apparent shear rate in slits having a fixed length-to-height ratio of 40 and three different heights for the case of isothermal walls.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity, ( c_p )</td>
<td>2450 J/kg ( \cdot ) K</td>
</tr>
<tr>
<td>Heat conductivity, ( k )</td>
<td>0.15 W/m ( \cdot ) K</td>
</tr>
<tr>
<td>Density, ( \rho )</td>
<td>800 kg/m(^3)</td>
</tr>
<tr>
<td>Power-law exponent, ( n )</td>
<td>0.3</td>
</tr>
<tr>
<td>Power-law consistency, ( K )</td>
<td>0.0278 MPa ( \cdot ) s(^n)</td>
</tr>
</tbody>
</table>

Table 4-3. Properties of a typical PP at 473 K.
It is noted that the calculated temperature rise is much higher for the case of adiabatic walls. It can be seen from Fig. 4-21 that the effect of viscous heating is more significant in slit dies having a larger height. If one assumes the absence of slip then, according to this result, one expects to obtain a height dependence for the flow curves. Temperature dependence of the viscosity was determined by a vertical shift of the flow curves corresponding to different temperatures and is usually represented by an exponential relationship:

\[
\sigma_{w,T} = \sigma_{w,T_0} \, e^{-A(T-T_0)}
\]  

(4-2)
where $\sigma_{w,T}$ and $\sigma_{w,T_0}$ are wall shear stresses at the corresponding temperatures, $T$ and $T_0$.

The value of the temperature coefficient of viscosity, $A$, was found to be about 0.015 K$^{-1}$. Equation 4-2 indicates that the higher the temperature, the lower the viscosity, thus the flow curve for a slit having a larger height shifts to lower values of shear stress, as illustrated by Fig. 4-22. The solid line is a power law with parameters from Table 4-3; it is the flow curve without slip and without viscous heating.
If slip is present, it will affect the flow curves in a different way: the flow curve for a slit having a smaller height shifts to lower values of shear stress. To estimate the effect of slip, a relation for the slip velocity must be assumed. Due to the absence of experimental data for wall slip of polypropylene, it is reasonable to take the available data for high density polyethylene. Hatzikiriakos and Dealy (1992a) reported that the slip velocity of HDPE can be fitted to a power-law equation:

\[ u_s = a \sigma_w^m \] (4-3)

It is applicable for \( \sigma_w > \sigma_c \), where \( \sigma_c \) is the critical shear stress for the onset of slip. For polyethylene \( \sigma_c \) was found to be about 0.1 MPa. More realistic behaviour of the slip velocity at very low shear stresses can be attained by introducing one more parameter which zeroes the \( u_s \) for \( \sigma_w < \sigma_c \) (Fig. 4-23):

\[ u_s = \frac{1}{1 + \left( \frac{\sigma_c}{\sigma_w} \right)^{100}} a \sigma_w^m \] (4-4)

---

Fig. 4-23. Case study: slip velocity function (Eq. 4-4).
Using Eq. 4-4 with parameters $a = 2.58 \text{ MPa}^{-m} \text{ m/s}$, $\sigma_c = 0.1 \text{ MPa}$, $m = 3.4$, together with Eq. 2-3 and 2-17, the slip can be imposed on the flow curves. Figure 4-24 shows the effect of slip on flow curves in the case when there is no viscous heating. Therefore, a height dependence of the flow curves is obtained which is opposite from what one gets if only viscous heating is taken into account. In a similar way, the effect of slip can be applied to the flow curves with viscous heating and the results are plotted in Fig. 4-25. Now, with viscous heating and wall slip acting in the opposite directions, the flow curves show almost no divergence.
From the case study discussed above it is clear that with certain values of parameters affecting viscous heating and wall slip, the flow curves for a given material can be superposed and lead us to wrong conclusions. This seems to be the case for capillary flow as the data of Fig. 4-14, 4-15 and 4-16 indicate. Normally, one expects that capillary data would not be much different than slit data. Therefore, it is the combined effect of slip velocity and viscous heating that superposes the data.

