Extrusion of Polypropylene. Part I: Melt Rheology

J. BRANDAO,*† E. SPIETH,** and C. LEKAKOU*

*Department of Materials Science and Engineering
University of Surrey
Guildford, Surrey GU2 5XH, United Kingdom

**POLIBRASIL - S.A.
Polo Petroquímico do Nordeste
Camacari-Bahia CEP 42810, Brazil

This paper considers the rheology of extruded polypropylene regarding melt flow index, shear viscosity, and die swell. Two grades of polypropylene are studied with differences in the molecular weight and rheology. An Instron capillary rheometer is used for the measurement of viscosity and die swell. A range of shear rates and temperatures is covered in these measurements. Die swell is also measured in polypropylene extruded through a commercial single screw extruder where the effect of varying conditions of cooling and annealing on die swell are tested. A detailed theoretical analysis is carried out for the die swell. Analytical expressions are employed for the description of viscosity and die swell with empirical constants which are determined from the experimental data.

INTRODUCTION

The purpose of this paper is to study experimentally and simulate computationally the extrusion of polypropylene in the metering zone and die. Similar studies have been carried out for polyethylene by Agur and Vlachopoulos (1, 2), Savolainen et al. (3), and Tanner (4). The present investigation is split into two parts: (i) measurements and modeling of rheology and (ii) process analysis. The studied rheological properties of polypropylene melts include viscosity, as a function of temperature and shear rate, and die swell. Chemical degradation and oxidation is a particular feature of polypropylene at elevated temperatures which results in lowering the viscosity. The polypropylene grades used in this study contained additives to prevent oxidation and degradation.

Rheological measurements presented in this paper involve the techniques of melt flow index and capillary rheometer. Experimental data have been formulated into constitutive relations of shear viscosity against shear rate and temperature, following the Power-law with exponential temperature dependence or a polynomial relation. These constitutive relations will be incorporated in the flow and heat transfer models in Part II of this study (5).

The mathematical modeling of the die swell is described, including elastic and Newtonian contributions. Two main relations for the die swell have been derived: the first corresponds to low and moderate wall shear stresses and the second corresponds to high wall shear stresses. These relations have been combined into a curve fitting the obtained experimental data of die swell for polypropylene.

CONSTITUTIVE RELATIONS FOR SHEAR VISCOSITY

Two types of empirical constitutive expressions have been used for the shear viscosity.

(a) the power-law relation in which the viscosity, $\eta$, is given as a function of shear rate, $\dot{\gamma}$:

$$\eta = m \dot{\gamma}^{n-1}$$

where $m$ is the consistency and $n$ is the power-law index. Temperature effects are included in the consistency, according to the equation:

$$m = m_o \exp \left[ \frac{\Delta E}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right]$$

Although the power-law is widely used for non-Newtonian fluids in many engineering applications, it has some drawbacks. The main one is that it does not predict the experimentally observed Newtonian plateaus at very low and very high shear rates.

(b) a polynomial relation which includes both shear rate and temperature effects:

$$\log \eta = b_o + b_1 \log \dot{\gamma} + b_2 (\log \dot{\gamma})^2 + b_3 T + b_4 T^2 + b_5 T \log \dot{\gamma}$$

---

* Present address. POLIBRASIL-S.A., Polo Petroquímico do Nordeste, Camacari-Bahia CEP 42810, Brazil.
Equation 3 is not precisely a well established constitutive equation but an empirical relation, successfully employed in previous extrusion simulations (2, 6, 7).

**MODELING OF DIE SWELL IN CIRCULAR DIES**

The term die swell has been employed to express the increase in the cross-section of extrudate as it exits the die and, quantitatively speaking for a die of circular cross-section, it is represented by the ratio of the extrudate diameter over the die diameter. Die swell shows a particular dependence on the ratio of die length to diameter and the melt viscosity. In fact, when the length to diameter ratio, \( L/D \), exceeds a certain value, the die swell tends to become independent of the die length. Die swell has been observed even in Newtonian fluids at low Reynolds numbers, lower than 16. In this case, the extrudate diameter increases by 12% at most (8). Inelastic shear-thinning fluids obeying the power law showed swell ratios smaller than Newtonian fluids (9, 10).

