Tubing Extrusion of a Fluoropolymer Melt

The tubing extrusion-forming process of a fluoropolymer (FEP) melt was studied both experimentally and numerically. The flow behaviour of a FEP resin was determined by using a tubular die used in industrial-scale operations and these data were compared with simulation results using (i) a viscous model (Cross) and (ii) a viscoelastic one (the Kaye–Bernstein, Kearsley, Zapas / Papanastasiou, Scriven, Maccor or K-BKZ/PSM model) in order to assess the viscoelastic effects. In all simulations, compressibility, thermal and pressure effects on viscosity were taken into account. It was found that the viscoelastic results for the pressure, and hence the stresses at the wall, were always higher than the viscous results. Both were higher than the experimental results. A quadratic slip model plus viscoelasticity was found necessary to reproduce the experiments. The smooth flow curves resulting from this industrial tubular-coating die are a further manifestation that this is an appropriate design for coating fluoropolymers at very high apparent shear rates, exceeding 5000 s⁻¹.

1 Introduction

Fluoropolymers are of great commercial and scientific interest due to their unique combination of properties. These include excellent chemical stability and dielectric properties, anti-stick characteristics, mechanical strength, and low flammability (Imbalzano and Kerbow, 1994; Ebnesajjad, 2003). Their most important uses are in electronics and electrical applications, especially for wiring insulation, chemical processing equipment, medical devices and laboratory ware and tubing (Ebnesajjad, 2003; Domininghaus, 1993; Dealy and Wisbrun, 1990). The main focus of this work is on the process of tubing extrusion of FEP copolymers (Baird and Collias, 1998; Tadmor and Gogos, 2006).

The capillary extrusion flow of this resin and its complete rheological characterizations was previously studied by Rosenbaum et al. (1995, 1998, 2000) and more recently by Mitsoulis and Hatzikiriakos (2012). These rheological data are used in the present study to formulate the constitutive equations needed for the flow simulations in tubing extrusion dies. In particular a viscous Cross model and a viscoelastic K-BKZ are used to address various effects discussed below (Rosenbaum, 2000; Mitsoulis and Hatzikiriakos, 2012).

The extrusion tubing process of polytetrafluoroethylene (PTFE) paste has been studied by Patil et al. (2006, 2008). Specifically, Patil et al. (2006) have derived an analytical expression to predict the pressure drop in annular dies for flow of PTFE paste. The model predictions were compared with experimental results in PTFE paste extrusion to examine formability of tubing through annular dies of various geometries (Patil et al., 2008). Due to its high melting point (greater than 340 °C), PTFE can only be processed in the form of paste at temperatures between 35 to 50 °C. However, copolymers of PTFE, such as the FEP resins considered in the present work, have considerably lower melting points (less than 260 °C) and thus their melt processing is possible. Melt tubing extrusion is the subject of the present study.

Ferrandino (2004a, 2004b) reviewed the extrusion tubing process from the point of view of material (melt) and control of extrusion process, and made specific recommendations to produce tubing with consistent properties, particularly in medical applications. Guo and Stehr (2001) presented a semi-analytical method for the design of crosshead annular dies by considering simplified versions of the equations of motion and energy as approximations of the flow channel using a series of varying annular slits, each having constant geometric parameters. The analysis was performed using a Cross model fitted to experimental data for an isotactic polypropylene (i-PP). They reported that the optimum die designs are related, but less sensitive to extrusion conditions within a certain range, i.e., pulling speeds of the tube. More recently, Kolitawong et al. (2011) studied the temperature distribution of a power-law fluid in a pressure-driven axial flow between isothermal eccentric cylinders. Eccentricity is used to balance the expected sagging during the cooling process. They found that the dimensionless temperature profile depends upon the radius ratio of the inner to outer cylinders, the eccentricity, the angular position, and the power-law exponent n. They have also reported that the temperature is a strong function of the gap between the cylinders. The temperature profiles are flat in the middle of the gap and then, near the wall, suddenly drop to the wall temperature.

The main objective of the study is to model the tubing process of melt-processible fluoropolymers. The flow model predictions are performed using both a viscous and a viscoelastic model and these are compared with experimental results obtained from industrial-scale tubing dies for a certain fluoropolymer (FEP). The tubing simulation model includes all important effects in a full numerical scheme, such as pressure- and temperature-dependence of viscosity, compressibility, vis-
cous dissipation, slip-at-the-wall, and viscoelasticity through an appropriate integral constitutive equation.

2 Experimental

Tubing extrusion experiments were performed for the FEP-4100 resin (a copolymer of tetrafluoroethylene and hexafluoropropylene) using a tubing extrusion die. This resin has been rheologically characterized previously in detail by Rosenbaum et al. (1995, 1998, 2000), and Mitsoulis and Hatzikiriakos (2012). It has a molecular weight of about 208,000 and a polydispersity index of about 2 (Ferrandino, 2004a; 2004b). The melting point of this resin is around 260°C, determined by differential scanning calorimetry (DSC) analysis. The rheological parameters determined by fitting the experimental results are summarized in Tables 1 to 3. These include the parameters of the Cross and power-law models for the viscosity of the fluoropolymer (Table 1), the parameters for the K-BKZ viscoelastic constitutive model (Table 2), and the physical properties of the FEP-4100 needed for the non-isothermal flow simulations (Table 3). The data in these Tables are also discussed in more detail below.

