Polymer communication

A simple constitutive model describing the steady state shear viscosity and its prediction of the first normal stress function in shear flow

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A B S T R A C T
To describe the nonlinear behavior of polymer melts with few parameters, a simple three-parameter model for the shear viscosity function is proposed and applied to the polymer melt viscosity prediction as well as the first normal stress coefficient prediction using Wagner's relationship. Its predictions were compared with experimental data. The nonlinear form of the model correlates the viscosity very well with the experimental data over many decades of shear rate. It demonstrates that a simple nonlinear term can replace the sum of the series of multiple linear spectra. From the first normal stress coefficient correlation with the experimental data, the damping constant of Wagner's equation was obtained. Another applicability is demonstrated by the description of the elongational viscosity.

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1. Introduction

Three independent stress functions, the shear stress and the first and second normal stress differences, are sufficient for the characterization of the steady shear flow of “simple” incompressible fluids [1]. From these functions, three important material functions for the flow (viscosity function, defined as the ratio of shear stress to shear rate, and the first and second normal stress functions, defined as the ratios of the first and second normal stress differences to the square of the shear rate) are obtained. The constitutive equations describing the viscous and elastic behavior of the fluid can be generally classified into two groups; semi-empirical constitutive equations which are convenient for calculations but based on rough molecular or thermodynamic ideas and more rigorous theoretical equations which are quite complex and hardly tractable for simple calculations [1]. Various viscosity function models were suggested such as the power-law model [2], the Cross model [3], the Bueche-Harding model [4], the Ellis model [5], the Eyring model [6] and the Carreau-Yasuda model [7,8] to name a few. The Eyring model has a theoretical basis and the others were derived empirically. These semi-empirical constitutive equations are based mainly on their predictions of stress and material functions and not on the accuracy of their description of molecular processes.

As a part of our continuous effort to get a better simulation of viscoelastic fluid behavior, this article aims to devise a model, which is simple and easily applicable to many practical problems, from the observation of experimental data so as to correlate accurately the behaviors of the viscosity function and the first normal stress function. For practical application, it should have as few parameters as possible. This model should be able to describe, quantitatively as well as qualitatively, the behaviors of the viscosity and the first normal stress coefficient in steady shear flow of the transition region. In the linear viscoelastic regime, the first normal stress coefficient can be derived from the relationship with the viscosity [9] and in the nonlinear viscoelastic regime it can be approximated using the relaxation spectrum [10] because there is a definite indication that the description of the relaxation spectrum by differential constitutive equations is of comparable significance to the description of the nonlinear behavior [11]. However, the first normal stress coefficient depends on a higher moment of the relaxation spectrum than does the shear viscosity [9,12]. The spectrum, in turn, is related to the molecular weight distribution, with a broader distribution leading to a broader spectrum of relaxation times. Therefore, the first normal stress coefficient will depend on the molecular weight distribution in a manner significantly different from the viscosity.

Stastna and De Kee [12] have compared several relationships that have been proposed to calculate the first normal stress

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in the sense that part of them may be in a state of high stress and unyielding regions; it can handle non-uniform stress in the material, where part of it may flow freely while others not. This is similar to the relaxation of chain entanglements whereby some of the melt viscosity. Thus, the shear-thinning behavior can be considered as the relaxation of chain entanglements whereby some of the molecules are in entangled state while others are not. This is similar to the yielding behavior of polymer solutions where parts of the fluid may flow while the rest acts like a solid. The typical Bingham fluid model has been widely applied to the flow curves of many yielding fluids [2,11]:

$$
\tau = \tau_{y} + \eta \dot{\gamma}; \quad \tau \geq \tau_{0} \\
\dot{\gamma} = 0 \quad \tau < \tau_{0}
$$

where $\tau$ is the shear stress, $\dot{\gamma}$ is the shear rate, $\tau_{y}$ is the yield stress, and $\eta$ is the plastic viscosity. However, it does not properly describe the dynamics of the yielding fluids. Papanastasiou explained that the difficulties of this case are ascribable to the necessity of tracking randomly distributed yield material surfaces due to a discontinuity in the stress at the critical shear rate [15]. To avoid the discontinuity in the flow curve owing to the incorporation of the yield criterion, Papanastasiou proposed a simple equation that can describe the entire yield flow curve, before and after yield [15]:

$$
\tau(\dot{\gamma}) = \tau_{y}[1 - \exp(-a\dot{\gamma})] + \eta \dot{\gamma} = \frac{\tau_{y}[1 - \exp(-a\dot{\gamma})]}{\gamma} + \eta \frac{\dot{\gamma}}{\gamma}
$$

where $\eta$ is the viscosity of the yielded material, $\tau_{y}$ is the yield stress and $a$ is the time constant. This model is suitable for both yielding and unyielding regions; it can handle non-uniform stress in a material, where part of it may flow and part may act like a solid [15]. Depending on the exponent $a$, quick stress growth can be achieved with a very small change of strain rate, consistent with the behavior of the material in its practically unyielded state.