**4.7 Rabinowitsch correction**

Once the slip effects are determined, one may calculate the viscosity. To do this, the Rabinowitsch correction should be applied, which for circular dies is given by:
Fig. 4-26. The viscosity of polypropylene at various temperatures using the time-temperature superposition principle.

\[ \dot{\gamma}_w = \left( \frac{3 + 1/\eta}{4} \right) \gamma_A \]  \hspace{1cm} (4-5)

where \( n \) is the power-law exponent, given by the slope of \( \log(\sigma_w) \) versus \( \log(\dot{\gamma}_A) \), assuming that the material under study is a power-law fluid. In fact, the graph of \( \log(\sigma_w) \) vs. \( \log(\dot{\gamma}_A) \) exhibits a slight curvature, and the local value of the slope was used to apply the Rabinowitsch correction along the entire curve. Due to the uncertainty of wall slip for wall shear stresses greater than about 0.13 MPa only data in the fracture-free region are considered in calculating the viscosity. The resulting viscosity values have been corrected.
for the effects of pressure and these are plotted in Fig. 4-26. The data for the other two temperatures, 230 and 260 °C, using the time-temperature superposition principle are also plotted.

![Graph showing viscosity vs. shear rate for PP Profax, T = 200 °C]

Fig. 4-27. The viscosity of Profax polypropylene at 200 °C.

The agreement between the data obtained using various capillaries is also verified for Profax polypropylene by plotting the viscosity data (Fig. 4-27). Again, the pressure and Rabinowitsch corrections were applied to the capillary data. A reasonable superposition is obtained for shear stresses not exceeding the onset of gross melt fracture (about 0.14 MPa).
4.8 Melt fracture

Samples of polypropylene extrudates produced at various shear rates using a capillary having a length-to-diameter ratio of 20 and diameter of 0.762 mm are shown in Fig. 4-28. It can be observed that there is a sudden transition from a smooth extrudate to a grossly distorted one. The types of gross distortions range from a helical screw thread appearance to severe irregular distortions. For polyethylenes, surface melt fracture (sharkskin) usually occurs before gross melt fracture [Ramamurthy (1986)]. However, this type of distortion does not occur in the case of polypropylene and the transition from a smooth surface to a grossly distorted one is rather abrupt.

![Fig. 4-28. Various samples produced by extrusion of PP from a circular die having $D = 0.762$ mm and $L/D = 20$ at 200 °C.](image)
Fig. 4-29. Critical shear stresses for the onset of melt fracture as a function of L/D and temperature.

The onset of gross melt fracture was detected to occur at critical shear stresses in the range of 0.12-0.15 MPa for capillary dies having L/D ratios from 10 to 100 and independent of temperature (Fig. 4-29). These values of $\sigma_c$ agree with those reported by other researchers. For example, Fujiyama and Kawasaki (1991) averaged their capillary rheometer data for isotactic PP obtained with capillaries having L/D ratios in the range from 2 to 10 to give a value of 0.13 MPa for the onset of fracture. Ui et al. (1964) found the critical shear stresses for the onset of melt fracture for a series of polypropylenes to be in the range between 0.1-0.13 MPa.
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\[ T = 200 \text{ C} \quad D = 0.762 \text{ mm} \]

\[ \dot{\gamma}_A = 208 \text{ s}^{-1} \]

| L/D | 20 | 40 | 70 |

Fig. 4-30. Samples of PP produced at a fixed shear rate in circular dies with different L/D at 200 °C.

It was also observed that the severity of extrudate distortion increases with L/D ratio at a given apparent shear rate, as illustrated in Fig. 4-30. This finding is rather surprising, as an increase of the L/D ratio and hence, of pressure, has been found to suppress the extrudate distortion in some cases in the extrusion of polyethylene/polypropylene blends [Vinogradov and Ivanova (1967)]. However, at a given apparent shear rate, the wall shear stress at the entrance of the die is higher for a longer capillary due to the effect of pressure on viscosity. This possibly gives an explanation as to why the L/D ratio has an effect on the severity of melt fracture.

