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Simple constitutive modelling of nonlinear viscoelasticity under general extension

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Abstract

We study the behaviour of a single integral constitutive equation, capable of providing analytic expressions for the viscoelastic stress in extensional flows of a variety of deformation histories and geometries, ranging from uniaxial to equibiaxial. It is based on the use of a stress damping function, with a *power-law* dependence on the elongation, λ: $h(\lambda) = 1/\lambda^n$. The parameter n ($0 \le n \le 2$) signifies the nonlinear viscoelastic character of the material and, therefore, is an inverse measure of network connectivity strength of the underlying microstructure. This renders the constitutive approach applicable to incompressible polymers of a variable degree of branching, strain hardening and stress thinning behavior. Methods of connecting n with the macromolecular architecture and the alignment strength of the flow are also explored.

Keywords: Extension; Elongation; Uniaxial; Biaxial; Planar; Nonlinear; Viscoelasticity; Constitutive relation; Strain damping function; Polymer; Branching; Alignment strength; Eyring plasticity; Melt strength

1. Introduction

Elongational flow dominates polymer processing technologies such as melt spinning, blow molding, sheet stretching, tube inflation, vacuum molding, extrusion coating and foaming [1]. This explains its attraction as a topic of theoretical and experimental study to engineering and materials scientists alike [2–37]. Essential for the success of the above applications is choosing materials with substantial elongational viscosity, that demonstrate strain hardening (SH, i.e., accelerated viscosity growth beyond a characteristic strain) and melt strength (MS), defined as the maximum force at which a molten thread can be drawn under standard conditions before it breaks. Imparting such properties on the polymer is most effectively accomplished by broadening the molecular weight distribution and/or adding long chain branches; either molecular change is manifested with an increase in the steady-state compliance, J_e^0 [38].

Constitutive equations encode information pertaining to the rheology of a material in a manner useful for process design and characterization. In the last 30 years, constitutive equations of the single integral K-BKZ type [39–41], with separable the time and strain contributions became popular on the basis of their simplicity, practicality and reasonable success in representing reality:

$$\underline{\underline{\sigma}} = \int_{-\infty}^{t} M(t-t')h(I_1, I_2)\underline{\underline{C}}^{-1}(t,t')\mathrm{d}t' \tag{1}$$

Here, $\underline{\underline{\sigma}}$ is the stress tensor, $M(t)$ the memory function, $\underline{\underline{C}}^{-1}$ the Finger strain tensor, $h(I_1,I_2)$ is the damping function, a measure of the viscoelastic nonlinearity of the material due to its fading memory at large deformations and, therefore, a decreasing function of the first (I_1) and second (I_2) invariants of $\underline{\underline{C}}^{-1}$. Eq. (1) was introduced by Wagner [42] on the grounds that, following step–strain excitations of variable magnitude, time–strain superposition was commonly observed in the stress relaxation response of branched and linear polymers [43,44].

For the case of linear chains, Eq. (1) soon found its molecular justification in the context of the theory of Doi and Edwards [45]. The damping function, h, represents the extent of destruction of the temporary polymer network due to loss of chain entanglement density and segmental orientation following a

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deformation. The strain invariants constitute the objective variables of h because they quantify the average extent of chain retraction after a sudden elongation, which is the main reason of entanglement dissolution and loss of segment orientation. This is because $(I_1-3)^{1/2}$ physically signifies the average change in length of a line element at point P in the material, averaged over all possible orientations: $(I_1-3)^{1/2}=\mathrm{d}L'/\mathrm{d}L$ [37]. By analogy $(I_2-3)^{1/2}$ signifies the average area change on all planes around point P: $(I_2-3)^{1/2}=\mathrm{d}A'/\mathrm{d}A$. For monodisperse polymer chains of uncomplicated linear architecture, the Doi-Edwards molecular theory suggests that h is only due to the survival of polymer segment orientation. Then, h is a nearly universal function of I_1 (mainly) and I_2; in the Larson approximation, $h\approx 5/(I_1+2)$ [40].

Material invariance of the damping function fails in the presence of broad polymer molecular weight distribution (MWD) and, most notably, in the presence of chain branching [24,43,46]. This is primarily due to the fact that stress survival after a sudden strain is now not only due to segmental orientation but also due to some remaining segmental deformation [47]. Therefore, the type and degree of branching as well as the branch length and relative location within the molecule (internal vs. external, i.e., crosslinked on both ends vs. tethered) improve the connectivity of the temporary polymer network, reduce entanglement destructibility upon deformation and, therefore, *smooth* the nonlinear viscoelastic character of the fluid.

