Start-up and Transient Flow Effects From the Molecular Weight Distribution

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Abstract. Start-up and transient shear-stress flows are modeled here using the recently generated constitutive model for linear viscoelasticity of polymers. The relation derived from control theory and the melt calibration procedure has been developed between the relaxation modulus, dynamic viscosity, and molecular weight distribution (MWD). This study extends the start-up, and transient effects of linear viscoelasticity on stress and viscosity from the novel viewpoint of the classical Boltzmann superposition principle. The shear viscosity measurements of well-characterized classical low-density polyethylene (LDPE IUPAC A) with a known MWD were used to obtain time-dependent stress and viscosity transitions. The developed formulas model the start-up situation with an overshoot effect and shear-stress growth coefficient. Simulations were performed for relaxation modulus measurements at different shear histories defined by the effective viscosity. As an example of practical application, injection molding for producing a cellular-phone cover were modeled to obtain the pressure loss and orientation level for every element in finite element models, which predicted the shrinking and warping of the end products.

Keywords: Polydispersity; Transient viscosity; Shear history; Simulations; Orientation.

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INTRODUCTION

Numerous studies have modeled the start-up effect using the tube concept of Doi and Edwards for linear monodisperse polymers. We have used an alternative procedure that starts directly from the molecular weight distribution (MWD) and viscoelastic properties in a polydisperse structure [1-2], which are converted here for shear viscosity and flows with different transitions. This is possible since viscoelastic and molecular weight fractions are linearly interrelated by control theory and melt calibration procedures.

We first present the formulas for steady shear viscosity, and then explain the use of the time-dependent linear transient viscosity rather than the shear stress. A wide range of modeled viscosity functions for the ramp test is presented. We introduce a novel way to explain and sum all shear histories based on the respective effective viscosity using a new version of the classical Boltzmann superposition principle. The importance of the effective relaxation state is highlighted before describing relaxation and other measurements. Some practical uses are presented in simulations of the filling of injection-molded parts [3].

THEORY AND RESULTS

The procedure used to derive the following characteristic formula for shear viscosity is similar to that presented earlier for relaxation modulus [1] and complex viscosity [2]:

\[
\log \frac{\eta(\dot{\gamma})}{\eta_0} = -\log \frac{\dot{\gamma}}{\dot{\gamma}_c} \int_0^1 \left( P^w(\log \psi) + P^r w(\log \frac{\psi}{R}) \right) d\log \psi
\]  

The rheologically effective distribution (RED), \(w(\log \dot{\gamma})\), is a function of shear rate on a logarithmic scale, and the characteristic shear rate, \(\dot{\gamma}_c\), is on the order of 1/s. Default value of \(R = 10^6\) for distance was set for the Rouse shear range distribution. An alternative model based on a more complex analytical formula inverted for shear
viscosity in a similar way can be used, but this produced no noticeable difference when modeling the viscoelastic properties over the measured ranges.

A simple relation can be written for the melt calibration, $M(\dot{\gamma})$, as a function of shear rate, where the value of $M$ is $M = M_f \left( \frac{\dot{\gamma}}{\dot{\gamma}_1} \right)^n$.

This formula can be used to convert MWD $w(\log M)$ into RED or $w'(\log \dot{\gamma}) = w(\log M)$, as needed in Eq. (1).

We model the time-dependent transient shear viscosity $\eta(t,\dot{\gamma})$ at different shear rates. To describe stress and viscosity at different induced shear rates, we use a caret to indicate the effective old viscosity $\hat{\eta}$ at $t=t_0$ developed at a shear rate $\dot{\gamma}_0$ or $\hat{\eta} = \eta(t_0, \dot{\gamma}_0)$, which reaches $\lim_{t \to \infty} [\eta(t, \dot{\gamma}_0)] = \eta(\dot{\gamma}_0)$ in the steady-state situation. Depending on the shear history, effective viscosity $\hat{\eta}$ at time $t=t_0$ may vary considerably from its steady-state limit $\eta(\dot{\gamma}_0)$.

