Study on the Viscoelastic Behaviors of PMMA

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Abstract. The polymer rheology is essential for plastic manufacturing. In order to master the rheological characteristics of polymethyl methacrylate (PMMA) a viscoelastic model of PTT is employed to describe its rheological behaviors in 1-D channel flow. The corresponding governing equations are established based on isothermal impressible fluid. Then construct a numerical method to calculate the viscosity change with shear rates so as to explore the influences of the nonlinear parameter and relaxation time spectrum. The rheological experiments were carried out with three PMMA brands in a capillary rheometer to measure the viscosity at different shear rate. The experimental results show the Newtonian region appears within the scope [0, 2.1] for shear rate, and the constitutive equation can correct describe the rheological characteristics if the parameters are set properly.

1. Introduction
PMMA are widely used in industries and biomaterials science, most of them are manufactured by injection molding process. The rheological behaviors of PMMA, however, have not received much attention because the process has only been applied in recent years. Some software such as Moldflow usually applies the uniform rheological model, for example, Cross-WLF model [1] to describe the rheological behaviors in the two different stages for convenience. But PMMA has special characteristic which are different from other polymers. It is necessary to characterize it with an appropriate model so as to control the manufacturing precisely. Over recent decades it has generally been recognized that some rheological complex fluids such as polymer melts cannot be adequately described by the Navier–Stokes theory. Because of this, several constitutive equations and flows for non-Newtonian fluids have been developed [2-3]. Therefore, a new viscoelastic model was studied in this study.

Although many attempts were performed to study the PMMA experimentally [4-5], a representative numerical model for the augmentation procedure does not exist. However, numerical techniques are the best approach to investigate the interaction of complex rheology (viscoelasticity) with realistic domain structure. Abbas et al. [6] studied two-dimensional magneto hydrodynamic boundary layer flow of an upper-convected Maxwell fluid in a channel with porous wall. Alenezi et al. [7] researched numerically and analytically the importance of the rheological parameters (viscosity and relaxation time) on the flow.

2. Viscoelastic Flow and Solution
Compared with tube-based models, the classical Phan-Thien–Tanner (PTT) model are not fully capable to describe the shear and the elongational behavior of branched polymer melts. Varchanis et al.[9] results show the model can make similar predictions for polydisperse linear polymers
characterized with multiple modes. In addition, if one considers that PTT and Giesekus feature only one nonlinear parameter to estimate for each mode, as well as all the difficulties of the nonlinear regression techniques, these simple models are found to be equally attractive with the more sophisticated tube models.

$$\left[1 + \frac{\lambda \alpha}{\eta} tr(\tau)\right] \tau + \lambda \frac{\nu}{\eta} \tau = 2\eta^2$$

(1)

here $\alpha$ is the nonlinear parameter to eliminate the singularity in extensional viscosity, $tr(\tau)$ denotes the trace of the viscoelastic tensor $\tau$, $\lambda$, $\eta$ represent the relaxation time and viscosity coefficient respectively. The upper convective derivative is defined as

$$\tau = \frac{\partial \tau}{\partial t} + v \cdot \nabla \tau - \nabla v \cdot \tau - \tau \cdot (\nabla v)^T$$

(2)

The governing equations reduces to

$$Q = 2\pi \int_{0}^{\mu} rv_z dr$$

(3)

$$- \frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \sigma_{rz}\right) + \frac{\partial}{\partial z} \sigma_{zz} = 0$$

(4)

For 1D viscoelastic symmetric flow, $\sigma_{zz} = \eta \frac{\partial v_z}{\partial r} + \tau_{zz}$, $\sigma_{\theta\theta} = 0$, the constitutive and momentum equations are reduced to

$$\tau_{rr} + \lambda \left( \frac{\partial \tau_{rr}}{\partial t} + v_z \frac{\partial \tau_{rr}}{\partial z} \right) + \frac{\lambda \alpha}{\eta} \left( \tau_{rr} + \tau_{zz} \right) \tau_{rr} = 0$$

(5)

$$\tau_{rz} + \lambda \left( \frac{\partial \tau_{rz}}{\partial t} + v_z \frac{\partial \tau_{rz}}{\partial z} - \frac{\partial v_z}{\partial r} \tau_{rr} \right) + \frac{\lambda \alpha}{\eta} \left( \tau_{rr} + \tau_{zz} \right) \tau_{rz} = \eta \frac{\partial v_z}{\partial r}$$

(6)

$$\tau_{zz} + \lambda \left( \frac{\partial \tau_{zz}}{\partial t} + v_z \frac{\partial \tau_{zz}}{\partial z} - 2 \frac{\partial v_z}{\partial r} \tau_{rz} \right) + \frac{\lambda \alpha}{\eta} \left( \tau_{rr} + \tau_{zz} \right) \tau_{zz} = 0$$

(7)

$$- \frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \left( \eta \frac{\partial v_z}{\partial r} + \tau_{rz} \right) \right) + \frac{\partial \tau_{zz}}{\partial z} = 0$$

(8)

The stress is the sum of each relaxation time component, i.e. $\tau^{(k)} = \sum_{k=1}^{N} \tau^{(k)}$, and each component $\tau^{(k)}$ is subject to the constitutive equation.

Integrate the momentum equation (8) twice, the formal expression for velocity $v_z$ in terms of pressures $p$ and stress $\tau$ can be obtained as follow

$$v_z = \int_{r}^{\mu} \left[ \frac{\tau}{2\eta_s} - \frac{\partial \tau_{zz}}{\partial z} - \frac{\tau_{zz}}{\eta_s} \right] d\tilde{r}$$

(9)

Substitute this formula into the mass equation (3) yields
\[ Q = 2\pi \int_0^R r^K \left[ \frac{\partial p}{\partial z} - \frac{\partial \tau_{rr}}{\partial z} \right] - \frac{\tau_{zz}}{\eta} \right] dr \]

If the stress is given, the pressure can be determined by Eq. (10). Then the velocity \( v \) can be calculated with Eq. (9) subsequently.

