Modeling of Paste Extrusion in Semi-Solid State

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ABSTRACT: A constitutive rheological equation is proposed for the paste extrusion of polytetrafluoroethylene (PTFE) that takes into account the continuous change of the microstructure during flow, through fibril formation. The mechanism of fibrillation is captured through a microscopic model for a structural parameter, ξ. This model essentially represents a balance of fibrillated and unfibrillated domains in the PTFE paste through a first-order kinetic differential equation. The rate of fibril formation is assumed to be a function of the strain rate and a flow type parameter, which describes the relative strength of straining and rotation in mixed type flows. The proposed constitutive equation consists of shear-thinning and shear-thickening terms, the relative contribution of the two being a function of ξ. Finite element simulations using the proposed constitutive relation predict correctly the variations of the extrusion pressure with the apparent shear rate and die geometrical parameters.

Key words: PTFE paste extrusion, semi-solid modeling, structure parameter, die design, numerical simulation

1 INTRODUCTION

Poly-tetra-fluoro-ethylene (PTFE or $-(CF_2-CF_2)_n-$) is a linear polymer of helical molecular conformation, high molecular weight (10^6-10^7), high melting point (342°C), and high melt viscosity (1-10 GPa·s at 380°C). The last two characteristics introduce an obstacle into its processing. So it is not possible to process PTFE resins by using polymer melt processing. There is still an advantageous alternative: because of its transition temperatures in its phase diagram at 19°C and at 30°C, above 19°C PTFE changes its crystallinity and becomes highly deformable. Then it can be processed as a paste by extrusion, mixed with appropriate lubricants in amounts of 16-40% wt. [1,2]. After paste extrusion, the extrudate is dried and sintered.

In the present study, such a PTFE paste is studied rheologically by extrusion through a capillary die. The transient pressures are recorded for different paste formulations and different processing conditions. Finally, an attempt is made at modelling the material through a rheological model that encompasses most of the phenomena encountered in paste extrusion.

2 EXPERIMENTS

The experiments are carried out first by premixing the lubricant with the polymer at 25°C. The polymer is a powder. The lubricant must coat the resin particles, must have a high vapour pressure, and must not leave a residue after evaporation [1]. The viscosities of the different types of lubricants range between 0.51-7.50 mPa·s. During pre-forming, the two-phase mixture (resin and lube) is compressed, and the lubricant migrates in all directions. Then during extrusion through a typical capillary rheometer, the pressure is recorded as a function of distance for different conditions. A typical behaviour is shown in Fig. 1(a) with 3 distinct regions: region (I) of a pressure build-up; region (II) of steady-state values; and region (III) of a final gradual pressure build-up again as the paste is depleted of the lubricant. Figure 1(b) shows actual results for different apparent shear rates. Rich phenomena are observed, with the pressure peaks about the same but at different times, while the steady-state values scale with the apparent shear rate as expected.

(a)

(b)

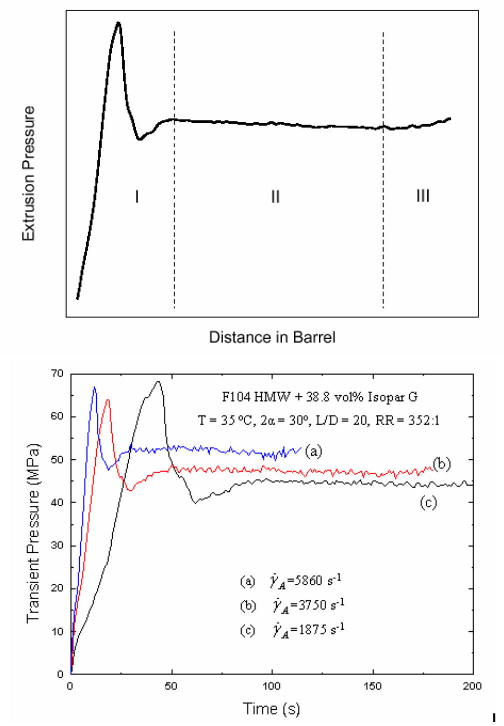

Fig. 1. PTFE paste extrusion at 35°C: (a) typical extrusion pressure vs. distance in the capillary, (b) effect of apparent shear rate $\dot{\gamma}_A$ on pressure transient (RR=area reduction ratio)