A schematic of the tubing extrusion die used in the experiments and the numerical simulations appears in Fig. 1 (Buckmaster et al., 1997; Dupont de Nemours, 1998). While the details of the design are given in Table 4. It is a special annular crosshead die attached to the rheometer to mimic the tubing extrusion process. This crosshead die included dies and tips (internal diameter) with equal entry cone angles of 2α = 60° and die land length L of 7.62 mm. In the present work we report data obtained with a die diameter D of 3 mm and a tip diameter d of 1.52 mm. The molten polymer enters the tapered die via the uppermost port and is forced around the wire tip guide towards the die orifice. The wire tip guide serves as a mandrel for the molten polymer, giving the extrudate a tubular shape. The die land passage forms the exterior surface of the tubular shape, and the exterior surface of the cylindrical exten-

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_0, C )</td>
<td>1542.3 Pa·s</td>
<td>This work</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>0.0049 s</td>
<td>This work</td>
</tr>
<tr>
<td>( \eta_C )</td>
<td>0.316</td>
<td>This work</td>
</tr>
<tr>
<td>( K )</td>
<td>11,931 Pa·s^n</td>
<td>This work</td>
</tr>
<tr>
<td>( n )</td>
<td>0.5</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 1. Parameters for the FEP melt obeying the Cross model (Eq. 8) and the power-law model (Eq. 10) at 371°C

<table>
<thead>
<tr>
<th>k</th>
<th>( \lambda_k ) (s)</th>
<th>( a_k ) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.337 \times 10^{-3}</td>
<td>0.49050 \times 10^{6}</td>
</tr>
<tr>
<td>2</td>
<td>0.178 \times 10^{-2}</td>
<td>0.22702 \times 10^{6}</td>
</tr>
<tr>
<td>3</td>
<td>0.865 \times 10^{-2}</td>
<td>66,224</td>
</tr>
<tr>
<td>4</td>
<td>0.562 \times 10^{-1}</td>
<td>4823.1</td>
</tr>
<tr>
<td>5</td>
<td>0.488</td>
<td>172.41</td>
</tr>
<tr>
<td>6</td>
<td>2.98</td>
<td>18,628</td>
</tr>
<tr>
<td>7</td>
<td>16.6</td>
<td>3,6235</td>
</tr>
</tbody>
</table>

Table 2. Relaxation spectrum and material constants for the FEP melt obeying the K-BKZ model (Eq. 13) at 371°C (\( \alpha = 7.174, \beta = 0.6, \theta = -0.11, \lambda = 0.76 s, \eta_0 = 1.613 Pa \cdot s) \)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_\text{c} )</td>
<td>0.00095 MPa^{-1}</td>
<td>Hatzikiriakos and Dealy (1994)</td>
</tr>
<tr>
<td>( \beta_0 )</td>
<td>0.03 MPa^{-1}</td>
<td>Rosenbaum et al. (1995)</td>
</tr>
<tr>
<td>( \eta_0 )</td>
<td>1.39 \times 10^{-4} Pa·s^{-1}</td>
<td>Mitsoulis and Hatzikiriakos (2012)</td>
</tr>
<tr>
<td>( \eta_b )</td>
<td>0.54</td>
<td>This work</td>
</tr>
<tr>
<td>( \beta_{st} )</td>
<td>400 cm/(s·MPa^{0.5})</td>
<td>This work</td>
</tr>
<tr>
<td>( b )</td>
<td>2.0</td>
<td>This work</td>
</tr>
<tr>
<td>( \rho )</td>
<td>1.492 g/cm³</td>
<td>Ebnesajjad (2000)</td>
</tr>
<tr>
<td>( C_p )</td>
<td>0.96 J/(g·K)</td>
<td>Van Krevelen (1990)</td>
</tr>
<tr>
<td>( k )</td>
<td>0.00255 J/</td>
<td>Van Krevelen (1990)</td>
</tr>
<tr>
<td>( n )</td>
<td>0.00095 MPa -1</td>
<td>Rosenbaum et al. (1995)</td>
</tr>
<tr>
<td>( E )</td>
<td>8.3143 J/(mol·K)</td>
<td>Dealy and Wissbrun (1990)</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>371°C (644 K)</td>
<td>Rosenbaum et al. (1995)</td>
</tr>
</tbody>
</table>

