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A simple improved mathematical model for polytetrafluoroethylene (PTFE) paste extrusion

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HIGHLIGHTS

- ▸ Performed experiments in PTFE paste extrusion using three different capillary rheometers.
- ▸ Demonstrate that the experimental results are consistent with the assumption of continuum.
- ▸ Modified an existing model (developed in our group) to produce more consistent modeling results.
- ▸ Performed successful scale up for the PTFE paste extrusion.

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ABSTRACT

The rheology of non-melt processable polytetrafluoroethylene (PTFE) pastes has been studied using three capillary rheometers having barrels of different diameters equipped with capillary dies of various designs. The pressure drop is measured as a function of apparent shear rate (flow rate), reduction ratio (cross sectional area of barrel to that of die), contraction angle, length-to-diameter ratio, and diameter of the barrel (scale-up). To describe the effects of die design for scale-up purposes, a simple phenomenological mathematical model has been developed. The model takes into account the elastic–plastic (strain hardening) and viscous nature of the material in its non-melt state, due to the creation of fibrils and the presence of lubricant, respectively. In addition, it takes into account the slip condition at the paste/wall interface. The model predictions are found to be consistent with experimental results obtained from macroscopic pressure drop measurements and it can be used for scale-up purposes.

1. Introduction

Polytetrafluoroethylene (PTFE) is a highly crystalline polymer with a high melting temperature of approximately 342 °C. It is not possible to process PTFE using conventional polymer melt processes due to this high melting temperature and melt viscosity (Sperati, 1989). Instead, techniques involving cold pressing, cold extrusion in the form of paste, and sintering have to be employed. This is possible because PTFE has two transition temperatures at approximately 19 °C and 30 °C (Blanchet, 1997). Below 19 °C, shearing will cause PTFE crystals to slide past each other, retaining their identity. However, above 19 °C, shearing will cause the unwinding of crystallites, creating fibrils interconnecting most of the PTFE particles in the flow direction (Mazur, 1995; Ebnesajjad, 2000; Ariawan et al., 2001, 2002a, 2002b). At temperatures greater than 30 °C, a higher degree of fibrillation can be achieved, which also depends on the surface tension and viscosity of the lubricant used (Ariawan et al., 2002b; Ochoa and Hatzikiriakos, 2004, 2005; Ochoa et al., 2006).

In PTFE paste extrusion, fine powder resin of individual primary particle diameter of approximately 0.2 μm is first mixed with a lubricating liquid (lube) at concentrations from 16% to 25% to form a paste (Mazur, 1995; Ochoa and Hatzikiriakos, 2004, 2005; Ochoa et al., 2006). The paste is then compacted at a typical pressure of 1–2 MPa to produce a preform that is nearly free of air void (Ariawan et al., 2001; Ochoa and Hatzikiriakos, 2004). The next step involves the extrusion of the preform using a ram extruder at a temperature slightly higher than 30 °C and a die, which typically includes a contraction, i.e., a cylindrical die whose surface is reduced by a factor known as the reduction ratio (Ebnesajjad, 2000). During flow in the contraction region, PTFE particles are squeezed under high pressure, and crystallites across the interface are mechanically interlocked and subsequently unwound to produce fibrils (Hatzikiriakos, 2012).

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Modeling efforts to describe adequately the flow of paste through a typical cylindrical die including a contraction are hampered by a number of unknown important parameters. First, a lack of appropriate constitutive rheological relations, which is the case for most pastes (Bridgwater, 1989; Benbow et al., 1989; Benbow and Bridgwater, 1993; Ariawan et al., 2002b; Wilson and Rough, 2012). As PTFE paste flows through tapered dies, fibrillation occurs continuously, and this changes the rheology of the paste increasing the flow complexity and making difficult the rheological characterization.

A simple approach is to use a rheological law that represents the PTFE paste average behavior through the whole flow domain. In such cases, analytical expressions can be derived for the extrusion pressure (Snelling and Lonz, 1960; Benbow et al., 1989; Benbow and Bridgwater, 1993; Ariawan et al., 2002b; Cheyne et al., 2005; Patil et al., 2006). Although these models give no information on the microstructure development of the material, nevertheless they are very helpful for scale-up purposes as they assess the physical mechanisms involved in the complex problem of PTFE paste flow. Another unknown significant parameter is slip at the wall. Since flow is lubricated, significant slip occurs at the wall and this should be taken into account.

In this work, we study experimentally the flow behavior of PTFE fine-powder resins in paste extrusion using three reservoirs of different diameters. This is done for the first time in the literature, and such data are extremely useful to check the suitability and capability of models for scale-up purposes. As it will be demonstrated here, the unique set of experimental data from three different reservoirs, have helped us to modify the model developed by Ariawan et al. (2002b). The resultant simple mathematical model is found to be consistent qualitatively and quantitatively with all experimental observations. Finally, this model is tested and found to be suitable to be used for scale-up of the process of PTFE paste extrusion.