New imposed shear rate $\dot{\gamma}$ results in the viscosity gradually approaching its limit $\lim_{t \to \infty} [\eta(t, \dot{\gamma})] = \eta(\dot{\gamma})$. The negative or positive viscosity difference $\Delta \eta = \eta - \hat{\eta}$ approaches zero as a function of normalized relaxation $g(t) = G(t)/G_0$. However, during a constant shear all of the molecules do not relax or orientate to every possible direction (or, at least, the effect is minimal in the perpendicular $z$ direction), and thus we need dimension exponent $D \sim 1/3$ since the relaxation of orientation change is in one direction. The shear rate and time-dependent transient viscosity are added to the effective viscosity: $\eta(t,\dot{\gamma}) = \hat{\eta} + \Delta \eta(t)$. At different shear rates the stress results from the continuous loading of the molecules rather than relaxation, and we get results shown in Fig. 1a by Eq. (3) for transient viscosity:

$$\eta(t,\dot{\gamma}) = \hat{\eta} + (\eta(\dot{\gamma}) - \hat{\eta}) (1 - g(t))^D$$

(3)

**The Boltzmann Superposition Principle for Shear Viscosity**

Now we rewrite the Boltzmann superposition principle for shear viscosity and molecular orientation: the total effect of applying several shear deformations and changes in molecular orientations is simply the sum of their individual effects. For continuous changes in viscosity and orientation, this sum is generalized to an integral as follows:

$$\eta(t) = \hat{\eta} + \int_{-\infty}^{t} (1 - g(t - \tau))^D \frac{d\eta(\tau)}{d\tau} \, d\tau$$

(4)

The Boltzmann superposition principle yields the linear viscoelasticity in a similar way as for all earlier presented formulas for control theory and melt calibration, and we can conclude that we now have linear viscoelasticity starting from the MWD to the transition effects.

**FIGURE 1.** Modeled viscosity curves for IUPAC A LDPE at 150°C. a. Transient viscosity $\eta(t,\dot{\gamma})$ over a wide range of $\dot{\gamma}$ values from the steady and effective shear rate $\dot{\gamma}_0 = \dot{\gamma} = 1/s$ at $t=t_0$. b. Start-up $\eta'(t,\dot{\gamma})$ viscosity curves at new induced lower and higher shear rates. The lower thick line corresponds to the induced $\dot{\gamma} = 1/s$ shear rate. The upper thicker line was calculated from the relaxation modulus using the classical equation.
**Start-up, Relaxation Modulus and Orientation Simulations**

Now in the start-up situation, shear stress growth coefficient \( \eta^*(t, \dot{\gamma}) \) shown in Fig. 1b, can be developed from a parallel model by the transient viscosity function \( \eta(t, \dot{\gamma}) \), where \( \dot{\gamma}_x = 3\dot{\gamma} \) is due to the elongation in one direction:

\[
\eta^*(t, \dot{\gamma}) = \frac{\eta(t, \dot{\gamma})\dot{\gamma}^3t}{\dot{\gamma}_x t + 1}
\]  

(5)

As we explained previously [1-2], the measurement of relaxation modulus requires at least two steps, including simulating the shear history and the shear of the initial ramp. We rewrote the procedure presented in our earlier papers to find effective viscosity \( \tilde{\eta} \) and effective zero relaxation modulus \( \tilde{G}_0 \) at \( t=t_0 \) instead of classical zero modulus \( G_0 \).

Now we use relaxation function \( G(t, \dot{\gamma}) = G_0(t) - \Delta G_0(t) \) with a principle by similar to that presented for the transient viscosity in Eq. (3):

\[
G(t, \dot{\gamma}) = G_0(t) + (G_0(t) - \tilde{G}_0(t))(1 - \frac{G_0(t)}{\tilde{G}_0})
\]

(6)

Relaxation function \( G(t, \dot{\gamma}) \) can be converted to a standard imposed-ramp relaxation function \( G(t, \gamma) \) as a function of strain using the information in Fig. 2a if the shear history, implied duration of strain, and amount of strain are known.

Whilst it is important to model the shear stress and viscosity, it is equally important to model the molecular orientation during these transitions [3]. Orientation levels represent the memory and source of viscosity. In the characteristic Eq. (1) not only sole integrand but complete integral is called the characteristic polymer structure function \( P(\dot{\gamma}) \), which is related to the orientation level shown in Fig. 2b. This yields an effective shear viscosity \( \dot{\gamma} = \eta_0 |P(\dot{\gamma})| \) according to Eq. (1) modified by some simple algebraic conversions.

**FIGURE 2.** IUPAC A LDPE simulations. a. Relaxation modulus \( G(t, \dot{\gamma}) \) simulations at different effective shear rates related to effective zero relaxation modulus \( \tilde{G}_0 \) at 150°C. b. Orientation simulation layer at \( t=0.1 \) s during the filling of an injection mold for a cellular-phone cover. Different colored regions and respective \( P=\text{values}/100 \) indicate orientation levels in the filled melt.

**REFERENCES**