Table 3. Values of the various parameters for the FEP melt at 371°C

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall die length</td>
<td>( Z_{max} )</td>
<td>60.6 mm</td>
</tr>
<tr>
<td>Channel entry gap</td>
<td>( H_{en} )</td>
<td>3 mm</td>
</tr>
<tr>
<td>Tapered length</td>
<td>( L_t )</td>
<td>15.25 mm</td>
</tr>
<tr>
<td>Half cone angle</td>
<td>( \alpha )</td>
<td>30°</td>
</tr>
<tr>
<td>Minimum tapered gap</td>
<td>( f )</td>
<td>1.2 mm</td>
</tr>
<tr>
<td>Die land length</td>
<td>( L )</td>
<td>7.62 mm</td>
</tr>
<tr>
<td>Outer die diameter</td>
<td>( D )</td>
<td>3 mm</td>
</tr>
<tr>
<td>Inner die (tip) diameter</td>
<td>( d )</td>
<td>1.524 mm</td>
</tr>
<tr>
<td>Die land gap</td>
<td>( h )</td>
<td>0.738 mm</td>
</tr>
<tr>
<td>Wire diameter</td>
<td>( d_w )</td>
<td>0.574 mm</td>
</tr>
<tr>
<td>Die temperature</td>
<td>( T_0 )</td>
<td>371°C (644 K)</td>
</tr>
</tbody>
</table>

Table 4. Design parameters of the Nokia Maillefer 4/6 crosshead die (Dupont de Nemours, 1998)

Fig. 1. Nokia Maillefer 4/6 crosshead die design for tubing coating with dimensions in mm (not in scale) (Dupont de Nemours, 1998). Data given in Table 4

3 Governing Equations and Rheological Modelling

We consider the conservation equations of mass, momentum and energy for weakly compressible fluids under non-isothermal, creeping, steady flow conditions. These are written as (Mitsoulis et al., 1988; Tiu et al., 1989; Tanner, 2000):

\[
\begin{align*}
\bar{u} \cdot \nabla \rho + \rho (\nabla \cdot \bar{u}) &= 0, \\
0 &= -\nabla p + \nabla \cdot \bar{\varepsilon}, \\
\rho C_p \bar{u} \cdot \nabla T &= k \nabla^2 T + \bar{\varepsilon} : \nabla \bar{u},
\end{align*}
\]

where \( \rho \) is the density, \( \bar{u} \) is the velocity vector, \( p \) is the pressure, \( \bar{\varepsilon} \) is the extra stress tensor, \( T \) is the temperature, \( C_p \) is the heat capacity, and \( k \) is the thermal conductivity. For a \textit{weakly compressible} fluid, pressure and density are connected as a first approximation through a simple linear thermodynamic equation of state (Tanner, 2000):

\[
\rho = \rho_0 (1 + \beta_\varepsilon p),
\]

where \( \beta_\varepsilon \) is the isothermal compressibility with the density to be \( \rho_0 \) at a reference pressure \( p_0 (= 0) \).

The viscous stresses are given for inelastic non-Newtonian compressible fluids by the relation (Tanner, 2000):

\[
\bar{\varepsilon} = \eta(|\dot{\gamma}|) \left( \dot{\gamma} - \frac{2}{3} \left( \nabla \cdot \dot{\bar{u}} \right) I \right),
\]

where \( \eta(|\dot{\gamma}|) \) is the non-Newtonian viscosity, which is a function of the magnitude \( |\dot{\gamma}| \) of the rate-of-strain tensor \( \dot{\gamma} = \nabla \bar{u} + \nabla \bar{u}^T \), which is given by:

\[
|\dot{\gamma}| = \sqrt{\frac{1}{2} \Pi_{\dot{\gamma}}} = \left( \frac{1}{2} \left( \frac{\nabla \cdot \dot{\gamma}}{\dot{\gamma}} \right) \right)^{1/2},
\]

where \( \Pi_{\dot{\gamma}} \) is the second invariant of \( \dot{\gamma} \):

\[
\Pi_{\dot{\gamma}} = \frac{\nabla \cdot \dot{\gamma}}{\dot{\gamma}} = \sum_i \sum_j \gamma_{ij} \dot{\gamma}_{ij}.
\]

The tensor \( \bar{\gamma} \) in Eq. 5 is the unit tensor.

To evaluate the role of viscoelasticity in flow through a tubbing die, it is instructive to consider first purely viscous models in the simulations. Namely, the Cross model was used to fit the shear viscosity data of the FEP melt. The Cross model is written as (Dealy and Wissbrun, 1990):

\[
\eta = \frac{\eta_{0C}}{1 + (\lambda \gamma)^{nC}},
\]

where \( \eta_{0C} \) is the Cross zero-shear-rate viscosity, \( \lambda \) is a time constant, and \( nC \) is the Cross power-law index. The experimental data of FEP were obtained at 300°C, 325°C, and 350°C (Rosenbaum et al., 1995), while the experiments with the tubing die were performed at 371°C. The data has been shifted to 371°C by using the Arrhenius relationship (Dealy and Wissbrun, 1990) for the temperature-shift factor \( \alpha_T \):

\[
\alpha_T(T) = \frac{\eta}{\eta_0} = \exp \left[ \frac{E}{R_g \left( \frac{1}{T} - \frac{1}{T_0} \right)} \right].
\]

In the above, \( \eta_0 \) is a reference viscosity at \( T_0 \), \( E \) is the activation energy, \( R_g \) is the ideal gas constant, and \( T_0 \) is a reference temperature (in K). The activation energy was calculated from the shift factors determined by applying the time-temperature superposition principle to obtain the curves at 371°C plotted in Fig. 2 (Dealy and Wissbrun, 1990; Mitsoulis and Hatzikiarikos, 2012). It was found that \( E = 50,000 \) J/mol. The newly fitted viscosity of the FEP melt by Eq. 8 is also plotted in Fig. 2 (line), while the parameters of the model are listed in Table 1. We observe that the FEP melt has a wide Newtonian plateau and then shows shear-thinning for shear rates above 10 s⁻¹ giving a power-law index \( n_C = 0.32 \). The Cross model fits the data well over the range of experimental results. The same is also true for the viscoelastic K-BKZ model (see below).

