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Transient modeling of viscosity

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The viscoelastic behavior of polymer melt is a significant factor during rheological characterization and should be taken into account during analysis and viscosity modeling.

Rheological characterization of a polymer melt is a common procedure for the analysis of polymer processing. The measurement of viscosity plays a central role in such analyses and this rheological property is a fundamental characteristic of the material.[1] Common uses of viscosity measurement include monitoring of lot-to-lot batch stability, incorporation into process simulations, and quality assurance of materials development.[2] Previous studies identified and characterized a relaxation response in capillary-derived viscosity in several polymers, including semicrystalline and amorphous polymers.[3] The viscosity of polymer melts also depends strongly on their temperature and deformation rate.[4,5] Consequently, many different constitutive models (i.e., which describe the stress–strain relationship in a material) have been developed to characterize the shear rate and temperature dependence of the viscosity.

A model that has been widely implemented in various process simulations due to its intuitive form and excellent predictive capability across a relatively wide range of processing conditions is the Cross-WLF model. It is named after a combination of two constitutive models: a 'Cross' model that describes the shear rate dependence and a 'WLF' (Williams, Landel, Ferry) model that describes the temperature dependence.[6–8] However, rheologists have observed that there can be a significant transient response (or stress relaxation response) in the settling of viscosity when transitioning between shear rates. The purely viscous Cross-WLF model fits observed data but does not capture this transient behavior (see Figure 1). Consequently, there is considerable interest in developing high-fidelity models that take relaxation behavior into account.

The viscoelastic behavior of fluids has been long recognized. Isayev[9] aptly states that "[a] basic characteristic of polymer systems is their relaxation spectrum, which determines all manifestations of their viscoelastic properties." From first principles, Maxwell showed that imposed stresses in a viscoelastic material should decay at an exponential rate.[10] According to Maxwell, a solid body free from viscosity will exhibit a stress, σ, proportional to strain, ε, wherein $\sigma = E\varepsilon$ for a coefficient of elasticity, E. Any changes in the strain will cause a proportional change in the stress, such that $d\sigma/dt = E d\varepsilon/dt$. If the body

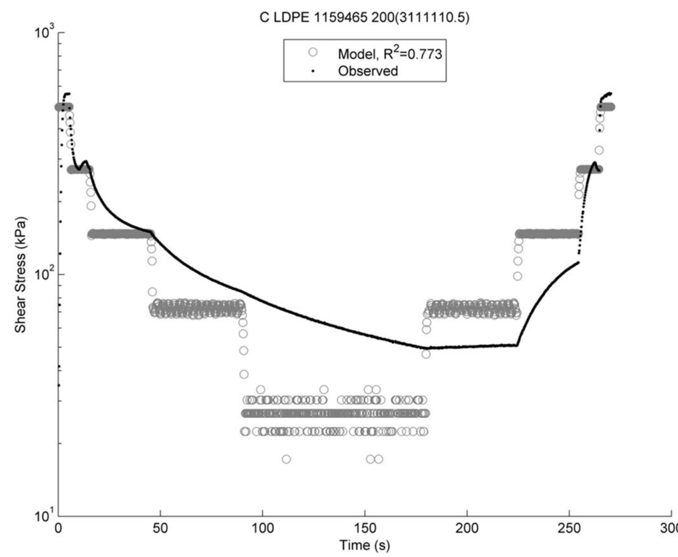

Figure 1. *Observed shear stress as a function of time throughout a hysteresis test of low-density polyethylene (LDPE). The polymer exhibits a significant transient response. The purely viscous Cross-WLF (for Williams, Landel, Ferry) model predicts shear stresses having a step response in accordance with the applied apparent shear rates. The coefficient of determination, R^2, between the observed and modeled stress is 0.773.*

is viscous, the stress will not remain constant but will tend to disappear at a rate depending on the value of stress and the nature of the body. Maxwell proposed that this rate of relaxation is proportional to the imposed stress, such that:

$$\frac{d\sigma}{dt} = E\frac{d\varepsilon}{dt} - \frac{\sigma}{\lambda} \quad (1)$$

where λ is a characteristic relaxation time. For a constant applied strain, the stress relaxation is:

$$\sigma = E\varepsilon e^{-t/\lambda} \quad (2)$$

with the viscosity defined as $\eta = E\lambda$ in the presence of a steady flow, i.e., constant $d\varepsilon/dt$.

We wished to extend Maxwell's model of linear viscoelasticity to a nonlinear analysis through the use of numerical simulation that

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incorporates a constitutive model describing the relaxation time as a function of applied stress. In the study presented here, we conducted rheological capillary and parallel plate characterization for a low-density polyethylene.[11] The objective was to identify the simplest reasonable viscoelastic analysis that captures the transient shear stress behavior observed in Figure 2. We assumed no steady conditions, and we analyzed transient data, with time steps between 0.0001 and 0.2s, using a nonlinear, viscoelastic constitutive model in which the relaxation time was modeled as a function of the applied stress.

Maxwell[6] proposed a theory of linear viscoelasticity by suggesting that the rate of relaxation is proportional to the applied stress according to Equation 1. For transient analysis of the dynamic rheological data, an incremental solution of the stress is sought that allows for ongoing analysis of varying strain. Accordingly, multiplying Equation 1 by the time constant, λ, provides:

$$\lambda \frac{d\sigma}{dt} = \lambda E \frac{d\varepsilon}{dt} - \sigma \qquad (3)$$

For a simple shear flow, the rate of change of strain with respect to time is the shear rate. The viscosity, η, can also be substituted according to Maxwell's definition of viscosity as the product of the modulus and the time constant, $E\lambda$. The resulting model is:

$$\lambda \frac{d\sigma}{dt} = \eta\dot{\gamma} - \sigma \qquad (4)$$

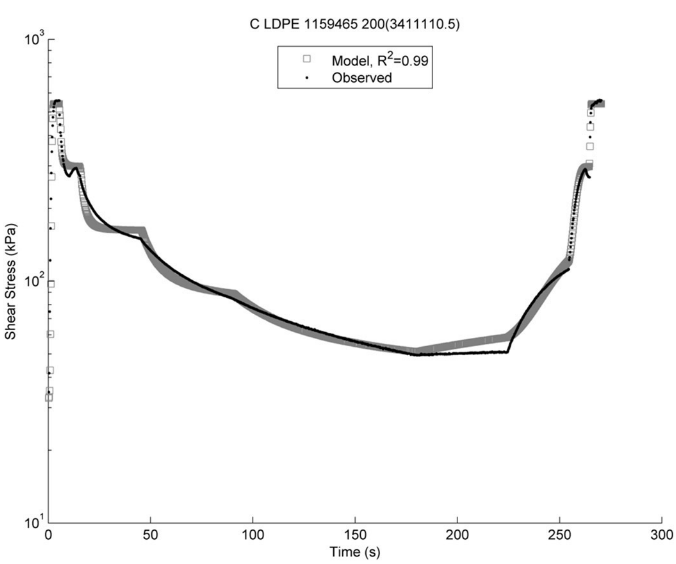

Figure 2. *Observed shear stress as a function of time, including the modeled stress predicted with viscoelasticity but without compressibility, pressure dependence, and viscous heating.*

where $\dot{\gamma}$ is shear rate. Simple rearrangement provides an incremental formulation of the stress:

$$\dot{\sigma} = \frac{1}{\lambda}(\eta\dot{\gamma} - \sigma) \qquad (5)$$

The described transient analysis thus implements linear viscoelasticity when λ is a constant, or nonlinear viscoelasticity with λ as a function of the stress or other states. A salient feature of this analysis is that it can model the shear stresses observed during a dynamic rheological experiment wherein the material will tend to relax even as new stresses are applied. The model is fully consistent inasmuch as it supports pure stress relaxation without flow, shear stress development from a relaxed state, and steady shear flow.

The fit model, plotted in Figure 2, explains more than 99% of the transient variation in the capillary and parallel plate rheometers that we observed. The results indicate that the described constitutive model closely predicts the observed viscoelastic behavior of the polymer melt tested. Furthermore, the results indicate that the relaxation spectrum modeled with the transient analysis of the capillary rheological data is closely correlated to the results predicted by the same transient analysis of parallel plate rheological data.

In summary, constitutive modeling describes the viscoelastic behavior in both capillary and parallel plate rheometers. Moreover, our analysis and results suggest that the viscoelastic behavior of a polymer melt is a significant factor during rheological characterization, and that the modeling of the transient response should be taken into consideration during rheological analysis to provide high-fidelity models. In future work we will extend the experimental portion of the work, and we will examine the nonlinear Maxwell model for transient analysis of rheological data for different grades of polymers with varied molecular weight and morphology.

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