Therefore, it is the elastic component of shear-thinning viscoelastic fluids, such as polymer melts, that should account for the measured large swell ratios, usually up to 400%, and not the viscosity dependence on shear rate. An important parameter in assessing elasticity is the recoverable shear or strain, defined by Eqs 4 and 5, respectively:

\[
\gamma_r = \frac{\tau_{12}}{G} \quad (4)
\]

\[
\varepsilon_r = \frac{\tau_{11} - \tau_{22}}{2\tau_{12}} \quad (5)
\]

depending whether shear or normal stresses are important.

The die swell of polymer melts in laminar flow can be analyzed into three parts: a small Newtonian swell, a sudden elastic recovery at the die exit, and an additional swelling due to slow stress relaxation. The sudden elastic recovery is related to the molecular recoiling as soon as the wall shear stress is removed at die exit. The additional swelling is due to the slowly relaxed first normal stress difference, usually developed at die entry. In long dies, the memory effect of the first normal stress difference has faded by the time the melt exits the die and, as a result, the additional swelling is small. The swell ratio, then, reaches an asymptotic value.

\[
\tau_{11} - \tau_{22} = A \tau_{12}^6
\]

where both elastic and Newtonian swelling are considered.

Tanner (12) has suggested a double empirical power-law for the first normal stress difference. In this study, only the contributions of \( B_{\text{Newt}} \) and \( B_{\text{elast}} \) are considered, since there are no reliable estimates of \( B_{\text{inelast}} \) and \( B_{\text{relax}} \) and, in some cases, \( B_{\text{inelast}} + B_{\text{relax}} \) is small. The contribution of \( B_{\text{Newt}} \) has been given the constant value of 0.12.

In the modeling of \( B_{\text{elast}} \), the flow in the die is considered isothermal and incompressible and the inertial, gravity, and surface tension forces are neglected. The model is based on the elastic recovery theory of Tanner (12), which in turn is based on the theories of Lodge (13, 14), Kaye (15), and Zapas (16). Lodge showed the role of elastic recovery and sidewise swelling when the stress is released instantaneously. Furthermore, a small delayed recovery occurs after the instantaneous recovery. The constitutive equation employed by Tanner takes into account strain tensors at a past time measured relative to the material configuration at the present time. The flow at exit may be approximated by a suddenly developed strain which takes the viscoelastic melt from the constrained viscous stress state inside the capillary "instantaneously" to the unconstrained atmospheric pressure state outside the capillary.

If it is considered that the shear stress varies linearly with the radius of the die, the general form of Tanner's theory is expressed by the equation:

\[
B_\varepsilon = \left[ \int_0^1 \left( N1(\tau_{12}) + G(\tau_{12}) - \frac{\tau_{12}^2}{G(\tau_{12})} \tau_{12} \right) d\tau_{12} \right]^{1/6}
\]

By assuming an empirical power-law type of relation between the first normal stress difference and the shear stress:

\[
\tau_{11} - \tau_{22} = A \tau_{12}^6
\]

a relationship for \( B_{\text{elast}} \) suggested by Racin and Bogue (17) can be derived:

\[
B_{\text{elast}} = \left[ 1 + \frac{A^2 (4 - a)}{4 (2 + a)} \right]^{1/16}
\]

Hence, the die swell can be expressed as:

\[
B_\varepsilon = \left[ 1 + \frac{A^2 (4 - a)}{4 (2 + a)} \tau_{12}^{2 + a} \right]^{1/6} + 0.12
\]

where both elastic and Newtonian swelling are taken into account.

Equation 10 usually yields good predictions of die swell at low shear stresses but, beyond a certain limit, it starts to predict smaller values than the experimental data as die swell increases too rapidly at high shear stresses. In order to improve the agreement between theory and practice, Dietz, White, and Clark (18) proposed a double empirical power-law for the first nor-
mal stress difference of the type

\begin{align}
\tau_{11} - \tau_{22} &= A_1 \tau_w^{a_1} \quad \text{if} \quad \tau_w < \tau_{wc} \\
\tau_{11} - \tau_{22} &= A_2 \tau_w^{a_2} \quad \text{if} \quad \tau_w > \tau_{wc}
\end{align}

(11)

where \( \tau_{wc} \) is a critical wall shear stress, above which die swell starts to increase too rapidly. Huang and White (19), using the theory of Dietz et al. (18), suggested the following expression to predict die swell:

\[ B_s = \left[ 1 + \frac{(a_2 - a_1)A_2^2 \tau_{wc}^{2a_2} + A_2^2 \tau_{wc}^{2a_2 - 2}}{4a_1 a_2 \tau_{wc}^{2a_2 - 2}} \right]^{1/6} + 0.12 \]

(12)

where \( a_1, a_2, A_1, A_2, \) and \( \tau_{wc} \) are characteristic empirical constants of the material.