As the constitutive equations are nonlinear, usually it can not be determined by analytical methods. In this study, the finite difference method is employed to discretize the equations as follows

\[
\tau_{ij}^n + \lambda \left( \frac{\tau_{ij}^{n-1} - \tau_{ij}^{n-1}}{\Delta t} + \nu_{ij}^{n-1} \frac{\tau_{ij}^{n-1} - \tau_{ij}^{n-1}}{\Delta z} \right) + \frac{\lambda \alpha (\tau_{ij}^n + \tau_{ij}^n)}{\eta} \tau_{ij}^n = 0
\]

\[
\tau_{ij}^n + \lambda \left( \frac{\tau_{ij}^{n-1} - \tau_{ij}^{n-1}}{\Delta t} + \nu_{ij}^{n-1} \frac{\tau_{ij}^{n-1} - \tau_{ij}^{n-1}}{\Delta z} \right) + \frac{\lambda \alpha (\tau_{ij}^n + \tau_{ij}^n)}{\eta} \tau_{ij}^n = 0
\]

The algebraic equations (11)-(13) are nonlinear and the Newton-Rapson iterative method is employed to determine the solutions. Once the stresses are determined the velocity and pressure can be calculated with Eqs. (9) and (10) as illustrated above.

3. Results and Discussions

To verify the proposed method, the rheological experiments were conducted with a Göttfert Rheograph 25-50 using PMMA (CM205, 207 and 211, Chi Mei Corporation) at 220 °C, 240 °C and 260 °C. The measured viscosities at different shear rates were recorded, and the data for low shear rates were used to fit the relaxation time spectrum. Then the calculations were conducted with same conditions, and the simulated data were compared with that of experiments in high shear rates to get the best fitted nonlinear parameter. The fitted parameters of viscoelastic model are listed in Table 1.

| Brand | Temperature(°C) | Relaxation time spectrum | \( \eta_i (\text{Pa}\cdot\text{s}) \) | \( \alpha \) |
|-------|----------------|--------------------------|------------------|---|
| CM205 | 220            | 0.08943                  | 7135.4           | 0.05 | 0.55 |
|       | 240            | 0.08657                  | 6596.6           | 0.234 | 0.71924 |
|       | 260            | 0.07657                  | 3696.6           | 0.61924 |
| CM207 | 220            | 0.0857                   | 2850             | 0.05 | 0.14 |
|       | 240            | 0.0857                   | 122              | 0.21924 |
|       | 260            | 0.05657                  | 496.563          | 0.61924 |
| CM211 | 220            | 0.067                    | 4016.6           | 0.05 | 0.48 |
|       | 240            | 0.067                    | 935.02           | 0.52 |
|       | 260            | 0.057                    | 1396.6           | 0.42 |
|       |                |                          | 461.02           | 0.42 |
Figure 1. The change of viscosity as a function of shear rate at different temperatures for PMMA CM 205

Figure 2. The change of viscosity as a function of shear rate at different temperatures for PMMA CM 207

Figure 3. The change of viscosity as a function of shear rate at different temperatures for PMMA CM 211
Both the experimental and simulated results show the viscosity decreases with increasing shear rate, which indicates this type of PMMA display the ‘shear shinning’ phenomenon. For the low shear rate region, the viscosity decreases slowly and the fluid exhibits Newtonian flow, which is regarded as Newtonian region. These regions for the three PMMA brands are [0, 8], [0, 6] and [0, 3] respectively. The Newtonian viscosity is greater than 1000 Pa·s, which means PMMA is high viscous material. These figures also indicate the high Newtonian viscosity expands the Newtonian region.

In this study the two relaxation time spectrum is applied to construct the viscoelastic model for PMMA. The fitted parameters in Table 1 and the viscosity plots show the three brands of material have similar rheological behaviors. PMMA 205 is more viscous than the others especially in low shear rate region, and needs larger nonlinear parameter α to balance the stress change. PMMA 207 has the lowest viscosity, so it is the most suitable one for injection molding. The good agreements between experiments and simulations indicate the viscoelastic model can describe the PMMA rheological characteristics and the numerical method is valid for the 1D viscoelastic simulation.

The viscosity plots also show the viscosity of PMMA closely depends on the temperature. The viscosity decreases rapidly with increasing temperature, but the decreasing gratitude is different for the three brands. When the temperature increases from 220 °C to 260 °C, the viscosity decreases from 11698 Pa·s to 3812 Pa·s at approximate zero shear rate, the reduced viscosity is 8273 Pa·s for CM 205. However, this value decreases to 2422 Pa·s for CM 207 and 2527 Pa·s for CM 211 respectively. Meanwhile the viscosity for low temperature decreases more deeply that of high temperature in the high rate region, and they approximate the same value at the end.

4. Conclusion
To investigate the viscoelastic of PMMA the PPT model is employed to describe the rheological behaviors, and a numerical method is proposed to get the solution in 1D viscoelastic flow. The rheological experiments were conducted to measure the viscosity at different shear rate under three temperatures. The results show PMMA exhibits Newtonian characteristic at low shear rate and non-Newtonian behavior at high shear rate. The viscosity decreasing speed at high shear rate depends on the melt temperature. Among the three brands of PMMA, CM 207 is more suitable for injection molding. The simulations and experiments agree well, which indicates the proposed method is valid for PMMA.

5. Acknowledgements
Financial support from the National Science Foundation of China (No. 11672271) for this research work is gratefully acknowledged.

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