4.9 Effects of surface coating

Coating the die walls with a fluoropolymer can provide the same benefits as using the fluoroelastomer as additive to the resin. For example, Hatzikiriakos et al. (1993) found
that processing aids such as Viton® and Teflon® PA (DuPont) could significantly lower the critical shear stress for the onset of slip. Using these fluoropolymers, they coated the surface of the plates in a sliding plate rheometer. They found that the critical shear stress for the onset of slip could be as low as 0.027 MPa with a Teflon® coating. In addition, in slit extrusion with Viton® coated surface, a reduction of the wall shear stress was obtained ranging from 20 to 50%, depending on the extrusion rate.

![Graph](image)

**Fig. 4-31.** Apparent flow curves for polypropylene at 200 °C determined by using a slit die with \( H = 0.254 \) mm.

The polymer-metal interface in the slit dies was modified by applying a Teflon® coating in order to examine its effect on the processing of PP and the critical conditions for
the onset of wall slip. The procedure used to coat the dies is as follows: the solution was applied to the surface at 160 °C and enough time was allowed for the solvent to evaporate and for the resulting film to stabilize. Viton® coating was obtained by dissolving the pellets in acetone and applying the solution at room temperature.

![Graph showing flow curves for polypropylene at 200 °C](image)

**Polypropylene, T = 200 °C**  
**H = 0.508 mm, L/H = 60, W/H = 9.8**

- **Clean surface**
- **Viton coating**

**Fig. 4-32.** Apparent flow curves for polypropylene at 200 °C determined by using a slit die with $H = 0.508$ mm.

The flow curves obtained using the two slit dies (#1 and 2, Table 4-2) with Viton® coating are shown in Fig. 4-31 and Fig. 4-32, respectively. It can be observed that the coating has a dramatic effect on the flow curves for a wide range of wall shear stresses up to $\approx 0.16$ MPa. Beyond that point the flow curves come close to each other, and simultaneously the flow curve for clean surface starts to bend down, considerably deviating...
from the power law. This observation may serve as another proof that polypropylene slips at a certain value of shear stress not far below 0.16 MPa.

Figure 4-33 shows the dependence of the shear stress response in slit extrusion on surface conditions as a function of time. The data was obtained by using a slit die #2. Each curve represents the extrusion of a fixed amount of the polymer (one full load of the barrel). After the response for the clean surface was obtained, the Teflon® coating was applied only once for all subsequent runs 1 to 6. It can be seen that the presence of Teflon® significantly decreases the shear stress, resulting in easier processing. As more polymer is extruded over the same coating, a further decrease in the shear stress is obtained. This indicates that initially the resulting coating is not as smooth as with further treatment. Some mechanical interlocking of the polypropylene molecules within the micropores of the
coating initially occurs. However, as extrusion continues the Teflon® coating becomes smoother and as a result the wall shear stress decreases. One could conclude that a steady-state had been reached in run #3. However, as runs 5 and 6 indicate, a further decrease in wall shear stress was obtained. It is not known with certainty if these values represent the final steady-state values. This is the main reason why flow curves with a Teflon® coated surface have not been plotted.

As it was mentioned above, a thin layer of fluorocarbons, acting as a slip promoter, suppressed the surface melt fracture of polyethylenes. However, experiments with the two polypropylenes used in this work have shown that the presence of a Teflon® or Viton® coating had no effect on the critical shear stress for the onset of melt fracture and did not allow elimination of the extrudate distortions or delay of the onset of these distortions to higher shear rates. An explanation of the behaviour of PPs in capillary extrusion with coated surfaces which is different from that of PEs is currently lacking, but of course it has to do with the molecular architecture of the two types of polymers.
5. WALL SLIP AND MELT FRACTURE OF MOLTEN POLYPROPYLENES: SLIDING PLATE RHEOMETER STUDIES

This chapter is devoted to the analysis of the data for the two polypropylenes obtained from a sliding plate rheometer. The flow curves, viscosity and occurrence of slip are determined and compared with the capillary rheometer data. Effects of processing aids on wall slip of polypropylene are also examined.

5.1 Experimental

A sliding plate rheometer (Interlaken Series 3200) was used to determine the viscosity of the materials and compare it with data obtained from the capillary rheometer. This piece of equipment was also used to determine the onset of slip at smaller shear rates for Teflon® and Viton® coated surfaces. The rheometer's design allowed for two different gap spacings, 0.45 and 0.20 mm. The same resins as in the capillary rheometer studies were used. The experiments were carried out at 200 °C only.

