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J. Non-Newtonian Fluid Mech. 145 (2007) 92–101

Journal of Non-Newtonian Fluid Mechanics

www.elsevier.com/locate/jnnfm

Unphysical phenomena associated with the extended pom-pom model in steady flow

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Received 20 February 2007; received in revised form 8 May 2007; accepted 8 May 2007

Abstract

The extended pom-pom (XPP) model was first introduced to eradicate perceived deficiencies of the original pom-pom model such as the lack of a second normal stress difference and a discontinuity in the derivative of the extensional viscosity. However, in this paper it is shown that the XPP model itself possesses some disconcerting attributes. In simple steady shear and uniaxial extensional flow, multiple solutions are found. Furthermore, the extended pom-pom model can predict positive as well as negative values for the second normal stress difference. Experimentally, the second normal stress difference is negative for polymer melts.

Keywords: XPP model; Shear viscosity; Extensional viscosity; Second normal stress difference; Multiple solutions

1. Introduction

There have been significant advances in the mathematical modelling of polymer melts over the last decade. The pom-pom constitutive model for branched polymers, developed by McLeish and Larson [8], has been successful where traditional models such as the Giesekus and K-BKZ models have failed, viz. in predicting the nonlinear behaviour of materials in both shear and extension simultaneously. The PTT model can be flexible enough to model high density polyethylene melt rheology [7]. The success of the pom-pom model is due to the incorporation of molecular dynamics from considerations of the polymer physics. Whilst the Giesekus model can give qualitatively both shear-thinning and extension-hardening, it lacks the flexibility to quantitatively fit polymer melt data. The K-BKZ model can fit uniaxial extensional and shear viscosities but will simultaneously fail to predict the correct planar extensional viscosity.

Modifications to the original pom-pom model [1,12] have allowed quantitative agreement between experiments and model predictions obtained using numerical simulation techniques. The inclusion of multiple modes [5,13,14] allows the fitting of low-density polyethylene data. The rheology of such a complex branched material (LDPE) spans frequencies of several orders of magnitude. This corresponds to the wide spectrum of relaxation times associated with the randomly branched topology of the molecules. In this way different parts of the molecule can be assigned different relaxation times, which relax on different time-scales. We model this mathematically by a linear superposition of several Maxwell modes of stress each with a characteristic relaxation time. The key features in the mathematical modelling of branched polymers are reptation and the topology of the polymer molecules. The importance of reptation in the mathematical description of linear polymers was identified by de Gennes [3] and later quantified by Doi and Edwards [4]. This concept assumes that individual polymer molecules are constrained to move in a tube formed by neighbouring polymer molecules. Effectively, the perpendicular motion of a polymer chain is restricted due to a constraining tube of fixed radius. Curvilinear motion along the tube of the linear polymer chain is allowed.

Branched polymers have more complicated relaxation processes than for linear polymers. A constitutive model was developed by McLeish and Larson [8] who identified the topology of branched polymer molecules as a key concept in the development of a mathematical model in addition to reptation theory. This came from the realisation that polymer chain segments that are trapped between branch points, contribute the most to extra-stress in a strongly deforming flow. The model assumes that the polymer chains are represented by a backbone

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doi:10.1016/j.jnnfm.2007.05.002

segment connecting two identical pom-poms each with q arms at the branch points. The drag that the melt exerts on these arms, as a result of friction, causes the backbone to stretch. The branched arms inhibit the reptation motion of the backbone section by pinning the molecule in place at the tube junctions. The free ends of the arms are still able to move however, and the arms gradually work their way out of the tubes in a similar way to star polymers, towards the branch points by a diffusion process called arm retraction [9]. The arm retraction process is speeded up by the self diluting action of the arm ends. They are able to explore configuration space rapidly and act to remove the constraints for neighbouring chains which results in dilated tubes, in a process of *dynamic dilution*. Once the arms have relaxed, the backbone can subsequently relax by diffusion of the branch points and reptation. The backbone can then be treated as a linear polymer with two diffuse 'blobs' comprising the diffusing arms, and the chain can be modelled as a dumbbell inside a tube. A key feature of the model is therefore distinct relaxation times for these two processes, i.e. the orientation and stretch of the backbone section. This separation of relaxation times gives the pom-pom model the flexibility to quantitatively describe polymer melt rheology. Due to balance of tension in the backbone of the molecule, and in the arms, the stretch is not allowed to be greater than q. At this point, the arms are retracted into the backbone tube and this ensures that the stretch is bounded, although retraction lengths are found to be very small [5].

