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Experimental validation of a tube based constitutive equation for linear polymer melts with inter-chain tube pressure effect

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Abstract – A polydisperse case of an entangled linear polymer melts constitutive equation was studied. This constitutive equation, proposed by S. Dhole et al. [J. Non-Newtonian Fluid Mech. 161 (2009) 10–18], based on the reptation theory and the tube model, was tested on a polystyrene in shear (capillary rheometry) and planar extension in a complex flow (fieldwise measurements in a contraction flow) for different level of strain rates. A good quantitative prediction of all the set of experiments was obtained, using no adjustable nonlinear parameters.

Key words: Polymer melts / constitutive equation / planar elongational flows / tube theory / interchain pressure effect

Résumé – Validation expérimentale d’une loi de comportement de polymères fondus linéaires basée sur la théorie du tube et incluant des effets de pression inter-chaînes. Une version polymoléculaire d’une loi de comportement de polymères fondus linéaires est étudiée. La pertinence de cette loi, proposée par S. Dhole et al. [J. Non-Newtonian Fluid Mech. 161 (2009) 10–18] et basée sur la théorie du tube, a été évaluée pour l’écoulement d’un polystyrène en cisaillement stationnaire (rhéométrie capillaire) et dans un écoulement complexe de contraction plane par des méthodes de mesures de champ. Cette loi a montré de bonnes prédictions quantitatives sans avoir recours à l’ajustement de ses paramètres non linéaires.

Mots clés : Polymères fondus / loi de comportement / écoulements d’élongation plane / théorie du tube / effets de pression inter-chaînes

1 Introduction

Recent advances in molecular theories [2] for polymer melts viscoelastic behaviour can now allow a good quantitative prediction of moderate strain rates flows using few macroscopic “molecular” parameters. In the case of “strong” flows (fast and large deformations, as encountered in polymer processing flows), constitutive equations might fail in predicting all types (shear, uniaxial and planar elongation) of flow characteristics. Many recent constitutive equations were then proposed [3–5] to take more advanced models into account, such as chain stretch and convective constrain release [6]. Such constitutive equa-

tions were validated in strong and/or complex flows in many recent studies [7–15]. However, the data of Bach et al. [16] have shown an unexpected elongational thinning behaviour in “strong” elongational flows (where the strain rate was larger than the inverse Rouse relaxation time). Such behaviour was only predicted by previous models using unrealistically low values of the chain finite extensibility parameter [1, 15]. A further model of interchain tube pressure effect was then proposed by Marrucci and Ianniruberto [17] to explain Bach et al. [16] results, followed by macroscopic constitutive equations from Wagner et al. [18] and Dhole et al. [1] that were able to quantitatively predict them. The present study aimed at checking the validity of the model of Dhole et al. in both rheometrical and complex flows, for a polydisperse polystyrene melt.

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Nomenclature

β	Convective constraint release parameter
$\dot{\gamma}$	Shear rate (s^{-1})
λ	Source wavelength (m)
σ	Cauchy stress tensor (Pa)
$\sigma_1 - \sigma_2$	First principal stress difference (Pa)
θ_i	Reptation time of mode i (s)
θ_p	Inter-chain pressure relaxation time of mode i (s)
θ_R	Rouse time of mode i (s)
b	Finite extensibility parameter
C	Conformation tensor
C_{opt}	Stress-optical coefficient (Pa^{-1})
f	Finite extensibility function
G_i	Elastic modulus of mode i (Pa)
I	Identity matrix
I_p	Polydispersity index
k	Fringe order
M_w	Weight-averaged molecular mass (kg.mol^{-1})
p	Pressure (Pa)
$\vec{V}$	Velocity vector (m.s^{-1})
$\nabla \vec{V}$	Velocity gradient tensor (s^{-1})
W	Slit width (m)
Z	Number of entangled segments
$\bar{Z}$	Number of entanglements per chain

