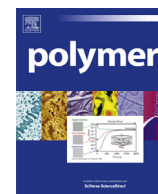




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Polymer

journal homepage: www.elsevier.com/locate/polymer

A constitutive analysis of the extensional flows of nearly monodisperse polyisoprene melts

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ARTICLE INFO

Article history:

Received 1 February 2016

Received in revised form

4 May 2016

Accepted 6 May 2016

Available online xxx

Keywords:

Polymer rheology

Extensional flows

Polyisoprene melt

Interchain pressure

ABSTRACT

Here two particular formulations [M.H. Wagner, S. Kheirandish, O. Hassager, *Journal of Rheology* 49 (6) (2005) 1317–1327; H.K. Rasmussen, Q. Huang, *Rheologica Acta* 53 (3) (2014) 199–208; G. Marrucci, G. Ianniruberto, *Macromolecules* 37 (10) (2004) 3934–3942] of the ‘interchain pressure’ [39], incorporated into the molecular stress function method [M.H. Wagner, S. Kheirandish, O. Hassager, *Journal of Rheology* 49 (6) (2005) 1317–1327], are used to assess the extensional [J.K. Nielsen, O. Hassager, H.K. Rasmussen, G.H. McKinley, *Journal of Rheology* 53 (6) (2009) 1327–1346; G. Liu, H. Sun, S. Rangou, K. Ntetsikas, A. Avgeropoulos, S.-Q. Wang, *Journal of Rheology* 57 (1) (2013) 89–104] and shear viscosities [D. Auhl, J. Ramirez, A.E. Likhtman, P. Chambon, C. Fernyhough, *Journal of Rheology* 52 (3) (2008) 801–835] of narrow molecular weight distributed (NMMD) polyisoprene melts. These two formulations are expected to represent the highest [M.H. Wagner, S. Kheirandish, O. Hassager, *Journal of Rheology* 49 (6) (2005) 1317–1327, G. Marrucci, G. Ianniruberto, *Macromolecules* 37 (10) (2004) 3934–3942] and lowest level [H.K. Rasmussen, Q. Huang, *Rheologica Acta* 53 (3) (2014) 199–208] of the ‘interchain pressure’. The needed Rouse times are here defined as $\tau_R/\tau_{max} \propto (M/M_e)^{-1.4}$ with a proportional factor of 1.4, achieved based on the viscosity measurement. τ_{max} is the maximal relaxation time, M the molecular weight and the entanglement molecular weight $M_e = (4/5)\rho RT/G_N^0$ [M. Doi M, S.F. Edwards, *The Theory of Polymer Dynamics*; Clarendon Press: Oxford (1986)], ρ is the density, R the gas constant, T the temperature and G_N^0 the plateau modulus. The method by [M.H. Wagner, S. Kheirandish, O. Hassager, *Journal of Rheology* 49 (6) (2005) 1317–1327, G. Marrucci, G. Ianniruberto, *Macromolecules* 37 (10) (2004) 3934–3942] predicts start-up of extensional viscosities significantly below the measured value. The formulations by [H.K. Rasmussen, Q. Huang, *Rheologica Acta* 53 (3) (2014) 199–208] seem to be in agreement with both the start-up of extension as well as the shear flow of all NMMD polyisoprenes. Potential non-isothermal effects were addressed computationally using the pseudo time principle, assuming the most critical case of adiabatic heating.

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1. Introduction

The idea of universality in the flow dynamics of entangled monodisperse polymer systems is appealing. Especially for the linear viscoelasticity (LVE), experimental and theoretical investigations have shown a unique dependence on the entanglement molecular weight, M_e . For polymers with a molar mass, M , above the entanglement molecular weight, the zero shear viscosity scales as $(M/M_e)^{3.4}$ [1] and each type of polymer has a well-defined plateau modulus [2] independent of length and molecular distribution. For entangled monodisperse polymer systems, theoretical

results, initiated by Doi and Edwards [3], agree with experimental findings. The concept of contour length fluctuations [4] was the first to explain the observed molar mass dependence in the power of 3.4 [5], but the area still evolves in its basic theoretical understanding [6].