**Experiments**

**Materials**

Two polypropylene grades have been tested in the experiments, GE6100 and TY6100, produced by Polibrasil S.A. Both of these grades contained additives to prevent thermal degradation under extrusion conditions. Molecular weight distributions of the two grades were obtained with gel permeation chromatography on a Waters 150C GPC instrument at 135°C. The results are shown in Fig. 1 and 2 for grades GE6100 and TY6100, respectively. Generally, the GE6100 grade is of higher molecular weight than the TY6100 grade.

**Measurements of Melt Flow Index**

Melt flow index (MFI) is the mass flow rate, expressed in grams, isothermally extruded in 10 min under constant load through a die of standard dimensions. The MFI measurements were carried out in a Davenport plastometer equipped with a capillary die of 8.000 + 0.025 mm length and 2.0955 + 0.0051 mm diameter. A pellet sample of 4 g was compacted and left to stabilize for 6 min at 230°C in the plastometer. It was then extruded through the die under a constant load of 2.16 kg.

**Measurements With Capillary Rheometer**

The shear viscosity data was obtained from rheological measurements in an Instron Capillary rheometer model 3211 with the following characteristics:

- Plunger diameter: 9.420 mm
- Barrel diameter: 9.525 mm
- Velocity range: 0.012-40 cm/min
- Load cell force range: 50 kg-2 ton.

Three capillary geometries with length to diameter ratios, \( L/D \), of 99.4, 133.3, and 199.8 were used in order to cover the shear rates of interest. The covered shear rates were in the range of 4 to 1700 s\(^{-1}\). The viscosity was measured at 200, 220, and 240°C. The experimental procedure was performed according to ASTM-D-3835. The Rabinowitsch correction was applied in the calculation of the wall shear rate, due to the non-Newtonian character of the tested melts. Effects of the capillary ends were neglected as the length to diameter ratios were sufficiently high.

**Measurements of Die Swell**

Die swell measurements for the two grades of polypropylene, GE6100 and TY6100, were performed employing the same capillaries that were used in the measurements of shear viscosity. In addition for the grade GE6100, die swell was measured after the material was extruded from a 60 mm extruder which is also used in the computer simulations of the extrusion of polypropylene in Part II (5). In all experiments in both capillary dies and extruder die, the difference between bulk and wall temperature was less than 15 K so that inelastic die swell (20) due to local thermal differences could be ignored.

In the experimental procedure employed in the capillary rheometer, first the pressure drop was allowed to reach its steady state value. Second, the first 5 cm of extrudate was cut and discarded. As the fresh extrudate emerged, a 4 cm sample was cut just after the die and left to cool in the air at room temperature. Then it was transferred to a silicone oil bath at 170°C to anneal for 15 min in order to release the frozen-in stresses built-up during the cooling stage and achieve an equilibrium state. The extrudate was then cooled in...
air at room temperature and its diameter was measured at 1 cm from the lower end of the extrudate with a micrometer to the nearest 0.01 + 0.005 mm.

Since the die swell measured as above refers to the frozen extrudate, a correction must be made to calculate the die swell of the molten extrudate at the extrusion temperature, taking into account the density difference between frozen and molten extrudates. The included correction was of the form (21, 22).

\[ B_{\text{molten}} = B_{\text{frozen}}\left(\rho_{\text{frozen}}/\rho_{\text{molten}}\right)^{1/3} \quad (13) \]

where \( \rho_{\text{frozen}} \) and \( \rho_{\text{molten}} \) are the density of the frozen polymer and the specific volume of the molten polymer, respectively.

In the die swell measurements carried out in the 60 mm extruder, a die of 4.1 mm diameter and 35 mm length was used. The die temperature was 230°C. The melt temperature as measured with a portable pirometer at die exit was 221°C. After the extrusion was stabilized, the first 10 cm of extrudate was discarded and from there on samples of 6 mm long were collected and quenched in a water bath to room temperature. Four groups of five samples each were then formed. The extrudate diameter in each group was estimated as the mean of the diameters situated at an angle of 90° from each other. This procedure was used in order to compensate for any distortion of the extrudate cross-section while carrying the strand from the die to the water bath.