For easy checks and simple analytical formulas, the high shear-rate range of the viscosity data can be fitted to the power-law model for the viscosity (Dealy and Wissbrun, 1990):

\[
\eta = K|\dot{\gamma}|^{n-1},
\]

where \( K \) is the consistency index and \( n \) is the power-law index. These values are also given in Table 1. We note here that the Cross model will turn into a power-law model for high shear rates so the power-law exponent in the Cross model should be the same as in the power-law model. We have tried to do this, but for narrow molecular weight distribution FEP melts with a Newtonian plateau over a wide range of shear rates and a small \( \lambda \) (0.0049 s), the power law gives a good fit only at extremely high shear rates beyond the range of available experimental data (above 5000 s⁻¹). Then the fitting misses all the points
for which runs were made. This is not the case with polydisperse polyethylenes (Ansari et al., 2010), where the onset of shear-thinning occurs early, \( \lambda \) is above 1 s, and the power-law fitting does a good job over a wide range of shear rates. We have thus fitted the power-law constants as shown in Table 1 and Fig. 2.

The viscosity of this resin also depends on the pressure for which the Barus equation can be used (Dealy and Wissbrun, 1990; Baird and Collias, 1998; Tadmor and Gogos, 2006; Sedlacek et al., 2004; Carreras et al., 2006):

\[
\eta_p = \eta_0 \exp \left( \beta_p p \right),
\]

where \( \eta \) is the viscosity at absolute pressure \( p \), \( \eta_0 \) is the viscosity at ambient pressure, and \( \beta_p \) is the pressure-shift factor. The latter was found to depend on pressure through the following equation (Mitsoulis and Hatzikiriakos, 2012):

\[
\beta_p = mp^{-n_p},
\]

where \( m = 1.39 \times 10^{-4} \text{ Pa}^{-n_p-1} \) and \( n_p = 0.54 \), with the pressure \( p \) given in Pa (Mitsoulis and Hatzikiriakos, 2012).

Viscoelasticity is included in the present work via an appropriate rheological model for the stresses. This is a K-BKZ constitutive equation (Eq. 13) as a contribution to the viscous dissipation term.

\[
\tau = \frac{1}{1-\theta} \int_{-\infty}^{t} \sum_{k=1}^{N} \frac{\alpha_k}{\alpha_0} \exp \left( -\frac{t-t'}{\lambda_k} \right) \left[ C^{-1}_i \left( t' \right) + \frac{\delta C_i}{\delta t} \right] dt',
\]

where \( t \) is the current time, \( \lambda_k \) and \( \alpha_k \) are the relaxation times and relaxation modulus coefficients, \( N \) is the number of relaxation modes, \( \alpha \) and \( \beta \) are material constants, and \( I_c, C^{-1}_i \) are the first invariants of the Cauchy-Green tensor \( C_i \) and its inverse \( C^{-1}_i \), the Finger strain tensor. The material constant \( \theta \) is given by

\[
\theta = \frac{N_2}{N_1} = \frac{\theta}{1-\theta},
\]

where \( N_1 \) and \( N_2 \) are the first and second normal stress differences, respectively. It is noted that \( \theta \) is not zero for polymer melts, which possess a non-zero second normal stress difference. Its usual range is between \( -0.1 \) and \( -0.2 \) in accordance with experimental findings (Dealy and Wissbrun, 1990; Tanner, 2000). The various parameters needed for this model are summarized in Table 2 (Kajiwara et al., 1995), where the relaxation times have been shifted to the new temperature of 371°C by diving the values at the reference temperature of 300°C by \( \alpha_T = 3.4 \).

Fig. 3 plots a number of calculated and experimental material functions for the FEP melt at 371°C. Namely, data for the shear viscosity, \( \eta_S \), the elongational viscosity, \( \eta_E \), and the first normal stress difference, \( N_1 \), are plotted as functions of corresponding rates (shear or extensional).

The non-isothermal modeling follows the one given in earlier publications (see, e.g., Luo and Tanner, 1987; Luo and Mitsoulis, 1990; Alaie and Papanastasiou, 1993; Barakos and Mitsoulis, 1996; Peters and Baaijens, 1997; Beaulne and Mitsoulis, 2007) and will not be repeated here. Suffice it to say that it employs the Arrhenius temperature-shifting function, \( \alpha_T \), given by Eq. 9. The various thermal parameters needed for the simulations are gathered in Table 3 together with their source (Van Krevelen, 1990; Hatzikiriakos and Dealy, 1994; Ebnesajjad, 2000; Mitsoulis and Hatzikiriakos, 2012). The viscoelastic stresses calculated by the non-isothermal version of the above constitutive equation (Eq. 13) enter in the energy equation (Eq. 3) as a contribution to the viscous dissipation term.