2 Molecular-based model of Dhole et al. [1]

The model of Dhole et al. was built using a classical expression of the stress tensor of the form:

$$\sigma = -pI + 3fG \left(C - \frac{1}{3}I \right) \quad (1)$$

$$f = \frac{b-1}{b - \text{tr}(C)} \quad (2)$$

where p is the pressure term, $G = 4\rho RT/5M_e$ is the elastic modulus (ρ and M_e being respectively polymer density and molecular mass between entanglements), b is the finite extensibility coefficient (in this study, we assumed that b is equal to the number of Kuhn segments between entanglements) and C is the conformation tensor. Evolution equation for the conformation tensor, in the so-called *affine stretching* version of the Dhole et al. [1] model, is given by:

$$\begin{aligned} \dot{C} = & \nabla \vec{V} C + C \nabla \vec{V}^T - \frac{1}{\theta} \left(fC - \frac{1}{3}I \right) \\ & - \frac{2}{\theta_p} \left(f^2 \text{tr} C^3 - \text{tr} C^{3/2} \right) \frac{C}{\text{tr} C} - \frac{1}{\theta_R} (f \text{tr} C - 1) \frac{C}{\text{tr} C} \end{aligned} \quad (3)$$

$$\frac{1}{\theta} = \frac{1}{\theta} + \frac{2\beta}{\theta_p} \left(f^2 \text{tr} C^3 - \text{tr} C^{3/2} \right) + \frac{\beta}{\theta_R} (f \text{tr} C - 1) \quad (4)$$

where θ is the reptation time (known to vary like Z^3 , Z being the number of entangled segments), θ_R is the

Rouse time (which varies like Z^2), θ_p is the inter-chain pressure relaxation time (proportional to θ_R , according to Marrucci and Ianniruberto [17]) and β is the convective constraint release parameter. The parameter β controls the rate of chains disentanglement in strong flows (i.e. large strain rates). This model predicts a shear-thinning effect in stationary shear beyond a shear rate value of $\dot{\gamma} = 1/\theta$, where β controls the value of the power law exponent on $\dot{\gamma}$ for moderate values of chain stretch (characterized by the trace of the tensor C). In transient flows, particularly elongational flows, θ_R controls the short time non linear response. In stationary elongation, this model predicts a strain hardening for strain rates larger than $1/\theta_R$ and a final saturation due to the finite extensibility (controlled by the parameter b). Between these two regimes, inter-chain pressure, controlled by θ_p , limits elongation softening, as observed by Bach et al. [16]. In this work, a multimode extension of this model was considered in order to take into account the polydispersity of the studied polymer.

3 Studied polymer: polystyrene

The studied polymer was a commercial polystyrene (Dow 648) of weight-averaged molecular mass $M_w = 295.6 \text{ kg.mol}^{-1}$ and polydispersity index $I_p = 2.17$, already studied in Boukellal et al. [15]. The number of Kuhn segments between entanglements is known to be 66 [1], molecular mass between entanglements is approximately 13 kg.mol^{-1} , then the mean number of entanglements per chain is $\bar{Z} = 23$ for this material. Classical rheological measurements were performed on this material: plate-plate oscillatory shear in the linear regime and capillary rheometry.

Figure 1 shows the master curve at 180°C of complex modulae as already obtained in [15]. One notices that the terminal relaxation zone is well defined.

Capillary rheometry, which consists in measuring pressure drop for a given flow rate imposed in a capillary geometry, was used to build steady shear viscosity curves at high shear rates. Figure 2 shows the steady shear viscosity curve at 180°C , obtained using capillary rheometry [15] in a 10 s^{-1} to 1000 s^{-1} range. One notices that the power-law exponent of the viscous curve is approximately -0.75 in this range of shear rates values. Capillary measurements were also superimposed with dynamic measurements using the Cox-Merz [19] plot (Fig. 2).