In the first group of frozen extrudates, group 1, the diameter was measured after the water bath. In the second group, group 2, the strands after the water bath were left to anneal at room temperature for 48 h before having their diameters measured. In groups 3 and 4, the extrudates were annealed at 170°C for 15 min in an oven and in a silicone oil bath, respectively. Finally, the die swells for all groups were corrected to the extrusion temperature as stated previously.

### RESULTS AND DISCUSSION

**Melt Viscosity**

The melt flow index (MFI) for the two polypropylene grades was measured at 230°C. GE6100 grade had an MFI of 0.7 g/10min and TY6100 had an MFI of 15.0 g/10min. The more viscous grade GE6100 has clearly a higher average molecular weight as is confirmed from the measurement of molecular weights during the characterization of the two polypropylene grades in Materials.

Figures 3 and 4 display the shear viscosity as a function of shear rate for polypropylene grades GE6100 and TY6100, respectively, at 200, 220, and 240°C as measured in the capillary rheometer. After a regression analysis the following Power-law relations were fitted for the two polypropylene grades:

**GE6100:**

\[ \eta = 18590 \exp[2778(1/T - 1/473)]\gamma^{-0.645} \quad (14) \]

**TY6100:**

\[ \eta = 2730 \exp[4865(1/T - 1/473)]\gamma^{-0.468} \quad (15) \]

where \( \eta \) is in Pa's and \( T \) is in K. In the considered range of temperatures the power-law index, \( n \), varied between 0.33 and 0.39 for GE6100 and between 0.49 and 0.56 for TY6100. An average \( n \) over the above range of temperatures was finally selected for each grade. GE6100, the grade with the higher average molecular weight, is more viscous and displays more shear thinning behavior, as expected.

The polynomial relation (Eq 3) was also fitted to the experimental data of shear viscosity for the two polypropylene grades and the results are summarized in Table 1. The polynomial relation (Eq 3) fits the experimental data better, with smaller deviations, over the covered range of temperatures and shear rates.

**Table 1. Calculated Constants in Eq 3 where \( \eta \) is in Pa's, \( T \) is in K and \( \gamma \) is in s⁻¹.**

<table>
<thead>
<tr>
<th>Constants</th>
<th>( b_0 )</th>
<th>( b_1 )</th>
<th>( b_2 )</th>
<th>( b_3 )</th>
<th>( b_4 )</th>
<th>( b_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GE6100</td>
<td>-4.33</td>
<td>-1.088</td>
<td>-0.048</td>
<td>0.040</td>
<td>-0.000047</td>
<td>0.00127</td>
</tr>
<tr>
<td>TY6100</td>
<td>12.22</td>
<td>-1.048</td>
<td>-0.069</td>
<td>-0.029</td>
<td>0.0000216</td>
<td>0.00017</td>
</tr>
</tbody>
</table>

**Fig. 3. Flow curve for polypropylene grade GE6100.**

**Fig. 4. Flow curve for polypropylene grade TY6100.**
Die Swell

Measurements of die swell were taken when the melt was extruded in the capillary rheometer under shear rates in the range of 4 to 450 s⁻¹ and at three temperatures, namely 473, 493, and 513 K. Equation 10 was tried first to fit the experimental data, including elastic and Newtonian swelling. A non-linear regression analysis yielded the following relations for the two polypropylene grades:

GE6100: \( B_\ast = [1 + 0.009276 \tau_W^{4.5844}]^{1/6} + 0.12 \) (16)

TY6100: \( B_\ast = [1 + 0.183756 \tau_W^{2.2076}]^{1/6} + 0.12 \) (17)

Figures 5 and 6 illustrate how the above best fitted relations compare with experimental data. It can be seen that for the grade TY6100 deviations exist after a certain critical shear stress, with the predictions being lower than the experimental data. Consequently, the alternative Eq. 12 suggested by Huang and White (19) was employed for TY6100 after \( \tau_W = 70 \) kPa, yielding the relation:

TY6100: \[ B_\ast = \frac{7.2935}{\tau_W} + 1.099 \times 10^{-5} \tau_W^{3.5866} \] + 0.12 for \( \tau_W > 70 \) kPa (18)

The combination of Eqs 17 and 18 resulted in predictions closer to the die swell measurements for TY6100. For GE6100 on the other hand, Eq 16 was considered satisfactory for the whole region of the shear stresses employed.