The various thermal and flow parameters are combined to give appropriate dimensionless numbers (Winter, 1977; Ansari et al., 2010). The relevant ones here are the Peclet number, \( Pe \), and the Nahme-Griffith number, \( Na \). These are defined as:

\[
Pe = \frac{\rho C_p Uh}{k},
\]

\[
Na = \frac{\eta EU^2}{kR_s T_0^2},
\]

where \( \eta = f(U/h) \) is a nominal viscosity given by the Cross model (Eq. 8) at a nominal shear rate of \( U/h \). In the above, \( U \) is the average velocity in the die \( [U = 4Q/(\pi(D^2-d^2))] \), where \( Q \) is the volumetric flow rate, and \( h \) is the die gap \( [h = (D-d)/2] \). The \( Pe \) number represents the ratio of heat convection to conduction, and the \( Na \) number represents the ratio of viscous dissipation to conduction and indicates the extent of coupling between the momentum and energy equations. A thorough discussion of these effects in non-isothermal polymer melt flow is given by Winter (1977).

With the above properties and a characteristic length the die gap \( h = 0.0738 \text{ cm} \), the dimensionless thermal numbers are in the ranges: \( 41 < Pe < 2860, 0.007 < Na < 10.9 \), showing a strong convection (\( Pe >> 1 \)), and a moderate to strong coupling between momentum and energy equations (\( Na >> 1 \)). A value of \( Na > 1 \) indicates temperature non-uniformities generated by viscous dissipation, and a strong coupling between momentum and energy equations. More details are given in Table 5.
Similarly, the compressibility coefficient $B_c$ is defined as:

$$B_c = \frac{\beta_c R}{h}.$$  (20)

The value $B_c = 0$ corresponds to the case of pressure-independence of the viscosity, and $B_c = 0$ to incompressible flow. For the present data, the range of values is: $5.4 \times 10^{-4} < B_p < 1.1 \times 10^{-2}$ and $1.7 \times 10^{-2} < B_c < 3.6 \times 10^{-4}$, showing a moderate dependence of viscosity on pressure and an even weaker compressibility effect in the range of simulations. More details are given in Table 5.

In the case of slip effects at the wall, the usual no-slip velocity at the solid boundaries is replaced by a slip law of the following form (Dealy and Wissbrun, 1990):

$$a_T u_s = -\beta_{sl} \sigma_n,$$  (21)

where $u_s$ is the slip velocity, $\sigma_n$ is the shear stress at the die wall, $\beta_{sl}$ is the slip coefficient, and $b$ is the slip exponent. It should be noted that the shift-factor $a_T$ is used here to take into account the temperature effects of the slip law at different temperatures.

In 2-D simulations, the above law means that the tangential velocity on the boundary is given by the slip law, while the normal velocity is set to zero, i.e.,

$$\beta_{sl} (\hat{n} \cdot \vec{c}) = a_T (\vec{c} \cdot \hat{n}) = 0.$$  (22)

where $\hat{n}$ is the unit outward normal vector to a surface, $\vec{c}$ is the tangential unit vector in the direction of flow, and the rest of symbols are defined above. Implementation of slip in similar flow geometries for a polypropylene (PP) melt has been previously carried out by Mitsoulis et al. (2005) and more recently in annular dies by Chatzimina et al. (2009).

The corresponding dimensionless slip coefficient, $B_{sl}$, is a measure of fluid slip at the wall:

$$B_{sl} = \frac{\beta_{sl} \hat{n}^b}{U} \left( \frac{U}{h} \right)^b.$$  (23)

The value $B_{sl} = 0$ corresponds to the no-slip boundary conditions and $B_{sl} \approx 1$, to a macroscopically obvious slip. For the present data, the range of values is: $0.129 < B_{sl} < 0.821$, showing a moderate to strong slip effect in the range of simulations. More details are given in Table 5. We also note in passing that the creeping flow approximation (for which the Reynolds number, $Re = \rho U h / \eta \approx 0$) is justified due to the high viscosity of the melt, which gives even for the highest apparent shear rate of experiments, $Re < 10^{-3}$.

### 4 Method of Solution

The solution of the above conservation and constitutive equations is carried out with two codes, one for viscous flows (u-v-p-T-h formulation) (Hannachi and Mitsoulis, 1993) and one for viscoelastic flows (Luo and Mitsoulis, 1990; Barakos and