3 MATHEMATICAL MODELLING

3.1 Conservation and constitutive equations

We consider the time-dependent Navier-Stokes equations for weakly compressible materials. The rheology of the material obeys the generalized Newtonian model [3]:

(mass conservation) $$\frac{\partial \rho}{\partial t} + \bar{u} \cdot \nabla \rho + \rho \left(\nabla \cdot \bar{u} \right) = 0 \quad (1)$$

(momentum conservation) $$\rho \frac{\partial \bar{u}}{\partial t} = -\nabla p + \nabla \cdot \bar{\bar{\tau}} \quad (2)$$

(rheological model) $$\bar{\bar{\tau}} = \eta \bar{\bar{\dot{\gamma}}} \quad (3)$$

(equation of state) $$\rho = \rho_0 \left(1 + \beta P \right) \quad (4)$$

where $\boldsymbol{u}$ = velocity vector, p = pressure, $\boldsymbol{\tau}$ = extra stress tensor, ρ = density, η = viscosity, $\dot{\gamma}$ = $\nabla u + \nabla u^T$ = rate-of-strain tensor, β = compressibility coefficient. We have assumed that the material flows under creeping conditions ($Re \approx 0$), which is a valid approximation in paste-processing.

3.2 Structure parameter, ξ

The rheology of the PTFE paste depends on the formation and evolution of a network of fibrils connecting PTFE polymer particles during the extrusion. To model this complex flow behaviour, a rheological constitutive equation is proposed which explicitly accounts for the evolution of fibrils. The rheology of the paste continuously changes as it flows through the conical sections. It starts as a two-phase fluid-like system, an oversaturated suspension and it ends as a highly fibrillated solid-like system. While the paste initially behaves as a shear-thinning fluid, after the appearance of fibrils in its structure, it behaves more and more as a shear-thickening fluid. Thus, it is assumed that the stress tensor consists of two contributions coming from the unfibrillated and fibrillated domains of the paste, represented, respectively, by a shear-thinning and a shear-thickening viscous stress. The relative significance of the two contributions should depend on the structural parameter, ξ. Recall that the structural parameter, ξ, is the percentage of the domains of the system that are fibrillated, and takes values between 0 and 1. Thus, the total viscous stress can be written in the following form:

$$\bar{\bar{\tau}} = \left[\left(1 - \xi \right) \eta_1 + \xi \eta_2 \right] \bar{\bar{\dot{\gamma}}} \quad (5)$$

where η_1 and η_2 are the shear-thinning and shear-thickening viscosities that are expressed by a Carreau model [3]:

$$\eta_i = \eta_{0,i} \left[1 + (\lambda_i |\dot{\gamma}|)^2 \right]^{\frac{n_i - 1}{2}} \quad (6)$$

where i=1 refers to shear-thinning (n_1<1) and i=2 refers to shear-thickening (n_2>1). The values used here are: $\eta_{0,1}$=4000 Pa·s, λ_1=0.3, n_1=0.5, $\eta_{0,2}$=1600 Pa·s, λ_2=1, n_2=1.3, and are taken from calibration trials.

The creation of fibrils has been attributed to the unwinding of mechanically locked crystallites due to the extensional nature of the flow in the conical region of the die. The extensional flow also causes elongation of newly formed fibrils, which might also break depending on the total local Hencky strain. Therefore, both creation and breakage are possible. A kinetic model is proposed for the structural parameter, which is a balance of the fibrillated and unfibrillated domains of the paste and whose dynamics are controlled by the rates of creation and breakage:

$$\bar{u}\cdot\nabla\xi = f - g \qquad (7)$$

where f and g denote the rate of creation and elimination of fibrillated domains in the paste. These functions are given by

$$f(\dot{\gamma},\psi) = \alpha\dot{\gamma}\sqrt{\psi}, \quad g(\dot{\gamma},\xi) = \beta\dot{\gamma}\xi \qquad (8)$$