The idea of universality in the flow dynamics of entangled polymer systems was a guideline for the theoretical considerations in the earliest tube theories [7–10]. It was challenged by the extension measurements of the start-up and steady extensional viscosities on solutions of narrow molecular weight distributed (NMMD) polymers and pure melts, respectively. These ruled out the possibility of a unified flow physics of melts and solutions based on entanglements. It motivated further theoretical developments [11–13] in an effort to create a unified theoretical framework.

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Recently, to investigate the particular consequences of the presence of the solvent, Huang et al. [14,15] made start-up and steady extension measurements on the most ideal dilutions: NMMD polystyrenes in their own styrene oligomer. The results were surprising. The measurements for diluents consisting of chains, in term of Kuhn steps, were in-between pure melts and corresponding solutions [16], all with the same number of entanglements. The flow physics of entangled monodisperse polymer systems is even more complicated than expected.

Despite the differences between melts and solutions, there seems to be a remarkable amount of experimental evidence, in shear as well as extension, of a correlation between the entanglement number and the time constant controlling the transition to the strain-hardening flow. For entangled monodisperse polymer systems the strain-hardening viscoelasticity seems to be controlled by a single time scale, commonly referred to as the Rouse time τ_R . It defines the transition from a pure configurational stress on large time scales [3] to a strain-hardening regime at small times [8,17–20].

Keeping the above efforts in mind, the first attempt to measure extensional viscosities on nearly monodisperse polymer systems was actually done previous to all of the above references, considering monodisperse systems. In the mid-seventies Vinogradov and co-workers [21] extended narrow molecular weight distributed (NMMD) polyisoprene uniaxially. The theoretical importance of their work was limited, probably due to low extensional strain values where only a few reached a value of 2. Notice that the extensional strain is defined as $\varepsilon(t) = \ln(l(t)/l(0))$, where $l(t)$ and $l(t=0)$ are the distances between two particles in the direction of the extension at time t and $t=0$, respectively. Within the recent years, new attempts to measure the extensional viscosities on NMMD polyisoprene have been made [22–25]. The purpose of this paper is to find out how these measurements relate to experimental rheometric investigation on other entangled polymer systems and recent theoretical ideas, both being unclear.

2. Non-isothermal extension

As the quantitative method to handle different underlying physical mechanisms the ‘molecular stretch’ representation from Wagner [26] will be applied. Its general functional representation seems to be a sufficiently accurate basis for the fluid mechanics of MNND polymers [27] and their solutions [28], although the actual underlying physical mechanisms are debated [26,28]. This ‘molecular stretch’ method is not unique. Other frameworks are likely to have an equal validity [29,30].

The ‘molecular stretch’ representation is formulated isothermally. As discussed later, the issue of potential non-isothermality during extension of NMMD melts may need to be addressed due to the heat of work. The well-established time-temperature superposition is only valid during isothermal conditions. The changing temperature during the stress build up will need a more comprehensive method. The experimental evidence is limited. Without considering specific constitutive equations only one paper has been published by Yu et al. [31]. Previous studies [32–34] were all based on the assumption of time and strain separability. This is only a correct assumption for small, i.e. linear, deformations.

For linear conditions Morland and Lee [35] introduced the ‘pseudo time’ principle, considering a ‘thermo-rheological simple’ material. The ‘pseudo time’, $\xi(\mathbf{x}, t, t')$, at the past time t' relatively to the present time t is defined as

$$\xi' \equiv \xi(\mathbf{x}, t, t'') = \int_{t'}^t \frac{1}{a_T(T(\mathbf{x}, t, t''))} dt'' \quad (1)$$

where a_T is the classical time-temperature superposition shift factor, calculated at the temperature, $T(\mathbf{x}, t, t')$, at the past time, t' . a_T is evaluated relative to the fixed temperature T_0 . The ‘pseudo time’ should be evaluated on all particle paths. Mathematically the reference state is the (Cartesian) particle coordinates $\mathbf{x}' = (x'_1, x'_2, x'_3)$ at the past time state displaced to the coordinates $\mathbf{x} = (x_1, x_2, x_3)$ at the present time. Notice $\partial \xi' / \partial t' = -1/a_T(T')$ and $\partial \xi' / \partial t = 1/a_T(T')$. The latter one evaluated at the present time where $t' = t$ is $\partial \xi' / \partial t = 1/a_T(T)$. A short notation for the present and past temperatures has been used, referring to the present particle \mathbf{x} , as $T = T(\mathbf{x}, t, t)$ and $T' = T(\mathbf{x}, t, t')$, respectively.