<table>
<thead>
<tr>
<th>Apparent shear rate, $\dot{\gamma}_A$ (s$^{-1}$)</th>
<th>Peclet number, $Pe$</th>
<th>Nahme number, $Na$</th>
<th>Compressibility parameter, $B_c$</th>
<th>Pressure-shift parameter, $B_p$</th>
<th>Slip parameter, $B_{sl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>41</td>
<td>0.007</td>
<td>$1.69 \times 10^{-5}$</td>
<td>$5.35 \times 10^{-4}$</td>
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</tr>
<tr>
<td>320</td>
<td>163</td>
<td>0.10</td>
<td>$5.59 \times 10^{-5}$</td>
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<tr>
<td>800</td>
<td>407</td>
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<tr>
<td>1600</td>
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</tr>
<tr>
<td>5600</td>
<td>2859</td>
<td>10.89</td>
<td>$3.57 \times 10^{-4}$</td>
<td>$1.13 \times 10^{-2}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Range of the dimensionless parameters in the flow of FEP melt at 371°C (die land gap $h = 0.0738$ cm)
Mitsoulis, 1996). The boundary conditions (BC) for the problem at hand are well known. Briefly, we assume no-slip (or slip when included) and a constant temperature $T_0$ at the solid walls; at entry, a fully-developed velocity profile is imposed, corresponding to the flow rate at hand and a constant temperature $T_0$ is assumed; at the outlet, zero surface traction and zero heat flux are assumed.

The viscous simulations are extremely fast and are used as a first step to study the whole range of parameter values and die designs. The viscoelastic simulations admittedly are harder to do and they need good initial flow fields to get solutions at elevated apparent shear rates. In our recent work (Ansari et al., 2010), we explained how it was possible for the first time to do viscoelastic computations up to very high apparent shear rates ($1000 \text{ s}^{-1}$) with good results. Briefly, the solution strategy starts at a given apparent shear rate from the viscous non-isothermal solution without pressure dependence, and then using this as an initial solution it continues for the non-isothermal viscoelastic solution with all effects present. When slip is present, the simulations are much faster as they require fewer iterations due to the less drastic conditions encountered in the flow field.

All velocities have been made dimensionless with the average velocity $U$. The lengths could have been made dimensionless either with die gap $h$ or with the wire radius $R_w$, which is $0.4 \text{ h}$. We have opted for the latter, since in wire coating it is customary to use the wire radius for dimensionalization. Then the pressures and stresses are made dimensionless by $\eta_0 U/R_w$, where $\eta_0$ is the zero-shear rate viscosity.

5 Experimental Results

Fig. 4 shows the apparent flow curves for the resin (FEP 4100) obtained with the tubular die using a $d = 1.524 \text{ mm}$ tip and $D = 3 \text{ mm}$ die at $T = 371^\circ \text{C}$. The apparent shear rate was calculated by using the formula which applies to slit dies (Dealy and Wissbrun, 1990):

$$ \dot{\gamma}_A = \frac{6Q}{0.25(D-d)^3\pi(D+d)} $$

where $Q$ is the volumetric flow rate, $d$ and $D$ is the tip and die diameter, respectively. The apparent wall shear stress was estimated as the average of the stress at the inner and outer walls by using the following formula for a power-law fluid (Hanks and Larsen, 1979):

$$ \tau_{rz} = \frac{A p D}{4L} \left(2r \right)^{1-n} \frac{3D}{2r} $$

where $\tau_{rz}$ is the shear stress at radius $r$, $A p$ is the pressure drop (measured experimentally by means of a load cell that measures the force needed to displace the polymer melt through the reservoir and die), $L$ is the length of the die land, and $c$ is a parameter which depends on the geometry and the power-law index. For a power-law index of $n = 0.5$ and a diameter ratio $\kappa = d/D = 0.508$, we find from tables $c = 0.7283$ (Hanks and Larsen, 1979).

A smooth flow curve is observed in Fig. 4 which increases monotonically, an indication of a good design. Together with the experimental data are shown simulation results by the purely viscous Cross model with no effects present (base case, $\beta_c = \beta_m = \beta_d = \alpha_T = 0$, see below). Obviously, the various effects at play must be taken into account to predict correctly the flow curve. This is done below.

6 Numerical Results

6.1 No Slip at the Wall

The first simulations were performed with no slip at the wall, although it is noticed that at such elevated apparent shear rates slip is almost always present (Rosenbaum et al., 1995; 1998; 2000). It is instructive to show results both with a purely viscous model and with a viscoelastic one so that the differences become apparent. The numerical simulations have been undertaken using either the purely viscous Cross model (Eq. 8) or the viscoelastic K-BKZ model (Eq. 13). Each constitutive relation is solved together with the conservation equations of mass and momentum either for an incompressible or compressible fluid under isothermal or non-isothermal conditions (conservation of energy equation) without or with the effect of pressure-dependence of the viscosity. The viscous results have been checked against each other either with a viscous code (Hannachi and Mitsoulis, 1993) or with the viscous option of the viscoelastic code (Luo and Mitsoulis, 1990) giving the same results.

