Polymer Rheology for Melt Processing: Complex Flows

The rheological behavior of polymer melts plays an important role during processing since it not only determines the extra stresses and pressure gradients and can reduce flow instabilities that yield process limits, but it also couples material, process, and production properties. Examples of (final) product properties determined by the process are frozen-in orientation, the structure of semicrystalline polymers, and long-term dimensional stability. For quantitative predictions of these qualities, the availability of reliable constitutive models is a prerequisite. Here, the performance of a new generation of constitutive differential equations (Verbeeten et al. 2000) based on the Pompom model (McLeish and Larson 1998) is presented.

1. Introduction

In recent years, significant progress has been made in the experimental and numerical analysis of viscoelastic polymer melt flow. From the numerical point of view, a number of well-established, mixed finite element formulations has been developed that are sufficiently stable, robust, and efficient to analyze a range of two- and three-dimensional flow problems. Typical examples are the so-called DEVSS/DG and DEVSS/SUPG methods. Experimentally, an increasing variety of flow geometries has become available, satisfying requirements such as near two-dimensionality of the flow (i.e., a depth-to-height aspect ratio of at least 8 in the whole flow domain). The measurement resolution of fringe patterns has improved significantly by the application of lasers (Schoonen 1998) such that accurate measurements can be made at critical locations in the geometry. Furthermore, the use of Mueller calculus allows the prediction of the observable fringe patterns in three-dimensional flow geometries (Bogaers et al. 1999b).

Crucial to the quantitative prediction of velocity and stress fields in inhomogeneous flows is the availability of reliable constitutive models. Within the class of differential models, the multimode versions of the Giesekus and PTT model have been the most widely applied. A new generation of models (Verbeeten et al. 2000) has been developed based on the concepts of the Pompom model (McLeish and Larson 1998). These Pompom-based models are a major step forward in describing the rheology of polyethylene melts.

The objective of this contribution is to investigate the performance of an enhanced, single-equation version of the Pompom model in predicting the response to a reversed shear flow, and predicting the inhomogeneous flow of a low-density polyethylene (LDPE) melt in the cross-slot geometry. This particular version quantitatively predicts all available rheometrical shear and elongation data of a set of polymer melts (see Verbeeten et al. 2000).

2. Enhanced Pompom Model

To describe stresses of polymer melts, the Cauchy stress tensor \( \sigma \) is decomposed as:

\[
\sigma = -pI + 2\eta_s D + \sum_{i=1}^{M} \tau_i
\]

Here, \( p \) is the pressure term, \( I \) the unit tensor, \( \eta_s \) denotes the viscosity of a purely viscous component, \( D = \frac{1}{4}(L + L^T) \) the rate of deformation tensor, in which \( L = (\nabla u)^T \) is the velocity gradient tensor, and \((\cdot)^T\) denotes the transpose of a tensor. The viscoelastic contribution of the \( i \)th relaxation mode is denoted by \( \tau_i \) and \( M \) is the total number of different modes. A multimode approximation of the relaxation spectrum is usually necessary for a realistic description of the viscoelastic contributions.

Here, the constitutive behavior of the viscoelastic contribution is described with the differential Pompom model. This model is (mainly) developed for long-chain branched polymers. The multiple-branched molecule can be broken down to the several individual molecules (Inkson et al. 1999). Every mode is represented by a backbone between two branch points, with on every end a number of dangling arms. The backbone is confined by a tube formed by other backbones. The original differential form by McLeish and Larson (1998), improved with local branch point displacement (Blackwell et al. 2000), is written in two decoupled equations and reads as follows:

\[
A + \frac{1}{\lambda_{ss}}[A - \frac{1}{2}I] = 0, \quad S = \frac{A}{\lambda_{ss}} \quad (2)
\]

\[
\dot{\Lambda} = \Lambda[D:S] - \frac{1}{\lambda_{ss}}(\Lambda - 1) \quad (3)
\]

\[
\lambda_s = \lambda_{ss}e^{-\lambda_{ss}q} \quad \forall \Lambda \leq q \quad (4)
\]

\[
\tau = S - G_s I = G_s(3\Lambda^2S - I) \quad (5)
\]

