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Entry flows of polylactides with slip

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ABSTRACT

The entry capillary flow of four different polylactides (previously characterized by Othman et al. (2012)) has been modeled with both a viscous (Cross) and a viscoelastic (K-BKZ) model. The modeling takes into account slip-at-the-wall, which was found to increase with decrease of molecular weight. The flow through different capillary dies and apparent shear rates show the excess pressure losses (ends correction), which are smaller than those for other similar linear polymer melts. The viscous simulations capture well the ends correction, while the viscoelastic simulations improve these predictions, as they also account for the viscoelastic nature of the polymer melts. It is concluded that solely viscous modeling can capture their flow behavior satisfactorily.

1. Introduction

Biodegradable polymers, such as poly(lactide) (PLA), have attracted an increasing amount of attention in the literature, due to environmental concerns [1,2]. Polylactides have found applications in packaging materials, such as films, bottles and food service products, as well as in drug delivery and medical fields where biodegradability and biocompatibility are desirable [3–5].

The rheology of PLAs has been extensively studied in the literature [6–12]. The K-BKZ constitutive equation was used to model the rheological data satisfactorily, including strain hardening which might occur in spite of the linear macrostructure of these polymers [7,11]. The processability of PLAs has also being studied in the literature, particularly its processing as can be assessed by melt fracture phenomena [12–14]. Ways to eliminate melt fracture instabilities in the capillary flow of PLAs have been reported in detail by Jazrawi et al. [14] using methods previously developed for polyethylenes [15,16].

It has been reported that PLAs with molecular weight greater than a certain value exhibit slip [12]. This might be expected due to their linear structure and similarities with other linear molecules that exhibit slip and melt fracture [17–24]. In flow simulations, such effects (slip) should be taken into account in order to model/describe experimental results accurately [25].

In this paper, we study numerically several commercial PLAs in terms of their entry flow in capillaries of various geometries. The experimental data used in the modeling of these polymers have been previously reported in the literature. Capillary rheometry is extensively used in both industry and academia to assess the rheological behavior of polymer melts at high shear rates as a method to bridge rheology with processing [26]. The K-BKZ constitutive equation is used to represent the rheology of PLAs and a slip boundary condition is used as a necessary ingredient to capture their flow behavior correctly. Therefore, the main objective of this study is to predict the flow behavior of commercial polylactides in capillaries of various geometrical characteristics, including contraction flows using the K-BKZ constitutive equation. If these flow simulations prove to agree with experimental data, they can be further used in the development and optimization of a number of applications of polylactides.

2. Materials and experimental methods

Four commercial PLAs were studied in this work, all obtained from NatureWorks LLC. These are summarized in Table 1. These commercial samples have different molecular weights and about the same polydispersity (Table 1). Details on the rheological characterization of these polymers can be found in Othman et al. [12].

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Table 1
Molecular characteristics and other properties of the PLAs used in this work.

Sample	10^3 M_w (g/mol)	M_w/M_n	T_m (°C)
PLA 7001D	110.1	1.59	149.0
PLA 2002D	106.9	1.82	152.4
PLA 3051D	92.5	1.82	150.0
PLA 3251D	55.4	1.62	167.9

Here we briefly discuss important aspects of these finding for the sake of clarity.

The capillary flow behavior of all commercial lactides listed in Table 1 were studied by using a pressure-driven Instron capillary rheometer equipped with a barrel having a diameter of 0.9525 cm [12]. Three series of dies having different diameters and various length-to-diameter ratios were used to determine and correct for the entry effects of the capillary data. The Mooney method was used to determine their slip behavior [17,19], while all the details on these measurements can be found elsewhere [12]. The dimensions of all dies used are listed in Table 2.

3. Governing equations and rheological modeling

We consider the conservation equations of mass and momentum for incompressible fluids under isothermal, creeping, steady flow conditions. These are written as [27,28]:

$$\nabla \cdot \bar{u} = 0, \tag{1}$$

$$0 = -\nabla p + \nabla \cdot \bar{\bar{\tau}}, \tag{2}$$

where $\bar{u}$ is the velocity vector, p is the pressure, and $\bar{\bar{\tau}}$ is the extra stress tensor.