A typical finite element grid is shown in Fig. 5 for the Nokia Maillefer 4/6 crosshead die of Fig. 1. The vertical entry of the crosshead has been converted into a parallel entry for ease of setting there a fully developed velocity profile at the designated apparent shear rate $\dot{\gamma}_A$. Enough entry length has been given to guarantee fully-developed conditions even for the viscoelastic runs. Then the crosshead tapers with an entrance angle $2a = 60^\circ$ at the inner wall and an outer angle of $2a = 64^\circ$ at the outer wall. The grid consists of 1568 elements, 6501 nodes, and 26462 unknown u-v-p-T degrees of freedom (d.o.f.), while a 4-times denser grid was also used, having been created by

![Fig. 4. The apparent wall shear stress of FEP 4100 melt as a function of the apparent shear rate using the Nokia Maillefer 4/6 crosshead of Fig. 1 at 371°C. The solid line corresponds to predictions by the viscous Cross model (base case, no effects present), open symbols correspond to smooth extrudates](image-url)
subdivision of each element into 4 sub-elements for checking purposes of grid-independent results. This checking consists of reporting the overall pressures in the system (pressure at the entry to the domain) from the two meshes and making sure that the differences are less than 1 % between the two results. Having fixed the model parameters and the problem geometry, the only parameter left to vary was the apparent shear rate in the die (Eq. 24). Simulations were performed for the whole range of experimental apparent shear rates, namely from 80 s$^{-1}$ to 5600 s$^{-1}$, where smooth extrudates were obtained with the presence of a small amount of processing aids, although the pressure drop remained the same with and without processing aid (Rosenbaum et al., 1995; 1998; 2000).

First, runs were carried out to study each effect separately, namely: (a) the effect of compressibility alone, (b) the effect of a pressure-dependent viscosity alone, (c) the effect of a temperature-dependent viscosity alone, and these were compared with the base case of no effects at all ($b_c = 0$, $b_p = b_{sl} = a_T = 0$).

Due to the high range of simulations, all effects were evident. However, compressibility played a minor role, as the results were little affected and they are not shown here. Admittedly, this is expected because the value of $b_c = 0.00095$ MPa$^{-1}$ for FEP is small, giving rise to small values for the dimensionless compressibility parameter $B_c$ in Table 5 in the range of simulations. The same was true for the LDPE and HDPE melts in our previous work (Ansari et al., 2010).

The effect of temperature-dependent viscosity (hence viscous dissipation) was strong in the range of simulations and gave high values for the temperature at the exit, reaching as high as 420 °C at 5600 s$^{-1}$ (viscoelastic run). This is not surprising given the high Na numbers of Table 5 and the predictions of Eq. 17 above. The results for the maximum temperature at the exit for different apparent shear rates are shown in Fig. 6 for both the viscous and viscoelastic runs, where it becomes evident that viscoelasticity produces higher temperature rises due to the enhanced stresses. The high temperature increase due to strong viscous dissipation effects at high extrusion rates in wire-coating applications is the reason for melt fracture suppression resulting in a smooth and stable process (Tadmor and Gogos, 2006).

The effect of pressure-dependent viscosity, with a variable value of $b_p$ obeying Eq. 12, also played a considerable role, which is counteracting the effect of temperature. The pressure (hence the shear stress) is higher than the base case for all apparent shear rates, due to the dominant effect of pressure-dependence of the viscosity, which is however counterbalanced by the effect of temperature.

Viscoelasticity enhances these trends as the viscoelastic stresses are higher than the viscous ones, and this becomes more evident at higher apparent shear rates. These trends are shown in Fig. 7, where the axial pressure distribution along the inner walls is plotted for both viscous and viscoelastic models. The pressure falls smoothly to zero at the exit, thus giving a further evidence of a good crosshead design. The small kinks around $z/R_w = -25$ are due to the sudden change in slope for the last part of the crosshead where it meets the die land. This is an indication that the die should be designed by rounding this entry to avoid the pressure kinks.

Collecting all these results together gives the apparent flow curves shown in Fig. 8. The experimental results are shown as symbols while the numerical results are shown as lines. These simulation results have been obtained with all parameters switched on, i.e., compressibility, pressure- and temperature-dependence of viscosity, but with no slip at the wall. We note that the curve from the K-BKZ model is higher than the one ob-
tained from the Cross model, although the shear behaviour is similar for the two models (see Figs. 2 and 3). Thus, one would expect the wall shear stresses predictions for the two different models to be nearly the same. But the apparent shear stresses are computed from the pressure drops, which are different for the two models, as shown in Fig. 7. The differences in the pressure drop are mainly dominated by the elongational viscosity in the K-BKZ model. The decreasing diameter in the crosshead will cause such normal stresses that become important at the high throughput values. The values for the pressure drops become of the same order as the differences in the pressure drops for the two different models (Fig. 7).

The results overestimate the experimental data appreciably. It is then at this point that we turn our attention to the slip results.

6.2 Slip at the Wall

Due to lack of different dies it was not possible to measure the slip effects in the crosshead die. It becomes then a task for the simulations to find the correct slip law that reproduces the experimental data. It is known that slip effects of FEP are present in flows through conventional capillary dies used in rheometry (Rosenbaum et al., 1995; 1998; 2000). In fact, Rosenbaum et al. (1995) have used capillary dies of various diameters to determine slip. The slip behaviour was found to be a sigmoidal double-valued function, which also explained the origin of the oscillating (stick-slip) melt fracture for this linear resin. In capillary flow, the flow curve consists of two distinct branches, namely a low flow rate and a high flow rate that are separated by a range of shear rates where stable flow is not possible (stick-slip). However, with the crosshead die the stick-slip melt fracture is absent, and the flow curve is a monotonically increasing function of shear rate. Thus, the slip velocity determined from capillary flow does not apply in annular. It should be stressed here that the flow curves, slip velocities and flow instabilities, such as melt fracture, obtained from various geometries, such as capillary, slit and annular dies, differ significantly; the origin of these differences is an open question in the literature (Delgadillo-Velazquez et al., 2008; Ansari et al., 2009; 2011).