The expression (5) for the extra stress differs (by a constant) from that proposed in McLeish and Larson (1998), but in Rubio and Wagner (1999), it has been shown that for the differential model, this is the correct form. Equations (2) and (3) are the evolution of orientation tensor \( S \) and backbone stretch \( \Lambda \), re-
spective. $A$ is an auxiliary tensor to get the backbone orientation tensor $S$. The upper convected time derivative of the auxiliary tensor $A$ is defined as:

$$\dot{A} = \frac{\partial A}{\partial t} + \tilde{v} \cdot \nabla A - L \cdot A - A \cdot L^\top$$  \hspace{1cm} (6)

The parameter $\lambda_{w}$ is the relaxation time of the backbone orientation. It is obtained from the linear relaxation spectrum determined by dynamic measurements. $I_3$ is the first invariant of tensor $A$, defined as $I_3 = \text{tr}(A)$. The backbone stretch $\Lambda$ is defined as the length of the backbone tube divided by the length at equilibrium. $\lambda_{w}$ is the relaxation time for the stretch $\Lambda$. A vector parameter, which, based on the ideas of Blackwell et al. (2000), is taken to be $2^q$, where $q$ is the amount of arms at the end of a backbone. Finally, $G_s$ is the plateau modulus, also obtained from the linear relaxation spectrum. Finite extensibility of the backbone is introduced by Eqn. (3), which only holds if the stretch $\Lambda$ is smaller or equal to the number of dangling arms $q$.

The expression (2) has a similar structure as the upper convected Maxwell (UCM) model, and becomes unbounded if $\lambda_{w} \gg 1$. To overcome this problem and to reduce the set of equations, the orientation and stretch equations will be written as a single equation by using Eqn. (5). Therefore, Eqn. (2) is rewritten in terms of $S$:

$$\dot{S} + 2[D: S]S + \frac{1}{\lambda_{w} I_3} [S - \frac{1}{3} I] = 0$$  \hspace{1cm} (7)

An expression is needed for $I_3$ to get a full coupling between the stretch and orientation. Introduce the following definitions:

$$A = \langle \tilde{x} \tilde{x} \rangle \quad \text{and} \quad S = \langle \tilde{u} \tilde{u} \rangle$$  \hspace{1cm} (8)

where $\tilde{x}$ is a vector of unknown dimensionless length, representing a part of the backbone, and $\tilde{u}$ is the unit vector. Assuming that the local vector $\tilde{x}$ has a length of the averaged stretch $\Lambda = \langle \Lambda \rangle \langle \tilde{x} \rangle = \Lambda \tilde{u}$, where $\Lambda$ is the local stretch of a part of the backbone, $I_3$ can be coupled with the stretch:

$$A = \langle \tilde{x} \tilde{x} \rangle = \Lambda^2 \langle \tilde{u} \tilde{u} \rangle = \Lambda^2 S \quad \text{and} \quad I_3 = \Lambda^2$$  \hspace{1cm} (9)

A second aspect of the Pompom model written in the form of equations (2) and (3) that needs improvement is zero second normal stress coefficient ($\Psi_2 = 0$) prediction by this form. To overcome this, the orientation equation (7) is modified to invoke a second normal stress coefficient. Instead of a UCM type, a Giesekus-like evolution equation for the orientation is proposed. Making use of expression (9), the equation now reads:

$$\dot{S} + 2[D: S]S + \frac{1}{\lambda_{w} I_3} [S - \frac{1}{3} I] = 0$$

Here, $\alpha$ is a material parameter, defining the amount of anisotropy is molecular friction and Brownian motion. If $\alpha = 0$, the orientation equation simplifies to the UCM-type orientation equation (7). For nonzero $\alpha$, also a nonzero second normal stress coefficient $\Psi_2$ is predicted. Moreover, $\Psi_2$ is proportional to $\alpha$.

By taking the derivative of Eqn. (5):

$$\dot{\lambda}(t)^{-1} + f(t)^{-1} I = 2G_m D$$  \hspace{1cm} (11)

with

$$\dot{\lambda}(t)^{-1} = \frac{1}{\lambda_{w}} \left[ \frac{\alpha}{G_m} \tau + f(t)^{-1} I \right]$$  \hspace{1cm} (12)

$$\frac{1}{\lambda_{w}} f(t)^{-1} = \frac{2}{K} \left( 1 - \frac{1}{\Lambda} \right) + \frac{1}{\lambda_{w}} \left[ \frac{1}{\Lambda^2} \left( \frac{\alpha}{G_m} \tau \right)^{-1} \right]$$  \hspace{1cm} (13)

and

$$\Lambda = \sqrt{1 + \frac{f(t)}{3G_m}} \quad \lambda = \lambda_{w} e^{-\alpha (\Lambda - 1)} \quad \text{and} \quad \nu = \frac{2}{q}$$  \hspace{1cm} (14)