The original pom-pom model suffers from three problems. First, the model predicts a zero second normal stress difference. Secondly, there is an unphysical discontinuity in the gradient of the extensional viscosity when the stretch is equal to q at steady state. Thirdly, the shear stress has a maximum. Verbeeten et al. [12] introduced a modified model, the eXtended Pom-Pom (XPP) model, to circumvent these three problems. A modification to the stretch equation, as introduced by Blackwell [1], which allows for branch point displacement, is used to overcome the discontinuity in the gradient of the extensional viscosity. The retraction of the arms into the tube has been neglected, and thereby the constraint that the stretch cannot be larger than the number of arms is removed. A Giesekus-like term has been added to the orientation equation, to introduce a non-zero second normal stress difference. Furthermore, the orientation equation is bounded for high strain rates. The XPP model has been successfully implemented in a finite element method and satisfactory quantitative agreement has been found in comparisons between experiments with LDPE melts and numerical simulations using a multi-mode XPP model (see Verbeeten et al. [13]).

2. The extended pom-pom model

2.1. The double extended pom-pom model

In the equations that provide a description of a multi-mode pom-pom model for branched polymer melts, $\lambda_{b,i}$ and $\lambda_{s,i}$ are the relaxation times of the backbone tube orientation and the backbone stretch for each mode, respectively. The evolution equations for the orientation tensor $\mathbf{s}_i$, and the backbone stretch λ_i, for the Double eXtended Pom-Pom (DXPP) model of Verbeeten et al. [12] are given by

$$\overset{\nabla}{\mathbf{s}}_i + f_i(\lambda_i, \mathbf{s}_i)\mathbf{s}_i + \frac{\alpha_i - 1}{3\lambda_i^2\lambda_{0b,i}}\mathbf{I} + \frac{3\alpha_i\lambda_i^2}{\lambda_{b,i}}\mathbf{s}_i \cdot \mathbf{s}_i = \mathbf{0}, \tag{1}$$

and

$$\frac{\partial\lambda_i}{\partial t} + \mathbf{u}\cdot\nabla\lambda_i = \lambda_i(\mathbf{d}:\mathbf{s}_i) - \frac{\lambda_i - 1}{\lambda_{s,i}}\,\mathrm{e}^{\nu_i(\lambda_i - 1)}, \tag{2}$$

where the function $f_i(\lambda_i, \mathbf{s}_i)$ is given by

$$f_i(\lambda_i, \mathbf{s}_i) = 2\mathbf{d}:\mathbf{s}_i + \frac{1}{\lambda_i^2\lambda_{b,i}}(1 - \alpha_i - 3\alpha_i\lambda_i^4\mathrm{tr}(\mathbf{s}_i\cdot\mathbf{s}_i)). \tag{3}$$

Here $\mathbf{d}$ is the is the rate of deformation tensor. The incorporation of an additional nonlinear term into the evolution equation for the orientation tensor provides the model with the features of a modified Giesekus equation, which introduces an anisotropy parameter, α. When $\alpha \neq 0$ a nonzero second normal stress difference is predicted, therefore giving a more complete physical description of the polymer melt. The parameter ν_i provides a measure of the influence of the surrounding polymer chains on the backbone tube stretch and is incorporated into the model to remove the discontinuity from the gradient of the extensional viscosity. Its value is obtained by data fitting and is found to be inversely proportional to the number of arms q_i, viz.

$$\nu_i = \frac{2}{q_i}. \tag{4}$$

The extra-stress tensor can be derived from the orientation tensor through the following relation

$$\boldsymbol{\tau} = \sum_{i=1}^{n} G_i(3\lambda_i^2\mathbf{s}_i - \mathbf{I}), \tag{5}$$

where G_i is the shear modulus from a linear relaxation spectrum. Note that for the XPP model, the orientation tensor exhibits a nonzero third normal stress component, τ_{zz}, even in 2D problems. The equation for this component may be eliminated from the system of equations since it is known that the trace of the orientation tensor, tr($\mathbf{s}$), is unity.

2.2. The single extended pom-pom model

The single equation variant of the extended pom-pom model combines the orientation tensor and the stretch into one equation for the extra-stress that has the same structure as the Giesekus or PTT models. It relates the polymeric stress to the rate of deformation tensor $\mathbf{d}$ through

$$f_i(\lambda_i, \boldsymbol{\tau}_i)\boldsymbol{\tau}_i + \lambda_{b,i}\overset{\nabla}{\boldsymbol{\tau}}_i + G_i(f_i(\lambda_i, \boldsymbol{\tau}_i) - 1)\mathbf{I} + \frac{\alpha_i}{G_i}\boldsymbol{\tau}_i\cdot\boldsymbol{\tau}_i = 2\lambda_{b,i}G_i\mathbf{d}, \tag{6}$$

in which the function $f_i(\lambda_i, \boldsymbol{\tau}_i)$ is given by

$$f_i(\lambda_i, \boldsymbol{\tau}_i) = 2\frac{\lambda_{b,i}}{\lambda_{s,i}}\mathrm{e}^{\nu_i(\lambda_i - 1)}\left(1 - \frac{1}{\lambda_i}\right) + \frac{1}{\lambda_i^2}\left[1 - \frac{\alpha_i\mathrm{tr}(\boldsymbol{\tau}_i\cdot\boldsymbol{\tau}_i)}{3G_i^2}\right]. \tag{7}$$