where α and β are the dimensionless rate constants for fibril creation and breakage, both assumed to be 1 in our simulations; ψ the flow type parameter and $\dot{\gamma}$ is the magnitude of the strain-rate tensor. The flow type parameter, ψ, indicates the relative strength of straining and rotation in a mixed flow. Its magnitude ranges from −1 to 1 depending on the flow type as shown in Fig. 2. Since fibrils are mainly created due to elongation and never due to rotation, ψ is taken to vary only between 0 and 1. Negative values of ψ are reset to 0. While the function f involves the formation of fibrils as unwinding of crystallites of neighbouring particles, the function g represents their breakage.

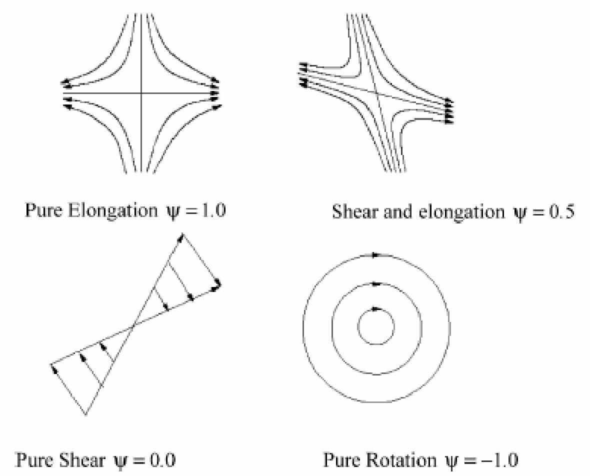

Fig. 2. Flow fields corresponding to different parameters ψ

A final remark for the parameter ξ is as follows. It represents the percentage of the domains of the system that are fibrillated, and as such should take values between 0 and 1. This can be fixed by limiting the ratio of $\alpha/\beta \leq 1$ (note that both parameters have been assigned the value of 1). For example at steady-state conditions, Eq. (7) results in $\xi = \alpha\sqrt{\psi}/\beta$, which essentially limits ξ to less than 1. Analytical solutions for one-dimensional axisymmetric flows, where the velocity profile can be taken approximately known (fully developed), can be derived for Eq. (7) and these show that ξ is always less than 1. It should be noted that ξ can take the value of 1 in pure elongational flow, where ψ becomes 1.

3.3 *Flow type parameter, ψ*

The concept of the flow type parameter, ψ, has been used to account for the dependence of the structural parameter on the relative amount of straining and rotation in the flow field. As an example, a linear planar flow has a velocity field $\mathbf{v} = \Gamma\cdot\mathbf{x}$, where Γ is the velocity gradient tensor:

$$\Gamma = \dot{\gamma}\begin{pmatrix} 0 & 1 \\ \psi & 0 \end{pmatrix} \qquad (9)$$

The flow of primary interest in our study is the strong flow for which $0 < \psi \leq 1$. Thus, for a planar flow, the largest eigenvalue of the velocity gradient tensor has the form of $\dot{\gamma}\sqrt{\psi}$. On the other hand the flow parameter ψ can also be written as

$$\psi = \frac{|\bar{\bar{D}}| - |\bar{\bar{W}}|}{|\bar{\bar{D}}| + |\bar{\bar{W}}|} \qquad (10)$$

where D and W denote the deformation and vorticity tensor, respectively. In the case of axisymmetric flow, the velocity gradient tensor has a different form than Eq. (9), and its the largest eigenvalue is no longer equal to $\dot{\gamma}\sqrt{\psi}$. Nevertheless, we can still define ψ according to Eq. (10) and therefore, it retains the significance of a flow type parameter. It appears reasonable to use such a ψ in our kinetic Eq. (8). The magnitude of D and W in cylindrical coordinates can be written as follows:

$$|D| = \sqrt{\left(\frac{\partial v_r}{\partial r}\right)^2 + \left(\frac{v_r}{r}\right)^2 + \left(\frac{\partial v_z}{\partial z}\right)^2 + \frac{1}{2}\left(\frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r}\right)^2} \qquad (11a)$$

$$|W| = \sqrt{\frac{1}{2}\left(\frac{\partial v_r}{\partial z} - \frac{\partial v_z}{\partial r}\right)^2} \qquad (11b)$$