5.2 Raw data

Figure 5-1 shows the response of the stress transducer at very low shear rates when the steady state is reached at small strains, with no or very small overshoots at the beginning. If the shear rate is increased, the overshooting becomes stronger (Fig. 5-2) and larger strains are required to reach a steady state. At very large shear rates over- and undershoots appear in the curves (Fig. 5-3). Analogous curves were obtained with a smaller gap between the plates (Fig. 5-4). This behaviour is due to the viscoelastic nature of the materials under study. At small rates the materials behave as viscous fluids (no overshoot), however, as the shear rate increases the response becomes more elastic and thus overshoots and undershoots appear in the shear stress response. These observations are typical for viscoelastic fluids.
Fig. 5-1. Typical responses obtained in a steady-shear experiment in a sliding-plate rheometer (small shear rates).

Fig. 5-2. Typical responses obtained in a steady-shear experiment in a sliding-plate rheometer (medium shear rates).
Fig. 5-3. Typical responses obtained in a steady-shear experiment in a sliding-plate rheometer (large shear rates).

Fig. 5-4. Typical responses obtained in a steady-shear experiment in a sliding-plate rheometer (large shear rates, smaller gap).
For an accurate determination of a steady-state value of the shear stress it is important to ensure that the sliding plate travels at a constant speed. Figures 5-5 and 5-6 plot the dimensionless shear rate (shear rate at a given time divided by a programmed shear rate) versus dimensionless time (scaled with respect to the total duration of each run) for a number of shear rates. It can be seen that in the case of 0.20 mm gap (Fig. 5-5) the plate reaches a constant speed at the beginning of the experiment even for the high values of the shear rate.
Fig. 5-6. Check for the displacement transducer linearity (larger gap).

However, in the case of 0.45 mm gap (Fig. 5-6) the plate inertia starts to affect its motion, and for higher shear rates the programmed value is not reached at all. Therefore, only the last 10% of the shear rate curve were considered for those shear rates, and appropriate corrections were made for the values of nominal shear rates that were used in the subsequent calculations. The nominal shear rates were calculated by differentiating the displacement data. The "jitter" in these graphs is explained by the fact that the data was generated by an analogue-digital converter used to process the signal coming from displacement transducers.
5.3 Flow curves

Figures 5-7 and 5-8 show the flow curves (steady-state shear stresses from Fig. 5-1 – 5-4 versus nominal shear rate) obtained in the sliding plate rheometer with two different gap spacings for the two polypropylene resins. It can be seen that these flow curves show no divergence for wall shear stresses less than about 0.13 MPa, implying the absence of slip in the pre-fracture region. These observations are in agreement with the data obtained by Hatzikiriakos (1991) for Profax 6631 polypropylene using both a sliding plate rheometer with various gap spacings and a capillary rheometer with capillaries of various diameters and $L/D$ ratios. He found that Profax 6631 did not slip for wall shear stresses less than about 0.16 MPa.

Fig. 5-7. Flow curves obtained in the sliding plate rheometer for polypropylene with different gap spacings.
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5.4 Viscosity measurements

Viscosity is frequently used to characterize thermoplastic resins. It is a function of flow conditions (shear rate, temperature, pressure) and resin composition (chemical structure, molecular weight distribution, presence of long chain branches, nature and concentration of additives) [Dealy and Wissbrun (1990)]. Steady shear experiments are used to determine the dependence of viscosity on various parameters.

The viscosity values for polypropylene at 200 °C are plotted in Fig. 5-9, along with the viscosity data obtained from the capillary rheometer at three temperatures. The capillary data have been corrected for the effects of pressure and the time-temperature superposition principle was applied to the data for the other two temperatures, 230 and
260 °C. Note the excellent agreement between the data obtained from the two instruments. Due to the uncertainty of wall slip for wall shear stresses greater than about 0.13 MPa only data in the fracture-free region are considered in calculating the viscosity.