For both polypropylene grades, die swell increased with increasing wall shear stresses and shear rates, as expected. The temperature dependence of die swell is illustrated in Figs. 7 and 8, showing that for a constant shear rate die swell decreases with increasing melt temperatures. This can be attributed to the lower molecular orientation at higher temperatures. The temperature dependence of die swell was less pronounced in GE6100, which has on average longer molecular chains. Generally, TY6100 displayed a smaller die swell than GE6100 under the same shear and temperature conditions. This can be explained by the fact that polymers with low molecular weights show smaller swell due to the absence of very long molecules which are mainly responsible for elastic effects in polymers melts. Furthermore, the lower viscosity of TY6100 reduced the wall shear stress, leading to a smaller extent of molecular orientation than in GE6100. At low shear stresses and especially high temperatures, the die swell ratio in TY6100 is very close to the Newtonian die swell of 1.12. The same behavior is not encountered in GE6100, implying a more elastic behavior for this grade due to its higher molecular weight.
In measuring the die swell in GE6100 after its extrusion in a commercial extruder, the effects of cooling and annealing after the die were investigated. Table 2 presents the measured die swell for the four methodologies employed. In a comparison between the results in groups 1 and 2, a very small decrease in die swell of 1.3% was observed 48 h after cooling due to post-crystallization. Comparing groups 4 and 5 with group 2, annealing in a hot oven and annealing in a silicone oil bath brought increases in die swell of 6.1 and 8.8%, respectively. Obviously, annealing in a silicone oil bath is more effective in relaxing the stresses than annealing in a hot oven.

## CONCLUSIONS

In this study, rheological measurements were carried out for two polypropylene grades of different molecular weights to determine the flow behavior and the die swell in extrusion over a range of shear rates and temperatures. The power-law index was found to be reasonably constant over the covered range of shear rates between 4 to 1000 s⁻¹. However, the power-law index changed when the temperature variation exceeded 20 K. Both consistency and power-law index varied with the molecular weight. With increasing Mw, the consistency increased and the power-law index decreased, displaying a higher extent of shear thinning behavior. The polynomial equation (Eq. 3) yielded a better agreement between experimental and predicted viscosities for the two grades of polypropylene than the power-law.

Four different techniques were tested in the measurement of die swell including various conditions of cooling and annealing. It was concluded that annealing in silicone oil plays an important role in the stress relaxation and increase of die swell. A correction factor was employed in order to take into account differences in density between the frozen extrudate and the molten extrudate at extrusion temperature.

A correlation for predicting the isothermal asymptotic die swell as a function of shear stress at the wall was derived for dies of circular cross-section by curve fitting Eqs 10 and 12 to experimental data of die swell. Equation 10 predicted the die swell of grade GE6100 reasonably well over the whole range of shear stresses employed. However, in the case of the lower molecular weight grade TY6100, the same equation did not hold over the entire range of shear stresses used. Hence, Eq 12 was employed to simulate the die swell above a critical wall shear stress which was found to be approximately 70 kPa. Both Eqs 10 and 12 did not include any contributions from the inelastic stress relaxation and the residual relaxation of the first normal stress difference. The latter is encountered when the die length to diameter ratio is small.

## NOMENCLATURE

\[ a, A = \text{Constants in Eq } 8. \]
\[ a_1, a_2, A_1, A_2 = \text{Constants in Eq } 11. \]
\[ B = \text{Die swell ratio.} \]
\[ B_\infty = \text{Asymptotic die swell ratio.} \]
\[ b_0, b_1, b_2, b_3, b_4, b_5 = \text{Empirical constants in Eq } 3. \]
\[ G = \text{Elastic shear modulus.} \]
\[ m = \text{Consistency.} \]
\[ n = \text{Power-law index.} \]
\[ N_1 = \text{First normal stress difference.} \]
\[ R = \text{Universal gas constant.} \]
\[ T = \text{Temperature.} \]
\[ v = \text{Specific volume.} \]

## GREEK SYMBOLS

\[ \dot{\gamma} = \text{Shear rate.} \]
\[ \gamma = \text{Recoverable shear.} \]
\[ \Delta E = \text{Flow activation energy.} \]
\[ \epsilon = \text{Recoverable strain.} \]
\[ \eta = \text{Viscosity.} \]
\[ \rho = \text{Density.} \]
\[ \tau_{11}, \tau_{22} = \text{Normal stresses.} \]
\[ \tau_{12} = \text{Shear stress.} \]
\[ \tau_{w} = \text{Wall shear stress.} \]
\[ \tau_{ws} = \text{Critical wall shear stress.} \]

## REFERENCES