The flow type parameter controls the magnitude of structural parameter inside the flow domain with the maximum amount of fibrillation to occur at the centre and much less at the die wall. This also ensures that the fibril creation and evolution mainly takes place inside the conical section; very little changes in fibril structure occur inside the die land where the flow becomes pure shear. This picture is supported by experimental evidence. This was confirmed by performing experiments with L/D ratios 0 and 20 [1,2]. Therefore, at least phenomenologically, the modelling concepts incorporated into our flow model agree well with the experimental observations.

3.4 *Boundary conditions*

The problem at hand is illustrated in Fig. 3. Due to axisymmetry a two-dimensional analysis is applied. The following boundary conditions are imposed:

(a) Slip conditions along the solid die walls. The slip velocity is assumed to obey a linear law:

$$V_s = C\tau_w \tag{12}$$

where C=1.92 m/MPa·s, found experimentally. At entry, a fully developed velocity profile is given based on the shear-thinning Carreau model and corresponding to the desired flow rate *Q*. Then the apparent shear rate is given by $\dot{\gamma}_A = 4Q/\pi R^3$.

(b) The no-fibrillation condition is also assumed, ξ=0.

(c) At exit, v_r=0 and T_r=0 are imposed, i.e., zero velocity and surface traction in the radial direction.

(d) At the symmetry line, v_r=0 and τ_{rz}=0 are imposed.

4 RESULTS AND DISCUSSION

The system of conservation, constitutive and structure equations (1-11) together with the boundary conditions is solved with the Finite Element Method for axisymmetric 2-D flows. Results are shown first in Fig. 3(a), where the development of fibrillated (red) regions with time is evident.

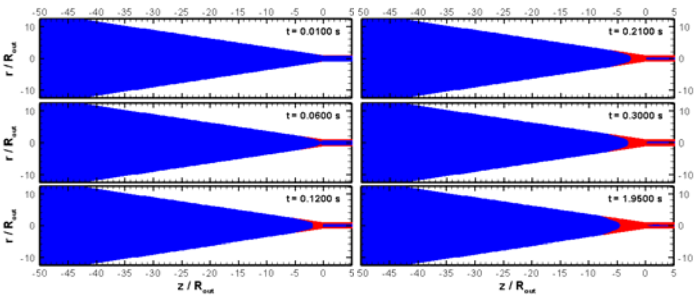

Fig. 3. Transient simulation results for the fibrillated (red) / unfibrillated (blue) regions for R_{res}/R=12.5, R=0.381 mm, $\dot{\gamma}_A$ =1390 s^{-1}, convergence angle 2a=30°

Figure 4 shows dimensionless pressure transients, which capture the maximum and the under-shoot, and are in qualitative agreement with the experiments. This is due to the combined effect of compressibility and structure, since neither of them alone can produce the phenomena of the 3 regions in the temporal pressure distribution.

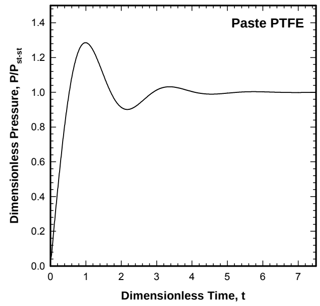

Fig. 4. Transient simulation results for the dimensionless pressure $P/P_{st\text{-}st}$ for R_{res}/R=12.5, R=0.381 mm, $\dot{\gamma}_A$ =1390 s^{-1}, convergence angle 2a=30°

5 CONCLUSIONS

The proposed model for paste extrusion seems capable of capturing the phenomena associated with structure and fibrillation. The difficulty remains to measure accurately and independently the parameters of the model, rather than guessing some of them. More work is needed to elucidate the development of structure in other types of flow than simple die extrusion.

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