4 Identification and validation procedure

4.1 Set of model parameters

By excluding the glassy zone, that was estimated to start at a pulsation $1/0.0076 \text{ s}^{-1}$, a classical fit of an eight mode spectrum was performed on the data of Figure 1 [15]. The set of G_i and θ_i is reported in Table 1. The mean (viscosity-averaged) relaxation time of this

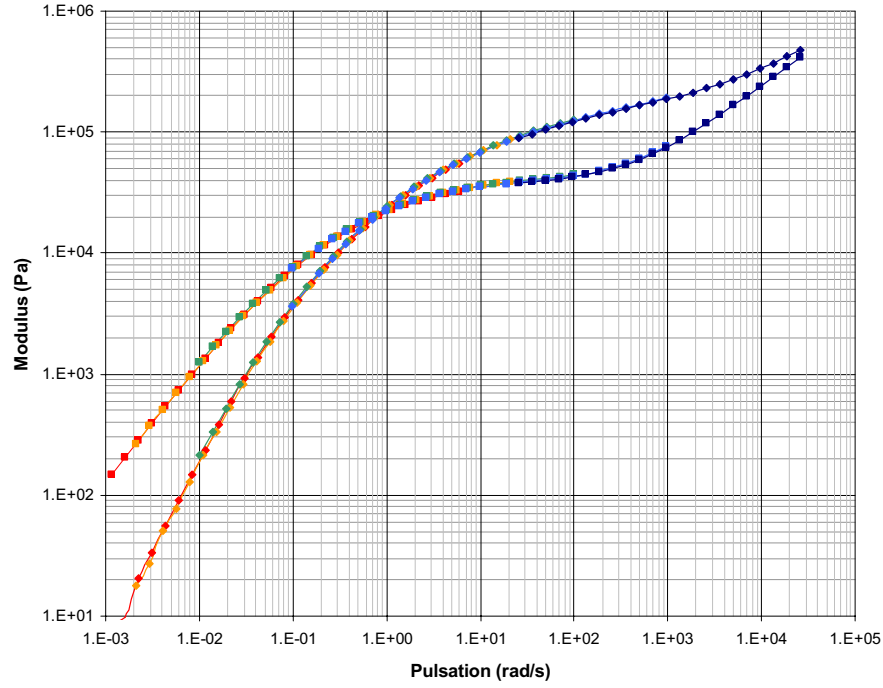


Fig. 1. G' and G'' master curve at 180 °C obtained from linear viscoelasticity measurements [15].

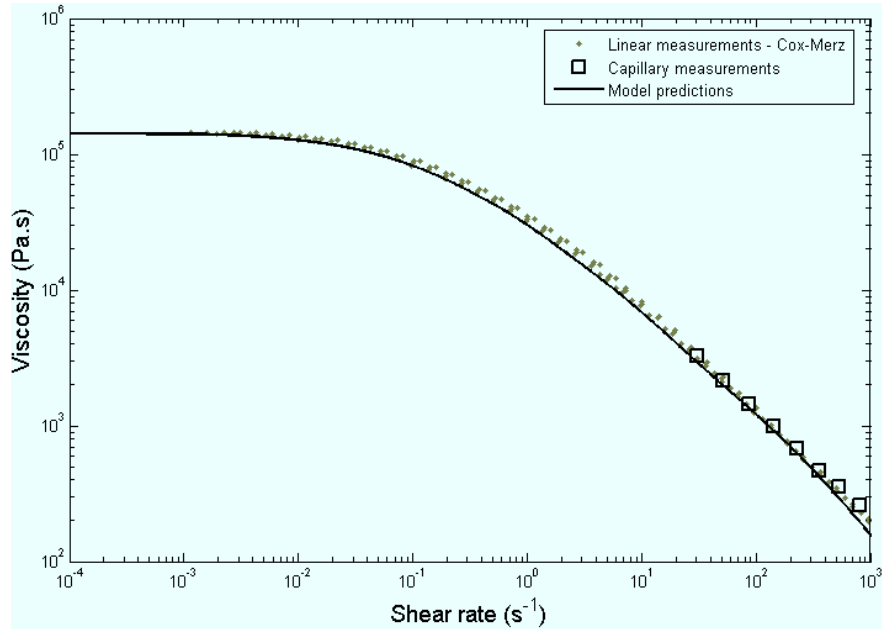


Fig. 2. Steady shear viscosity measurement, Cox-Merz plot and model prediction at 180 °C, showing that the Cox-Merz rule was well verified and that model predictions are in good agreement with measurements.