2. Flow model of PTFE paste

Snelling and Lontz (1960) first derived an equation for PTFE paste flow to describe the effects of die design and extrusion speed based on the ‘‘radial-flow’’ hypothesis (explained below in detail). However, this model does not take into account the frictional force, which becomes important when tapered dies of small entrance angle are used. Also, the analysis provided by these authors does not account for the pressure drop along the capillary length of the die that follows the entrance (contraction) region. Ariawan et al. (2002a) have proposed a viscoplastic model based on their previous experimental work (Ariawan et al., 2001, 2002a, 2002b) to predict the dependence of extrusion pressure on die geometrical parameters for rod extrusion. This approximate model captured the non-monotonic dependence of extrusion pressure on die entrance angle (critical testing of models for PTFE) and other geometrical characteristics of the cylindrical die. Similar to Snelling and Lontz (1960) model, its derivation is based on the ‘‘radial-flow’’ hypothesis for flow through a tapered die (Fig. 1), whose validity has been demonstrated experimentally (Ariawan et al., 2002a, 2002b) and numerically (Patil et al., 2006).

Important die geometrical characteristics that play a significant role in the PTFE paste extrusion include: the die diameter, D_a, the reduction ratio, RR, defined as the ratio of initial to final cross sectional areas ($RR \equiv D_b^2/D_a^2$), the contraction angle, 2α, and the length-to-diameter ratio, L/D_a (see Fig. 1b). According to ‘‘radial-flow’’ hypothesis all points located on virtual spherical surfaces of a constant radius r from the die apex have the same radial velocity (Binding, 1991). This also implies that PTFE paste slips massively on the die walls with a similar radial velocity. The mathematical form of the ‘‘radial-flow’’ hypothesis for a cylindrical die (Fig. 1a) can be written as

$$\frac{dr}{dt} = -\frac{Q}{2\pi(1-\cos\alpha)r^2}, \quad (1)$$

where Q is the volumetric flow rate and r is the distance from the die apex. Based on this hypothesis, the kinematics of PTFE flow can be calculated independent of any rheological constitutive law at a given volumetric flow rate. Then assuming a simple constitutive rheological law, analytical models for the pressure drop can be derived.

Although these models (Snelling and Lontz, 1960; Ariawan et al., 2002b) do not explicitly predict micromechanical details of the extrudates (fibrillation), they explicitly predict the extrusion pressure very well and therefore are useful in die design, particularly the latest models proposed by Ariawan et al. (2002a) and Patil et al. (2006). These models have considered an elasto-plastic and viscous contribution to stress, essentially a modified Kelvin stress–strain relation with an added power-law viscous term (Goh et al., 2004; Hoffman and Sachs, 1953; Ludwik, 1909). The stress expression can be written as

$$\sigma = C\gamma^n + K\dot{\gamma}^m, \quad (2)$$

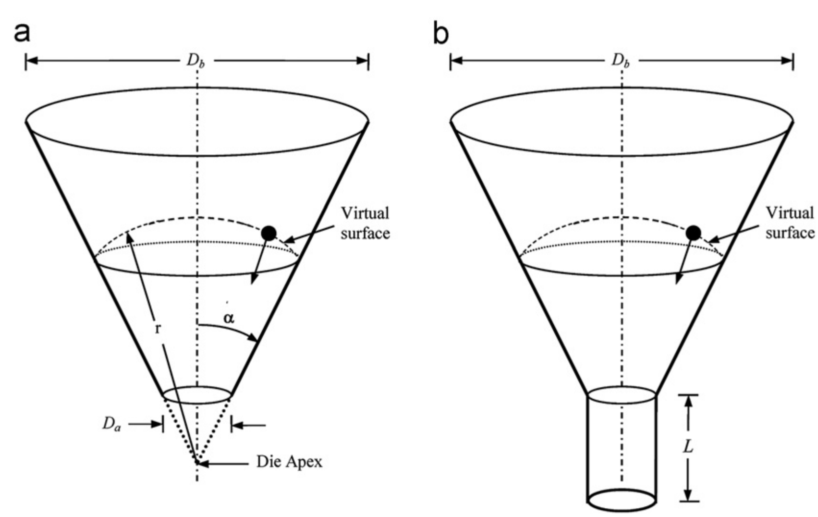

Fig. 1. (a) Schematic of a tapered orifice die showing the various characteristic dimensions and (b) schematic of a tapered die that includes a certain length of die land L.