The agreement between the data obtained in the two rheometers is also verified by plotting the viscosity data for Profax polypropylene (Fig. 5-10). Again, the pressure and Rabinowitsch corrections were applied to the capillary data. A reasonable superposition is obtained for shear stresses not exceeding the onset of gross melt fracture (about 0.14 MPa).

Fig. 5-9. The viscosity of polypropylene.
5.5 Effects of surface coating

The sliding plate rheometer which made it possible to carry out steady shear experiments at extremely low shear rates was used to determine the critical shear stress for the onset of slip with fluoropolymer-treated surfaces. Hatzikiriakos et al. (1993) used a similar sliding plate rheometer to study the effect of processing aids such as Viton® and Teflon® PA (DuPont) and found that they could significantly lower the critical shear stress for the onset of slip.

The procedures used to coat the surface of one of the plates with Teflon® and Viton® are the same as in the case of slit dies (see section 4-1). Figure 5-11 shows the flow curves obtained with clean and Teflon®-coated surfaces. It can be seen that the onset of slip can be as low as about 0.01 MPa, and above that point the flow curves for coated plates fall
below those for untreated surfaces. A region of flow instabilities can be observed at intermediate values of shear stress, where there is a considerable scatter in the data points. The responses for this region are shown in Fig. 5-12. It can be seen that no steady state is reached, and the shear stress for higher shear rates may be lower than that for lower shear rates. It is believed that the data points for Teflon®-coated surfaces for higher shear rates shown in Fig. 5-11 do not represent steady-state values. In section 4-9 it was shown that a very long time is required for the Teflon® coating to stabilize, and during that period the shear stress continues to drop, reaching values that are 50% below of those obtained with clean surfaces.

Fig. 5-11. Flow curves obtained in the sliding plate rheometer with clean and Teflon® coated plates.
Similar effect on the shear stress can be seen in the case of Viton®-coated surface (Fig. 5-13). The onset of slip was detected at the shear stress of 0.009 MPa, although at higher shear rates the decrease in shear stress is not so significant as in the case of Teflon® coating.

The effect of both coatings starts to be noticeable at very low shear stresses (about 0.01 MPa), and at higher shear rates a significant decrease in the shear stress is observed. All these observations point out the benefits provided by these processing aids, i.e. decreasing the power consumption in extrusion or in other polymer processing operations.

Fig. 5-12. Responses obtained in a steady-shear experiment with Teflon®-coated plates.
Fig. 5-13. Flow curves obtained in the sliding plate rheometer with clean and Viton® coated plates.
6. CONCLUSIONS

A sliding plate and capillary rheometers were used to determine the conditions for the onset of slip, surface and gross melt fracture for two polypropylene resins. It was found that surface melt fracture commonly observed in the processing of polyethylenes did not occur for these polypropylenes. Instead, a sharp transition from a smooth to a grossly distorted appearance was obtained. The onset of gross melt fracture was detected at a critical wall shear stress in the range from 0.12 to 0.15 MPa, independent of temperature and geometric characteristics of the dies.

An attempt was made to explain the diameter-independence of the flow curves of polypropylene in capillary flow. It was suggested that viscous heating is strong enough to mask this dependence under slip conditions and one should solve the full field equations including the energy equation to definitely assess its importance.

Finally, it was found that the presence of Teflon® and Viton® coatings on the polymer-wall interface significantly decreased the wall shear stress which implies that these materials are strong slip promoters. The onset of slip was found to occur at the critical shear stress of about 0.01 MPa, while the decrease in shear stress can be up to 50% in some cases. This results in the reduction of the driving pressure required to extrude the material and therefore in energy savings.

Recommendations for future work

Based on the experience gained during this study, the following recommendations for future work can be made.

- The diameter-independence of the flow curves of polypropylene in capillary flow was explained by viscous heating, which can be strong enough to mask the effect of wall slip. Moreover, it is still not known whether the slip occurs at the polymer-wall interface (adhesive failure) or within the polymer but close to the wall (cohesive
failure). New techniques should be devised to provide deeper insights into the nature of slip and to make its determination easier. Direct measurements of velocity profiles near the wall of a capillary/slit would be useful to prove this point experimentally and to resolve the remaining uncertainty. The possible methods could include laser velocimetry, radioactive tracer techniques, and scanning electron microscopy.

- It was shown that the effect of viscous heating was stronger in channels of a larger cross-section. In this regard it would be better to perform capillary rheometer experiments using capillaries and slits of a minimal diameter or a slit height. This will also allow a wider range of attainable shear rates.

- One of the methods used to detect the occurrence of slip in this work was roughening of the inner surface of a slit. Taking into account that pressure has a strong effect on the slip velocity, it would be useful to roughen plates in the sliding plate rheometer, where the sample is not subjected to an external pressure. The effect of pressure on the slip velocity results in the fluid acceleration as it approaches the exit of a capillary. This will be reflected in the local shear stress and pressure. Therefore, slits with stress and pressure transducers mounted on their walls to measure the shear stress and pressure locally would be helpful for this kind of study. Currently, such slit dies are used at McGill university to determine slip.

- The resins used in this work had close values of molecular weights, while other parameters such as molecular weight distribution, presence of chain branches, isomeric configuration of the molecules were not known. To relate the molecular characteristics of a resin with its rheological properties, melt fracture and slip behaviour, it is necessary to perform similar experiments with other polypropylene resins varying those parameters.
REFERENCES


Bartos, O., *Fracture of Polymer Melts at High Shear Stress*, J. Appl. Phys., 35 (9), 2767 (1964)


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NOTATION

\( A \)  temperature coefficient of viscosity, \( \text{K}^{-1} \)
\( a \)  parameter in the slip velocity equation (Eq. 4-4), \( \text{MPa}^m \cdot \text{m/s} \)
\( a_T \)  shift factor
\( b \)  Rabinowitsch correction
\( c_p \)  heat capacity, \( \text{J/}(\text{kg} \cdot \text{K}) \)
\( D \)  capillary diameter, \( \text{m} \)
\( H \)  slit height, \( \text{m} \)
\( h \)  gap between plates, \( \text{m} \)
\( I \)  melt polydispersity
\( K \)  power-law consistency index, \( \text{MPa} \cdot \text{s}^n \)
\( k \)  heat conductivity, \( \text{W}/(\text{m} \cdot \text{K}) \)
\( L \)  capillary or slit length, \( \text{m} \)
\( M_w \)  weight-average molecular weight, \( \text{kg/kmol} \)
\( m \)  parameter in the slip velocity equation (Eq. 4-4)
\( n \)  power-law exponent
\( N_{\text{MF}} \)  melt fracture number, \( \text{MPa} \)
\( P \)  absolute pressure, \( \text{Pa} \)
\( P_d \)  driving pressure, \( \text{Pa} \)
\( P_{\text{end}} \)  Bagley correction, \( \text{Pa} \)
\( Q \)  volumetric flow rate, \( \text{m}^3/\text{s} \)
\( R \)  capillary radius, \( \text{m} \)
\( T \)  absolute temperature, \( \text{K} \)
\( u \)  melt velocity, \( \text{m/s} \)
\( u_s \)  slip velocity, \( \text{m/s} \)
\( W \)  slit width, \( \text{m} \)
**Greek Letters**

- $\alpha$: pressure coefficient of viscosity, $\text{Pa}^{-1}$
- $\dot{\gamma}$: true shear rate, $\text{s}^{-1}$
- $\dot{\gamma}_A$: apparent shear rate, $\text{s}^{-1}$
- $\dot{\gamma}_{A,c}$: apparent shear rate, corrected for slip, $\text{s}^{-1}$
- $\dot{\gamma}_n$: nominal shear rate, $\text{s}^{-1}$
- $\dot{\gamma}_w$: wall shear rate, $\text{s}^{-1}$
- $\eta$: viscosity, $\text{Pa} \cdot \text{s}$
- $\eta_0$: zero-shear viscosity, $\text{Pa} \cdot \text{s}$
- $\eta^0$: viscosity at ambient pressure, $\text{Pa} \cdot \text{s}$
- $\rho$: density, $\text{kg/m}^3$
- $\sigma_c$: critical shear stress for the onset of melt fracture, $\text{MPa}$
- $\sigma_w$: wall shear stress, $\text{MPa}$
- $\sigma_{w,T}$: wall shear stress with viscous heating, $\text{MPa}$