Using high strain extensional experiments on a long chain branched polyethylene and a broadly distributed linear polystyrene melt Yu et al. [31] confirmed that polymer melts can be considered as ‘thermo-rheological simple’ even at high strain values. The ‘molecular stretch’ representation of the stress tensor, σ_{ij} , in a non-isothermal representation based on the pseudo time is given as

$$\sigma_{ij} = \frac{\rho T}{\rho_0 T_0} \int_0^\infty M(\xi(\mathbf{x}, t, t')) f(\mathbf{x}, t, t')^2 \int_{|\mathbf{u}|=1} \frac{[\mathbf{E}(\mathbf{x}, t, t') \cdot \mathbf{u}] [\mathbf{E}(\mathbf{x}, t, t') \cdot \mathbf{u}]}{|\mathbf{E}(\mathbf{x}, t, t') \cdot \mathbf{u}|^2} d\xi' \quad (2)$$

The initial value of $f(\mathbf{x}, t, t) = 1$ and $M(\dots)$ represents the memory function determined at the fixed temperature T_0 . Notice that all stresses are temperature corrected to the present temperature, T , using the ratio $\rho T / (\rho_0 T_0)$ where ρ_0 is the density at the fixed temperature T_0 and ρ is the density at the present temperature T . All the angular brackets are unit sphere integrals defined as $\langle \dots \rangle = 1/4\pi \int_{|\mathbf{u}|=1} \dots d\mathbf{u}$ where \mathbf{u} is a unit vector. The components of

the displacement gradient tensor $\mathbf{E}(\mathbf{x}, t, t')$ are $E_{ij}(\mathbf{x}, t, t') = \partial x_i / \partial x'_j$, $i, j = 1, 2, 3$. To integrate Equation (2) in real time $\partial \xi' / \partial t' = -1/a_T(T')$ is inserted.

$$\sigma_{ij} = \frac{\rho T}{\rho_0 T_0} \int_{-\infty}^t M(\xi(\mathbf{x}, t, t')) f(\mathbf{x}, t, t')^2 \int_{|\mathbf{u}|=1} \frac{[\mathbf{E}(\mathbf{x}, t, t') \cdot \mathbf{u}] [\mathbf{E}(\mathbf{x}, t, t') \cdot \mathbf{u}]}{|\mathbf{E}(\mathbf{x}, t, t') \cdot \mathbf{u}|^2} \frac{1}{a_T(T(\mathbf{x}, t, t''))} dt' \quad (3)$$

The ‘stretch evolution’ equation for, ideally, monodisperse linear polymers in a non-isothermal as well as generic formulation is

$$\frac{\partial}{\partial \xi} f(\mathbf{x}, t, t') = f(\mathbf{x}, t, t') \frac{\partial}{\partial \xi} \langle \ln |\mathbf{E}(\mathbf{x}, t, t') \cdot \mathbf{u}| \rangle - \frac{g(f(\mathbf{x}, t, t'))}{\tau_R} \quad (4)$$

g is a non-negative function where $g(1) = 0$ and $dg(f)/df = 1$ for $f = 1$. τ_R is a time constant, referred to as the Rouse time, determined at the fixed temperature T_0 . In the present model this is scaled based on the equality $dg(f)/df = 1$ for $f = 1$. g is currently undefined but will be defined explicitly later on. Alternatively, Equation (4) can be written in the real time

$$\frac{\partial}{\partial t} f(\mathbf{x}, t, t') = f(\mathbf{x}, t, t') \frac{\partial}{\partial t} \langle \ln |\mathbf{E}(\mathbf{x}, t, t') \cdot \mathbf{u}| \rangle - \frac{g(f(\mathbf{x}, t, t'))}{\tau_R \cdot a_T(T(\mathbf{x}, t, t))} \quad (5)$$

as $\partial \xi' / \partial t = 1/a_T(T)$ evaluated at $t' = t$.

3. Entanglements

Currently it seems that no published constitutive model is

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