Several phenomenological models handle these h variations empirically, thus adding flexibility to the predictive capacity of integral equations. Most notably Wagner et al. suggest [48,49]:

$$h\approx \exp(-a'\sqrt{b'(I_1-3)+(1-b')(I_2-3)}) \tag{2}$$

while Papanastasiou et al. [50]:

$$h\approx \frac{1}{1+a''(I_1-3)+b''(I_2-3)} \tag{3}$$

which along with improvements [51] are the most frequently used in fluid mechanical calculations [22,52]. Considerable advances have also been made over the years in molecular theory inspired modeling, albeit, at the cost of added complexity [53–60,28].

For extensional flows in particular, and with engineering practitioners in mind that relish simplicity in the constitutive approach, closed form solutions, a minimum number of material parameters, and connection of these parameters to microstructure, we have recently introduced [62] the simplest possible form of $h(\lambda)$, the *power-law* damping function, applicable for a range of degrees of chain branching and, therefore, strain hardening and stress thinning responses:

$$h(\lambda)=\frac{1}{\lambda^n} \tag{4}$$

Eq. (4), when combined with the integral constitutive Eq. (1) and an exponentially decaying $M(t)$ may be solved analytically. Justifying its use based on evidence, studying its stress predictions under a variety of flow histories and geometries, and further comparison of these predictions with experience are the scope of this paper. Discussion concerning the physical significance of the material parameters involved emphasizes its application on polymer fluids; nevertheless, we see no reason preventing its use as an approximate model for viscoelastic elastomers, glasses, rocks or metals, provided that one considers isotropic structure and incompressibility.

2. Strain measures in extensional flow [40,41]

Let $\underline{\underline{D}}$ be the rate of strain tensor which is defined as the symmetric part of the velocity gradient tensor. For an incompressible fluid in a general extensional flow defined by the velocity field $U_i=e_iX_i$, where $i=1, 2, 3$, and $e_1+e_2+e_3=0$:

$$\underline{\underline{D}}=\begin{bmatrix} e_1 & 0 & 0\\ 0 & e_2 & 0\\ 0 & 0 & e_3\end{bmatrix}=\begin{bmatrix} \dot\varepsilon & 0 & 0\\ 0 & m\dot\varepsilon & 0\\ 0 & 0 & -(m+1)\dot\varepsilon\end{bmatrix} \tag{5}$$

Here, $e_1\geq e_2\geq e_3$ and $-0.5\leq m\leq 1$. For uniaxial (i.e. axisymmetric) extension, for example, $m=-0.5$, for planar extension (pure shear) $m=0$, for ellipsoidal extension $m=0.5$, and for biaxial compression $m=1$.

Let $\underline{\underline{C}}(t')$ be the Cauchy tensor, expressing deformation at past time t' relative to the configuration at the present time $t>t'$ and $\underline{\underline{C}}^{-1}(t')$ is the Finger tensor, expressing deformation at present time t relative to the configuration at past time t'. In a general extensional flow the relative Hencky (or logarithmic) strain, ε, and the relative extension ratio (or principal stretch ratio), λ, are correspondingly equal to $\lambda=\exp(\varepsilon)=\exp\left(\int_{t'}^{t}\dot\varepsilon(t'')\mathrm{d}t''\right)$. Then, the Finger tensor is:

$$\underline{\underline{C}}^{-1}(t')=\begin{bmatrix} \lambda^2 & 0 & 0\\ 0 & \lambda^{2m} & 0\\ 0 & 0 & \lambda^{-2(m+1)}\end{bmatrix} \tag{6}$$

with its first and second invariants, respectively, equal to $I_1=\lambda^2+\lambda^{2m}+\lambda^{2(m+1)}$ and $I_2=\lambda^{-2}+\lambda^{-2m}+\lambda^{2(m+1)}$, and eigenvalues equal to the square of the principal stretch ratios, λ, λ^m and, $\lambda^{-(m+1)}$. The (I_1-I_2) difference decreases with m and is a measure of the alignment strength of the flow; its relative value is often invoked as the reason that flows of similar intensity but different geometry generate dissimilar stress response [40].

3. The power-law damping function: justification and significance

For the stress calculation, we use Eq. (1), combined with Eq. (4):

$$\underline{\underline{\sigma}}=\int_{-\infty}^{t}M(t-t')\begin{bmatrix}\lambda(t,t')^{2-n} & 0 & 0\\ 0 & \lambda(t,t')^{2m-n} & 0\\ 0 & 0 & \lambda(t,t')^{-2(m+1)-n}\end{bmatrix}\mathrm{d}t' \tag{7}$$