Since some polymer chains in the shear flow are entangled while others are not, the situation is analogous to the yielding fluid in the sense that part of them may flow freely while others not. Based on this analogy, we premise that the stress can be similarly expressed as a function of shear rate, i.e., we use a slightly modified version of Eq. (2) for the shear flow,

$$
\tau_{12}(\dot{\gamma}) = \frac{G_{0}(1 - \exp(-\lambda \dot{\gamma}))}{\gamma (\lambda \dot{\gamma})^{n}} \dot{\gamma} = \eta_{12} \dot{\gamma}
$$

where $\lambda$ is the time constant (not necessarily a relaxation time), $G_{0}$ is the modulus, $\eta_{12}$ is the shear viscosity exponent. Exponent $n$ controls the stress decrease with the shear rates. The power-law form of the shear rate in the denominator is used to control the rapid fall-off of the shear stress, similar to Carreau model [2]. The viscosity function in the shear viscosity is then expressed as

$$
\eta_{12}(\dot{\gamma}) = \frac{G_{0}(1 - \exp(-\lambda \dot{\gamma}))}{\gamma (1 + (\lambda \dot{\gamma})^{2})^{n}}
$$

This is a three-parameter model. At low shear rate, the shear viscosity approaches

$$
\lim_{\gamma \to 0} \eta_{12} = \lambda G_{0}
$$

Once the viscosity in the low shear rate (zero shear rate viscosity, $\eta_{0}$) is known from measurements, this model becomes in fact a two-parameter model because the zero shear rate viscosity can be approximated as $\eta_{0} = \lambda G_{0}$. Then each parameter ($\lambda$ and $n$) in Eq. (4) controls one particular aspect of the fluid curve shape. At large shear rates, this viscosity function drops to zero. Addition of the viscosity at infinite shear rate ($\eta_{\infty}$) to Eq. (4) can improve the model’s prediction at high shear rates,

$$
\eta_{12}(\dot{\gamma}) = \frac{G_{0}(1 - \exp(-\lambda \dot{\gamma}))}{\gamma (1 + (\lambda \dot{\gamma})^{2})^{n}} + \eta_{\infty}
$$

However, the data at low shear rates and in the neighborhood of the reciprocal of the time constant are most critical in obtaining meaningful values of the parameters. Unless specifically mentioned, Eq. (4) is mainly used for the model prediction.

As we mentioned above, the first normal stress coefficient depends on a higher moment of the relaxation spectrum than does the shear viscosity. Wagner [10] showed that, in steady shear flow, a relation between the first normal stress function and the viscosity function can be presented as

$$
\psi_{1} = -\frac{1}{m} \frac{d\psi}{d\dot{\gamma}}
$$

which results from a K-BKZ type single integral constitutive equation. The material parameter, $m$ (damping constant), is associated with the strain dependence of the memory function. This relation has been successfully used to describe the first normal stress function of polymer melts and solutions [10]. Substituting Eq. (4) into Eq. (7) gives

$$
\psi_{1} = -G_{0}(1 + (\lambda \dot{\gamma})^{2})^{-n} \dot{\gamma} \left[2(\lambda \dot{\gamma})^{2} \exp(-\lambda \dot{\gamma}) - \frac{2(\lambda \dot{\gamma})^{2} \exp(-\lambda \dot{\gamma}) - 1}{\lambda \dot{\gamma}} \frac{1}{1 + (\lambda \dot{\gamma})^{2}} \right]
$$

The damping constant $m$ can be determined by the fitting of experimental data with this equation.

3. Comparison with experimental data and discussion

In order to see how the model works, we compared the calculation with experimental data reported in the literature. Here, the same set of data as used by Wagner [10] and Souvaliotis and Beris [16] was used. These data obtained for low density polyethylene...
used by Wagner [10] and another low density polyethylene which has been extensively studied by Laun and Münstedt [17–21]. Shown in Fig. 1 are Laun’s data [17] for a melt of very polydisperse long chain branched low density polyethylene (LDPE-I) and another low density polyethylene melt of Chen and Bogue’s data used by Wagner [10]. The solid lines are optimized fittings. Though Eq. (4) is just a three-parameter model, the calculation affords good fits with experimental data. The nonlinear form of the model correlates the viscosity very well with the experimental data over many decades of shear rate for very polydisperse LDPE-I melt as well as other LDPE melts. Optimal parameter values are in Table 1. The zero shear rate viscosity (η0) values by the present model and Wagner’s fitting by Carreau’s model [10] are naturally in good agreement. It decreases with the temperature which reflects the decrease of the viscosity with temperature. This good agreement was not possible using a single mode extended White-Metzner model or Phan-Thien-Tanner model as shown by Souvaliotis and Beris [16]. The result is quite encouraging.

