Modelling of rheological properties in polystyrene with long-chain branching

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ABSTRACT

Numerical simulations with the so-called pom-pom differential constitutive model are compared to experimental data obtained with the filament stretching rheometer (FSR) for branched polystyrene polymer melts having narrow molecular weight distributions (MWDs).

INTRODUCTION

The observation of an overshoot in the transient stress-growth function measured in uniaxial extension of LDPE polymer melts was originally reported by Raible et al.[2]. Wagner et al.[3] applied a KBK-Z type integral model to demonstrate qualitative agreement by an appropriate choice of damping function. A steady state viscosity was predicted but not measured due to limitations in the original Meissner extensional rheometer[1]. The advent of the Filament Stretching Rheometer (FSR) for melts[7] made it possible to maintain an extensional flow sufficiently long to obtain a steady state viscosity. The original stress overshoot observation in LDPE was then confirmed by Rasmussen et al.[8]. Based on some appealing molecular ideas introduced by McLeish and co-workers[4,6] the so-called pom-pom model was used later to describe qualitatively the overshoot phenomena in Hoyle et al.[10]. In the present work we apply similar techniques to describe the stress overshoot observations made by Nielsen et al.[9] for branched polystyrene (PS) polymers.

MULTIMODE POM-POM MODEL

Inkson et al.[5] proposed an expression for the stress tensor of a multimode pom-pom model. Here, we use the later revised model by Hoyle et al.[10]. The stress is defined by

$$\boldsymbol{\sigma} = \sum_i^n \sigma_i = \sum_i^n g_i \lambda_i^2\,(t)\mathbf{S}_i\,(t) \tag{1}$$

where, n is the total number of modes, and g_i, λ_i and S_i represent the modulus, the evolution of the back-bone stretch and the evolution of orientation for each mode *i*. $\mathbf{S}_i$ and λ_i are expressed in the Eqs. (2) and (3) respectively.

$$\mathbf{S}_i = \frac{3\mathbf{A}_i}{trace(\mathbf{A}_i)} \tag{2}$$

$$\frac{\partial \lambda_i}{\partial t} = \lambda_i(\mathbf{k}:\mathbf{S}_i) - \left(\frac{1}{\tau_{s,i}} + \frac{1}{\tau^*}\right)(\lambda_i - 1)e^{\nu_i(\lambda_i - 1)} \tag{3}$$

where,

$$\frac{\partial \mathbf{A}_i}{\partial t} = \mathbf{k}.\mathbf{A}_i + \mathbf{A}_i.\mathbf{k}^T - \frac{1}{\tau_i}(\mathbf{A}_i - \mathbf{I}) \tag{4}$$

is the orientation tensor. The tensor $\mathbf{k}$ is the transpose of the velocity gradient tensor, τ_i and $\tau_{s,i}$ are the relaxation times for backbone and stretch while $\nu_i = \frac{2}{(q_i - 1)}$, where q_i is the number of branches in each mode. The relaxation rate $\frac{1}{\tau^*}$ was introduced by Hoyle et al.[10]. They assumed that the additional relaxation mechanism may occur due to the advection of flow which should be proportional to the extension rate along the tube segment. The additional relaxation time can be expressed as

$$\frac{1}{\tau^*} = (\boldsymbol{S}:\boldsymbol{S}^T)^{\alpha}|\mathbf{S}:\mathbf{k}| \qquad (5)$$

The parameters C_R and α are non-linear parameters that determines the overshoot behaviour.

RESULTS

In Fig. 1 we compare experimental data[9] with numerical simulations using the above model for a particular set of parameters.

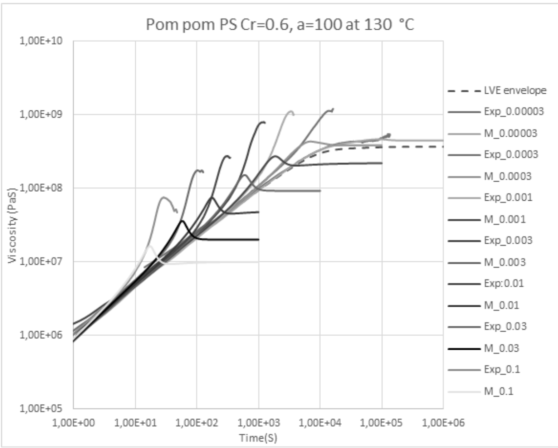

Figure 1. Experimental data from Nielsen et al.[9] and simulations using the Pom-Pom model with a specific set of parameters.

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REFERENCES

1. Meissner, J. (1969), "Rheometer zur Untersuchung der deformationsmechani-schen Eigenschaften von Kunststoff-Schmelzen unter definierter Zugbeanspruch-ung", *Rheol. Acta*, **8**:78-88.

2. Raible, T., Demarmels, A. and Meissner, J. (1979), "Stress and Recovery Maxima in LDPE Melt Elongation", *Polymer Bulletin,* **1:**397-402.

3. Wagner, M.H., Raible, T. and Meissner, J. (1979), "Tensile stress overshoot in uni-axial extension of a LDPE melt", *Rheol. Acta*, **18**:427-428.

4. McLeish, T.C.B., and Larson, R.G. (1998), "Molecular constitutive equations for a class of branched polymers: The pom-pom polymer", *J. Rheol.*, **42**:81-110.

5. Inkson, N.J. and McLeish, T.C.B. (1999), "Predicting low density polyethylene melt rheology in elongational and shear flows with "pom-pom" constitutive equations", *J. Rheol.*, **43**:873-896.

6. Blackwell, R.J., McLeish, T.C.B. and Harlen, O.G. (2000), "Molecular drag-strain coupling in branched polymer melts", *J. Rheol.*, **44**:121-136.

7. Bach, A., Rasmussen. H.K. and Hassager, O. (2003), "Extensional viscosity for polymer melts measured in the filament stretching rheometer", *J. Rheol.*, **47**:429-441.

8. Rasmussen, H.K., Nielsen, J.K., Bach, A. and Hassager, O. (2005); "Viscosity overshoot in the start-up of uniaxial elongation of low density polyethylene melts", *J. Rheol.*, **49**:369-381.

9. Nielsen, J.K., Rasmussen, H.K., Denberg, M., Almdal, K. and Hassager, O. (2006), "Nonlinear Branch-Point Dynamics of Multiarm Polystyrene", *Macromolecules*, **39:**8844-8853.

10. Hoyle, D.M., Huang, Q., Auhl, D., Hassell, D., Rasmussen, H.K., Skov, A.L., Harlen, O.G., Hassager, O. and McLeish, T.C.B. (2013), "Transient overshoot extensional rheology of long-chain branched polyethylenes: Experimental and numerical comparisons between filament stretching and cross-slot flow", *J. Rheol.*, **57**:293-313.