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, $\xi$. 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 $\xi$. 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 $-(\text{CF}_2-\text{CF}_2)_n-$) 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.

![Extrusion Pressure vs. Distance in the Capillary](image1)

**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]:

\[
\begin{align*}
\text{(mass conservation)} & \quad \frac{\partial \rho}{\partial t} + \rho \mathbf{u} \cdot \nabla \rho + \rho (\nabla \cdot \mathbf{u}) = 0 \\
\text{(momentum conservation)} & \quad \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} + \nabla p = -\nabla \cdot \mathbf{\tau} \\
\text{(rheological model)} & \quad \mathbf{\tau} = \eta \mathbf{\dot{\gamma}} \\
\text{(equation of state)} & \quad \rho = \rho_0 (1 + \beta p)
\end{align*}
\]

where \( \mathbf{u} = \) velocity vector, \( p = \) pressure, \( \mathbf{\tau} = \) extra stress tensor, \( \rho = \) density, \( \eta = \) viscosity, \( \dot{\gamma} = \nabla \mathbf{u} + \nabla \mathbf{u}^T = \) rate-of-strain tensor, \( \beta = \) 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, \( \xi \)

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, \( \xi \). Recall that the structural parameter, \( \xi \), 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:

\[
\mathbf{\tau} = \left[ (1-\xi) \eta_1 + \xi \eta_2 \right] \mathbf{\dot{\gamma}}
\]

where \( \eta_1 \) and \( \eta_2 \) are the shear-thinning and shear-thickening viscosities that are expressed by a Carreau model [3]:

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

where \( i=1 \) refers to shear-thinning \((n_i<1)\) and \( i=2 \) refers to shear-thickening \((n_i>1)\). The values used here are: \( \eta_{0,1}=4000 \text{ Pa·s}, \lambda_1=0.3, n_1=0.5, \eta_{0,2}=1600 \text{ Pa·s}, \lambda_2=1, n_2=1.3, \) 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: