A non-affine transient network model

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Abstract A new formulation of non-affine motion for the network model is proposed and its applications are presented in this manuscript. The major improvement is that a finite elongational viscosity is predicted for finite elongational rates contrary to the infinite elongational viscosities existing at some elongational rates predicted by previous network models. Comparisons with experimental data of the shear viscosity, normal stress coefficient and elongational viscosity are given, in terms of the same set of model parameters. Model predictions for the stress growth are also shown.

Key words Non-affine motion · Transient network · Elongational viscosity

Introduction

The need to develop new constitutive equations that can adequately describe the rheological properties of polymeric materials was recently stressed by Caswell (1996). The transient network model, which is a modification of the network theories of rubber elasticity, was originally proposed by Green and Tobolsky (1946). Since then several improvements have been proposed and these are discussed in Bird et al. (1987b) and Chan Man Fong and De Kee (1999). However, there is still ample room for further improvement.

One of the possible limitations of most network models is that the elongational viscosity can tend to infinity at a finite extensional rate. It is also observed that polymer melts cannot be extended indefinitely. Beyond a certain critical strain the materials rupture (Malkin and Petrie 1997). Most of the recent experiments have been limited to small extensional rates and to the measurements of transient elongational viscosity. In many cases a steady state is unattainable. Solomon and Muller (1996) have summarized the results in this area. These experimental observations may imply that an infinite stress is required to extend some polymeric materials beyond the critical strain. This is consistent with an infinite extensional viscosity at a finite strain rate.

However, Mackay et al. (1995) using the opposing jet method found that for three polymer melts (linear low-density polyethylene, low density polyethylene and polypropylene) the extensional viscosity initially increases with increasing extensional rates, reaches a maximum and then decreases with further increases to the extensional rate. The extensional rates in their experiments extended to $10^3 \text{ s}^{-1}$. This behavior does not necessarily imply that the molecular segment can be extended indefinitely (James and Sridhar, 1995); it could also mean that the motion of the segments is non-affine. Here, we present a non-affine network model that predicts a finite extensional viscosity at all extensional rates. Wedgeood and Geurts (1995) have considered an alternative non-affine network model and their model also predicts a finite elongational viscosity at all extensional rates.

Formulation

We assume that the polymeric material is represented by a network of temporary junctions. The creation and destruction of junctions is attributed to Brownian motion and to the imposed deformation.

If $\mathbf{R}$ is the end-to-end vector of a segment and $\Psi(\mathbf{R}, t)$ is the probability of having a segment in the range $\mathbf{R}$ to
(R + dR), a balance of segments yields (Bird et al. 1987b):
\[
\frac{\partial \Psi}{\partial t} = -\frac{\partial}{\partial \mathbf{R}} \cdot (\dot{\mathbf{R}} \Psi) + c - \ell \tag{1}
\]
where the dot denotes a derivative with respect to time, c and \(\ell\) are the rates of creation and loss of segments respectively. We assume that the segments move non-affinely and that the slip depends on \(R^2\). Physically we expect that the slip increases with the length of the segments. This, as mentioned in the introduction, allows for high extensional rates without the segments having to undergo large extensions. We postulate that \(\mathbf{R}\) is given by:
\[
\dot{\mathbf{R}} = \left[ \mathbf{L} - \frac{1}{2} \dot{\xi} (1 + b R^2) \right] \cdot \mathbf{R} \tag{2}
\]
where \(\mathbf{L}\) is the velocity gradient tensor, \(\xi\) and \(b\) are constants and \(\dot{\xi}\) is the rate-of-deformation tensor.

Note that if \(b = 0\), the present model simplifies to the previous non-affine model (Chan Man Fong and De Kee 1999). We assume that c and \(\ell\) can be written as:
\[
c = k_c \Psi_0 + k_1 f_2(\gamma) \Psi \tag{3a}
\]
\[
\ell = k_c \Psi + k_2 f_1(\gamma) \Psi \tag{3b}
\]
where \(k_c, k_1\) and \(k_2\) are constants, \(\Psi_0\) is the equilibrium configuration distribution, \(\gamma\) is the second invariant of \(\dot{\xi}\), \(f_1\) and \(f_2\) are functions to be prescribed and they satisfy \(f_1(0) = f_2(0) = 0\) .

Substituting Eqs. (2) and (3a, b) into Eq. (1), multiplying the resulting expression by \(\mathbf{R R}\), integrating over the configuration space and assuming that Peterlin’s approximation acceeds, gives:
\[
\frac{d}{dt} \langle \mathbf{R R} \rangle = \langle \dot{\mathbf{R}} \cdot \mathbf{R R} + (\mathbf{R R}) \cdot \mathbf{R} \rangle \\
- \langle \dot{\xi} (1 + b R^2) \dot{\xi} \rangle (\mathbf{R R}) + \langle \mathbf{R R} \rangle \cdot \dot{\mathbf{R}} \\
+ k_c \langle \mathbf{R R} \rangle_0 + k_1 f_2(\gamma) \langle \mathbf{R R} \rangle \\
- k_c \langle \mathbf{R R} \rangle - k_2 f_1(\gamma) \langle \mathbf{R R} \rangle \tag{5}
\]
where \(\langle \cdot \rangle\) denotes the average over the configuration space and \(T\) denotes the transpose.

We assume that the segments are Hookean and that the total stress \(\Pi\) can be written as:
\[
\Pi = -H \langle \mathbf{R R} \rangle \tag{6}
\]
where \(H\) is a constant.

It follows from Eq. (6) that
\[
\langle \mathbf{R R} \rangle_0 = J_0 \delta \tag{7}
\]
We follow the usual procedure and write:
\[
\Pi = \mathbf{P} \delta + \tau \tag{8a}
\]
\[
\langle \mathbf{R R} \rangle_0 = J_0 \delta \tag{8b}
\]
where \(\mathbf{P}\) is the equilibrium pressure, \(\delta\) is the unit tensor and \(J_0\) is a constant. Substituting Eqs. (6), (7), (8a, b) into Eq. (5) yields:
\[
\dot{\tau} + \lambda \tau + 3 \eta_m \beta (\gamma \cdot \tau + \gamma) - \lambda \beta (\text{tr} \tau) (\gamma \cdot \tau + \gamma) \\
= -\eta_m \dot{\gamma} [(1 - \xi) - (6 \eta_m \beta / \lambda) + 2 \beta (\text{tr} \tau)] \tag{9}
\]
where \(\lambda = 1 / k_c, \alpha = 1 + \lambda (k_1 f_1 - k_2 f_2), \beta = b \xi / 2 H\) and \(\eta_m = J_0\). \(\gamma\) is the Gordon-Schowalter derivative of \(\tau\) and is given by:
\[
\dot{\gamma} = (D \tau / D t) - \langle \dot{\mathbf{R}} \cdot \mathbf{R R} - \mathbf{R R} \cdot \dot{\mathbf{R}} \rangle \cdot \tau - \tau \cdot (\mathbf{L}^T - \xi \gamma / 2) \tag{10}
\]
where \(D / D t\) is the material derivative.

## Results and discussion

**Steady-shear flow**

The velocity components of a steady-shear flow can be written as:
\[
v_1 = \dot{\gamma} x_2, \quad v_2 = v_3 = 0 \tag{11}
\]
where \(\dot{\gamma}\) is the shear rate. The relevant stress equations are:
\[
\alpha \tau_{11} + \dot{\gamma} \tau_{12} [-2 \lambda + \lambda \xi + 6 \eta_m \beta - 2 \beta (\text{tr} \tau)] = 0 \tag{12a}
\]
\[
\alpha \tau_{22} + \dot{\gamma} \tau_{12} [\lambda \xi + 6 \eta_m \beta - 2 \beta (\text{tr} \tau)] = 0 \tag{12b}
\]
\[
\alpha \tau_{12} + \dot{\gamma} [\tau_{22} + \xi (\tau_{11} + \tau_{22}) / 2] + 3 \eta_m \beta \dot{\gamma} (\tau_{11} + \tau_{22}) \\
- \lambda \beta \dot{\gamma} (\tau_{11} + \tau_{22})(\text{tr} \tau) \\
= -\eta_m \dot{\gamma} [(1 - \xi) - 6 \eta_m \beta + 2 \beta (\text{tr} \tau)] \tag{12c}
\]
\[
\tau_{33} = \tau_{12} = \tau_{23} = 0 \tag{12d, e, f}
\]
The viscosity \(\eta\) is given by
\[
\eta = -\tau_{12} / \dot{\gamma} \tag{13}
\]
Combining Eqs. (12a–f) and (13) yields a cubic equation in \(\eta\) which can be written as
\[
16 \lambda^2 \beta^2 \beta \eta^3 [\alpha + \lambda \xi \gamma / \alpha] \\
+ 4 \lambda \beta \eta^2 [2 \alpha C_1 + (1 + 1 / \alpha) A_1 \lambda \xi \gamma^2] \\
+ \eta \alpha [\alpha C_1 + A_1 \lambda \xi \gamma^2 (\lambda \xi + 2 \eta_m \beta)] - \alpha^2 \eta_m A_1 = 0 \tag{14a}
\]
\[
A_1 = (1 - \xi) - 6 \eta_m \beta / \lambda \tag{14b}
\]
\[
B_1 = \alpha + \lambda \xi (1 - \xi) - 12 \eta_m \beta \xi \tag{14c}
\]
\[
C_1 = \alpha + \lambda \xi (\lambda \xi + 6 \eta_m \beta / \alpha) \tag{14d}
\]
The first and second normal stress coefficients are respectively given by
\[
\Psi_1 = 2 \lambda \eta / \alpha \tag{15a}
\]
\[
\Psi_2 = -\eta \{\lambda \xi + [6 \eta_m \beta \alpha + 4 \lambda^2 \beta \eta^2 (1 - \xi)] \\
/ (\alpha + 4 \lambda \beta \eta^2) \} / \alpha \tag{15b}
\]