Since we are sure that the proposed model works correctly for the shear viscosity function, we apply it for the prediction of the first normal stress function using Wagner’s relationship. Comparisons of calculations by Eq. (6) and experimental data are shown in Fig. 2. Overall agreement is excellent for LDPE-I in Fig. 2(A). The parameter values are those of the viscosity function, Souvaliotis and Beris [16] had to use different parameter values to achieve the best fit of Ψ1 and η. Current model proves superior to the spectrum fitting because Wagner [10] had to use five relaxation modes to get a good agreement for the first normal stress coefficient function at both low and high shear rates. The proposed model works very well for all shear rate ranges. Also it does not show obvious artificial maximum in the first normal stress coefficient function which appeared when the Carreau or Cross models were used [10,16]. The values of the damping constant, m, from this study was 0.12 while that from Wagner was 0.13 [10]. As Stastna and De Kee [12] reported, Wagner’s method depends on the viscosity model. Considering the damping constant values were determined by different methods, this agreement is quite promising. This implicates that our damping coefficient value can be used in Wagner’s constitutive equation. Therefore, once we have the shear viscosity and the first normal stress coefficient data in shear flow, we can obtain a reliable damping coefficient or, if the damping coefficient is provided by other experiments with the shear viscosity function data, we can predict the first normal stress coefficient. The comparison for the first normal stress coefficient function of another low density polyethylene shows also good correlation in Fig. 2(B). Due to the inflexion point, it shows a slope variation with the shear rate this time. Again, the adjusted damping coefficient, m, by the current model was 0.12, close to that of Wagner, 0.13.

Although we investigated the material function for shear flow only, the proposed model can be used for other flow types, too. As an example, it can be applied to the elongational flow behavior. Similar work was reported for the Cross model [22]. Consider a simple nonlinear model, namely the White-Metzner model [2,9]. In this model, the relaxation time is not a constant but depends on the rate of strain, particularly on the second invariant of the rate of strain tensor which is the shear rate in shear flow but root-three times the extension rate in uniaxial extensional flow (taking the second invariant of the deformation rate tensor is not always appropriate as explained by Souvaliotis and Beris [16]). Then the expression for the extensional viscosity is written as follows [1]

\[ \eta_\varepsilon = 2\eta_\varepsilon(\Pi_D) / \left[ 1 - 2 \frac{\lambda_E(\Pi_D)\Pi_D}{\sqrt{3}} \right] + \eta_\varepsilon(\Pi_D) / \left[ 1 + \frac{1}{\sqrt{3}} \lambda_E(\Pi_D)\Pi_D \right] \]

(9)

where \( \Pi_D \) is the second invariant of the deformation tensor. To account for the fact that high strain rates reduce the relaxation time, Barnes and Roberts [22] (a special case of Ide and White [23]) proposed an equation for the relaxation time:

\[ \lambda_E(\Pi_D) = \lambda_0 / (1 + K\Pi_D) \]

(10)
where \( \lambda_0 \) and \( K \) are parameters with the dimensions of time. By keeping the value of \( 2 \lambda_0 / \sqrt{3} K \) less than 1, extensional viscosity becomes finite \([16,22]\). Fig. 3 shows an example of the comparison between the calculated values and the experimental data of Laun \([17]\). The shear viscosity was fitted first, then, using the obtained parameter values, the extensional data were fitted. The agreement is quite good and shows the fast rises in extensional viscosity. At low deformation rates, the ratio of extensional viscosity to shear viscosity becomes 3 which can be easily surmised from Eq. (9). At high deformation rates the curves are parallel which can also be deduced from Eq. (9). This means that the Trouton viscosity will reach a constant value at high deformation rates as noted by Barnes and Roberts \([22]\).

We demonstrate here that the current three-parameter model can describe extensional flow behavior as well as shear flow. If we use the White–Metzner model to predict transient behavior, we should change the relaxation time dependence on the second invariant of the rate of strain tensor because it does not satisfy the well-posedness of the flow problem \([16]\). To correct this problem, Souvaliotis and Beris \([16]\) explained why the relaxation time should be a function of the invariants of the stress matrix. Even though the proposed models are not derived from rigorous mathematical theory, they describe the polymeric fluids behavior very well. This will be useful in the characterization of polymeric materials' rheological properties.

4. Conclusion

It has been demonstrated that the proposed three-parameter model for the viscosity function in shear flow can correctly describe the fluid behavior over a shear rate range of several orders of magnitude for low density polyethylene melts. Furthermore, it affords to correlate the first normal stress coefficient with experimental data very well and show that can be applied for engineering work. Prediction of the first normal stress coefficient using Wagner's relationship affords good agreement with experimental data. We confirm that Wagner's relationship is valid for predicting the first normal stress coefficient as a function of the shear rate. It is also good for the description of elongational flow as well as shear flow. From the exemplary comparison, the Trouton ratio reaches constant values at high and low deformation rates. The proposed model is quite compact and might be useful for simple modeling and simulation as well as for polymer's rheological property characterization.

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