3. Computational Method

Numerous numerical formulations have been proposed for the analysis of viscoelastic fluid flow, see Bailleux (1999b) for a review. The two most frequently used mixed finite element methods are both based on the DEVSS (Discrete Elastic–Viscous Stress Splitting) formulation, first introduced by Guénette and Fortin (1995). If a continuous stress interpolation is applied, the SUPG method is generally applied to handle the convective terms in the constitutive model, giving the DEVSS/SUPG method, while the discontinuous Galerkin (DG) method is the method of choice for discontinuous stress interpolations, giving the DEVSS/
DG method. If a separate interpolation of the velocity gradient tensor $L = (\nabla u)^T$ is used in the constitutive equation, the so-called G versions (i.e., DEVSS-G/SUPG) appear. In this work, the DEVSS/DG method is applied because of its good convergence properties in both smooth and nonsmooth geometries (Baaijens 1999a), while a particularly efficient implementation in smooth and nonsmooth geometries (Baaijens et al. 1999b) is suggested to adapt the solution to the solution $\tau$; however, it has been shown in Eqn. (13) that this may give rise to numerical instabilities for transient flows.

The stabilization parameter $\eta$ may, in principle, be chosen arbitrarily, but is set to $\eta = \sum G_\mu^\phi / G_\mu$. It has been suggested to adapt $\eta$ to the solution $\tau$; however, it has been shown in Eqn. (13) that this may give rise to numerical instabilities for transient flows.

The governing equations are integrated in time by a backward Euler scheme. To obtain the solution of the nonlinear set of equations at each time step, a one-step Newton–Raphson iteration process is implemented. The resulting set of equations is solved in a decoupled fashion, as described in detail in Bogaers et al. (1999a). This procedure allows an efficient solution of the subproblems using dedicated iterative solvers.

4. Parameter Identification

The parameters of the EPP (Extended PomPom) model are identified as follows. The linear relaxation spectrum is determined in the standard fashion based on linear viscoelastic data. The nonlinear parameter $q$ and ratio $\dot{\lambda}_{\text{vis}} / \dot{\lambda}_{\text{ext}}$ are fitted on the uniaxial elongational data only, while $x$ is chosen as 0.1/q. Parameter sets were determined for two different LDPEs (Lupolen 1819H, BASF, and Stamylan LD2008 XC43, DSM) that were used in two different experiments, reversed shear flow and flow through a cross-slot device, respectively (see next section). Results are only given for the DSM LDPE melt. The steady $\eta_0$ and the transient $\eta(t)$ uniaxial elongation viscosities are given in Fig. 1, all at a temperature of 150°C.

Other data, such as the shear viscosity and first normal stress coefficient, are not used in the parameter identification process. The predictions for these quantities, shown for the steady case only, are given in Fig. 2. In the current fit, only four relaxation times have been used, which has been found sufficient for the range of shear and elongation rates in the cross-slot flow experiment. The relative sudden drop in predicted viscosity at shear rates beyond $10^5$ s$^{-1}$, observed in Fig.

![Figure 1](image.png)

(a) Transient and (b) steady-state uniaxial elongation viscosity for the Stamylan LD2008 XC43 LDPE melt at 150°C. The solid line represents the fit of the EPP model.
2(a), is due to the limited number of relaxation times used, and can easily be improved by increasing the number of relaxation times to describe the linear spectrum.

The Lupolen 1819 LDPE melt was fitted with six relaxation times (Verbeeten et al. 2000).

5. Complex Flows

The predictive performance of the EPP model is shown for two critical flows: the reversed shear flow and the cross-slot flow. Experimental data for the reversed shear flow is available from Kraft (1996) for a LDPE

Figure 3
Reversed flow $\dot{\gamma} = 1(s^{-1})$. (a) Shear stress, (b) first normal stress difference $N_1$, (c) orientation angle for difference initial strains $\dot{\gamma} = \dot{\gamma} t^*$. $t^* = 4, 10, 15, 20, 40s.$
melt (Lupolen 1918H, BASF). This flow is known to be a very critical test for a constitutive model. Comparison (Fig. 4) shows that all experimentally observed features, the stresses and the orientation angle, are predicted rather well by the model. For the prediction, a six-mode fit was used.