Therefore in the absence of a slip velocity model, simulations are used to determine one by matching experimental results with simulations. We started off with a linear slip law \( (b = 1 \text{ in Eq. 21}) \), but the curvature of the experimental data was not obtained. On the contrary, a quadratic law \( (b = 2) \) gave the correct curvature. Then the \( \beta \)–slip coefficient was allowed to vary to match the experimental data from the viscoelastic simulations. Its value was found to be 400 cm/(s · MPa) and the matching was excellent as will be shown below. Obviously, the same could be done for the viscous simulations (Cross model), but we have chosen here to match the viscoelastic simulations because we believe that they more accurately reflect the viscoelastic character of the FEP melt.

When using slip at the wall, the velocity vectors at the wall are tangential to it and are found as part of the solution. This is shown in Fig. 9, where the velocity vectors are given from the viscoelastic K-BKZ simulations for the lowest and highest apparent shear rates of 80 s\(^{-1}\) and 5600 s\(^{-1}\). Slip changes drastically the velocity profiles across the die. Thus, we observe that at 80 s\(^{-1}\) slip at the die wall is small and the general annular profile is maintained, while at 5600 s\(^{-1}\) slip is strong and makes the profiles much flatter (more plug-like) due to the severe flow conditions taking place in the die. Again, due to the decreasing diameter in the crosshead the normal stresses become important at the high throughput values. Moreover, when slip dominates (Fig. 9B) these stresses will overrule shear
stress contributions and add to the pressure drop. We also observe that due to the abrupt change of slope at the entrance to the die, the slip velocities there are much higher than the rest. A curved design at that point is desirable in order to eliminate such abnormally high velocities.

It is again instructive to compare temperature and pressure distributions between the viscous and viscoelastic models with all effects present including slip. This is done in Fig. 10, where we show the maximum temperature at the exit from the Cross and the K-BKZ models. Now, the maximum temperatures have been reduced substantially, reaching at most 376 °C for 5600 s⁻¹ for the viscoelastic case, a rise of only 5 °C. In reality, this value is expected to be somewhat higher as the boundary condition of constant temperature at the wall is not exactly right, and a thermal balance would be more appropriate (Winter, 1977; Mitsoulis et al., 1988).

Fig. 11 shows the axial pressure distribution along the inner walls for different apparent shear rates. As with the temperatures, the pressures are much lower now, reaching at the highest rate 20 MPa as opposed to 60 MPa when no slip was assumed, a very substantial change. The viscoelastic pressures are higher than the viscous ones, and this becomes more apparent at elevated shear rates (maximum difference of 25% at 5600 s⁻¹). Again, the pressure falls smoothly to zero at exit, thus giving evidence of a good crosshead design. The kinks around z/Rw = −25 are now a bit more pronounced due to slip because of the sudden change in slope for the last part of the crosshead where it meets the die land.

Collecting again all these results together gives the apparent flow curves shown in Fig. 12. As expected, the agreement is excellent from the viscoelastic simulations, since the slip law was based on matching these simulations with the experiments. On the other hand, the same slip law with the viscous model underestimates appreciably the experimental data.

Fig. 9. Velocity vectors near the entrance to the die showing the acceleration of the velocity and the non-zero vectors at the walls due to slip for the FEP melt at 371 °C with the K-BKZ model: (A) \( \dot{\gamma}_A = 80 \) s⁻¹, (B) \( \dot{\gamma}_A = 5600 \) s⁻¹.
Both viscous and viscoelastic models were found to over-predict significantly the experimental apparent flow curve (shear stress vs. shear rate) in a wide range of extrusion rates reaching up to 5600 s\(^{-1}\), where the experiments produced smooth extrudates. The temperature rises were substantially high for such high apparent shear rates. Viscoelasticity gave higher results than the purely viscous Cross model.

The smooth experimental curve and the good condition of the extrudates made the addition of slip at the wall a necessity, given the fact that this melt appears to slip in capillary dies. Due to lack of experimental data, a quadratic slip law was assumed, which gave the correct predictions for the experiments by using the viscoelastic K-BKZ model. Then the same slip law used with the Cross model gave under-predictions as expected. Obviously, the opposite would have happened if we had chosen to match the viscous simulations (Cross model), but we believe that the K-BKZ model more accurately reflects the viscoelastic character of the FEP melt. The numerical simulations gave a good understanding of the various effects at play (weak compressibility, temperature- and pressure-dependence of viscosity, slip effects) and provided hints for die design optimization. Furthermore, it has been verified that this is a good design producing smooth results at high shear rates with small to moderate temperature rises due to significant slip effects.

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