The viscous stresses are given for inelastic non-Newtonian incompressible fluids by the relation [27,28]:

$$\bar{\bar{\tau}} = \eta(|\dot{\gamma}|)\bar{\bar{\dot{\gamma}}}, \tag{3}$$

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

$$|\dot{\gamma}| = \sqrt{\frac{1}{2}II_{\dot{\gamma}}} = \left(\frac{1}{2}(\bar{\bar{\dot{\gamma}}} : \bar{\bar{\dot{\gamma}}})\right)^{1/2}, \tag{4}$$

where $II_{\dot{\gamma}}$ is the second invariant of $\bar{\bar{\dot{\gamma}}}$

$$II_{\dot{\gamma}} = \left(\bar{\bar{\dot{\gamma}}} : \bar{\bar{\dot{\gamma}}}\right) = \sum_i \sum_j \dot{\gamma}_{ij}\dot{\gamma}_{ij}. \tag{5}$$

To evaluate the role of viscoelasticity in the prediction of entrance pressure correction, 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 PLA melts. The Cross model is written as [26]:

$$\eta = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^{1-n}}, \tag{6}$$

where η_0 is the zero-shear-rate viscosity, λ is a time constant, and n is the power-law index. The fitted viscosity of the PLA melts by Eq. (6) is plotted in Fig. 1, while the parameters of the model are listed in Table 3. The η_0 values used for the Cross model are of the same order with those used in the K-BKZ model (see below), however the λ values are very different and are not ranged in the same order. The low values of n are a peculiarity of the Cross model and do not coincide with the n-values found from a power-law model (usually around 0.5). In spite of that, the Cross model fits the data well over the whole range of experiment results.

Table 2
Characteristic dimensions of capillary dies used.

Diameter (mm)	L/D	Entry angle (°)
0.43	16	180
0.76	1.8	180
0.76	5.3	180
0.76	16	180
0.76	33	180
1.22	16	180

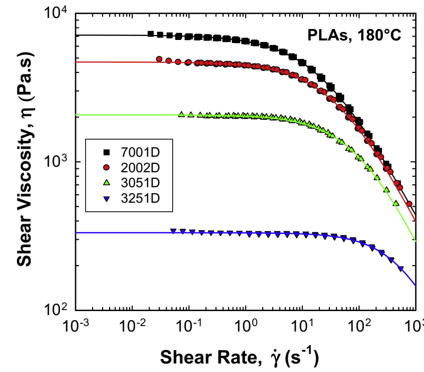

Fig. 1. The shear viscosity of the PLA melts at 180 °C fitted with the Cross model (Eq. (6)) using the parameters listed in Table 3.

Table 3
Parameters for the PLA melts obeying the Cross model (Eq. (6)) at 180 °C.

Parameter	PLA 7001D	PLA 2002D	PLA 3051D	PLA 3251D
η_0 (Pa s)	7136	4699	2072	333
λ (s)	0.043	0.02267	0.00925	0.00144
n	0.274	0.2354	0.185	0.0577

Viscoelasticity is included in the present work via an appropriate rheological model for the stresses. This is a K-BKZ equation proposed by Papanastasiou et al. [29] and modified by Luo and Tanner [30]. This is written as:

$$\boldsymbol{\tau} = \frac{1}{1-\theta}\int_{-\infty}^{t}\sum_{k=1}^{N}\frac{a_k}{\lambda_k}\exp\left(-\frac{t-t'}{\lambda_k}\right)\frac{\alpha}{(\alpha-3)+\beta I_{C^{-1}}+(1-\beta)I_C} \times [\mathbf{C}_t^{-1}(t') + \theta\mathbf{C}_t(t')]dt', \tag{7}$$

where t is the current time, λ_k and a_k are the relaxation times and relaxation modulus coefficients, N is the number of relaxation modes, α and β are material constants, and I_C, I_C^{-1} are the first invariants of the Cauchy-Green tensor $\mathbf{C}_t$ and its inverse $\mathbf{C}_t^{-1}$, the Finger strain tensor. The material constant θ is given by

$$\frac{N_2}{N_1} = \frac{\theta}{1-\theta}, \tag{8}$$

where N_1 and N_2 are the first and second normal stress differences, respectively. It is noted that θ 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 [26,27].

As discussed above, experiments were performed in the parallel-plate and extensional rheometers for the PLA melts to rheologically characterize them [12]. Fig. 2a–d plots the master dynamic moduli G' and G'' for all PLAs, listed in Table 1 in decreasing order of molecular weight at the reference temperature of 180 °C, respectively. The model predictions obtained by fitting the experimental data to Eq. (7) with a spectrum of relaxation times, λ_k, and coefficients, a_k, determined by a non-linear regression package [31], are also plotted. The parameters found from the fitting procedure for all commercial PLAs are listed in Table 4. It is worthwhile