Among the most frequently investigated flow geometries for polymer melts is the $n$:1 planar contraction, with, typically, $n = 4$. The advantage of such a configuration is that it resembles a number of actual processing configurations, such as extrusion. It is, however, not an optimal test geometry (Schoonen 1998). A particularly challenging aspect of simulating inhomogeneous flows is the ability to predict both shear- and elongation-dominated flow regions simultaneously at finite strains. Although along the centerline of the 4:1 contraction, high elongational rates are achieved at the contraction region, the
residence time of fluid particles is low and only moderate strain levels are attained. A similar situation holds for the flow past a confined cylinder (Baaijens et al. 1997). Again, at the wake of the cylinder, high elongation rates are achieved, but the residence time is too short to achieve large strains. At the rear stagnation point, with infinite residence time, the elongation rate is zero. The cross-slot flow geometry (Schoonen 1998, Bogaerds et al. 1999a, Peters et al. 1999) does not have these limitations. At the stagnation point, a finite elongational rate exists. Moreover, the elongational rate is fairly homogeneous in a region surrounding the stagnation point and the residence time in this region is sufficiently long to reach large strains. Sufficiently far upstream and downstream of the stagnation point, a fully developed shear flow exists, while elsewhere away from the stagnation point a combined shear/elongational flow is found. In conclusion: in contrast to many other geometries that have been investigated, the cross-slot geometry allows the investigation of steady elongation with large strains and combined shear/elongational flows.

To make a direct comparison of two-dimensional calculations with experimentally obtained birefringence data when using polymer melts, it is of critical importance that the flow geometry has a depth-to-height ratio of at least 8 throughout the domain of interest, otherwise three-dimensional effects have too large an influence on the experimental results. In fact, only the isochromatic fringes can be interpreted in a straightforward manner. Isoclinics can not be used to separate shear stresses from normal stresses due to end effects (see Schoonen 1998). If the aspect ratio is too small, or if the flow geometry is essentially three-dimensional, Mueller calculus can be used to convert computed stress data to experimentally observable fringes (see Bogaerds et al. 1999a).

Figures 4(a) and 4(b) compare the predicted and the measured birefringence pattern using the Giesekus and the PTT model, respectively, at a Weissenberg number of 4.3. Figure 4(c) shows the results for the EPP model. Remarkably good agreement exists in the whole domain for the EPP model, while both the Giesekus and the PTT model are unable to predict the fringe patterns near and at the stagnation point. This is reflected more quantitatively in Fig. 5 where, for a number of models, the stress along the symmetry line is depicted. Of all models investigated (i.e., the Giesekus, PTT, Feta-VD (Peters et al. 1999), and the EPP model), the EPP model shows the best performance.

Figure 5
Normal stress along the symmetry line.

6. Conclusions

The enhanced Pompom model not only provides an excellent description of all available rheometrical data for a variety of polyethylene melts, as shown in Verbeeten et al. (2000), it also predicts the response of the reversed shear flow and the complex stress patterns in the inhomogeneous cross-slot flow geometry accurately. Even the stresses at the stagnation point, corresponding to a steady planar elongation flow, and the subsequent stress relaxation in the downstream section, are predicted with remarkable accuracy. Among the advantages of the enhanced version of the Pompom model—the EPP model—are that (i) the model only has a single differential equation, combining stretch and elongation, which is attractive from the computational point of view, (ii) the resulting equation does not show the unbounded behavior in elongation as the original Pompom model (due to the UCM-like expression for the evolution of the orientation tensor), (iii) a second normal stress difference is included, considered realistic for polymer melts, and (iv) the EPP model provides an improved description of the rheometrical data.

Numerical algorithms, such as the DEVSS/DG method, have been developed to the state where the analysis of a range of viscoelastic polymer melt flows is feasible with sufficient reliability, robustness, and efficiency. In fact, three-dimensional simulations using multiple relaxation times are possible and, moreover, birefringence data generated in such configurations can be interpreted using computational methods (Bogaerds et al. 1999a). Nevertheless, ample room for improvements persist since, for instance, unacceptably low limits in achievable Weissenberg numbers still exist, in particular for flows with geometrical singularities, while computational resource requirements (in terms of both memory and computing time) are quite demanding.
See also: Polymer Rheology for Melt Processing: Molecular Modeling; Foams, Microrheology of; Polymer Film Casting: Modeling; Polymer Fiber Processing: The Rheotens Test; Polymer Injection Molding: Modeling for Properties

Bibliography


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