Table 1. Set of linear and nonlinear model parameters at 180 °C, it was taken $b_i = 66$ and $\beta_i = 0$ for all i , interchain pressure and Rouse relaxation times satisfy the $\theta_{pi} = 10 \theta_{Ri}$ relationship from Dhole et al. [1].

Mode i	1	2	3	4	5	6	7	8
G_i (Pa)	8.86×10^5	5.35×10^5	2.09×10^5	1.08×10^5	8.41×10^3	1.71×10^3	5.02×10^2	9.31×10^1
θ_i (s)	7.60×10^{-3}	1.09×10^{-1}	6.72×10^{-1}	1.35	4.93	1.70×10^1	3.81×10^1	1.79×10^2
θ_{Ri} (s)	7.60×10^{-3}	4.48×10^{-2}	1.51×10^{-1}	2.40×10^{-1}	5.70×10^{-1}	1.30	2.23	6.24
θ_{pi} (s)	7.60×10^{-2}	4.48×10^{-1}	1.51	2.40	5.70	1.30×10^1	2.23×10^1	6.24×10^1

polymer was found to be 0.789 s. All other (actually non-linear) parameters were deduced from classical molecular theories and from the paper of Dhole et al. [1]. More precisely, in the case of this polydisperse polystyrene, θ_{Ri} were computed using the scaling:

$$\theta_{Ri} = \theta_{R1} Z^2 \cong \theta_{R1} \left(\frac{\theta_i}{\theta_{R1}} \right)^{\frac{2}{3}} \quad (5)$$

where θ_{R1} is the Rouse relaxation time estimated at the beginning of the glassy zone ($\theta_{R1} = 0.0076$ s). Moreover, for each mode and following Dhole et al., inter-chain pressure relaxation times were set to $\theta_{pi} = 10\theta_{R1}$, finite extensibility coefficients were set to $b_i = 66$, and convective constraint release parameters were set to $\beta_i = 0$. All parameters are reported in Table 1. It is then important to notice that no nonlinear parameter were adjusted, the only difference between this polystyrene and the one used by Bach et al. [16] and identified by Dhole et al. [1] being its molecular mass distribution, from which depends only the viscoelastic spectrum.

A first noticeable observation (Fig. 2) is that the prediction for steady shear and Cox-Merz plot shows a good quantitative agreement using the set of nonlinear parameters suggested by Dhole et al.

4.2 Fieldwise measurements in a contraction flow

Additional rheological measurements at 180 °C were performed in [15] using fieldwise measurement techniques in a planar contraction, shown in Figure 3. Laser Doppler velocimetry and flow induced birefringence were used to measure, respectively, velocity and first principal stress difference using stress-optical law on the flow symmetry axis, upstream the contraction.

Twelve measurements were conducted along the flow symmetry axis, for twelve different flow rates (from 0.15 g.s⁻¹ to 0.70 g.s⁻¹), corresponding to planar elongation rates of mean value (elongation rates were not uniform on the flow symmetry axis, but increased with downstream distance) of 1 s⁻¹ to 10 s⁻¹. Using flow-induced birefringence measurements, first principal stress difference $\sigma_1 - \sigma_2$ was deduced from the stress optical rule:

$$\sigma_1 - \sigma_2 = \frac{k\lambda}{C_{opt}W} \quad (6)$$

where k , λ , C_{opt} and W are, respectively, the fringe order, the source wavelength set to 0.589×10^{-12} m, the stress optical coefficient set to -4.0×10^{-9} Pa⁻¹ [19, 20] and the slit width. First principal stress difference measurements are shown in Figure 4, on positions from 5 mm to 17 mm upstream the contraction. Let us notice that first principal stress difference was systematically increasing downstream the measured window, as strain rate was also increasing (the increase was measured to be nearly exponential up to the contraction).

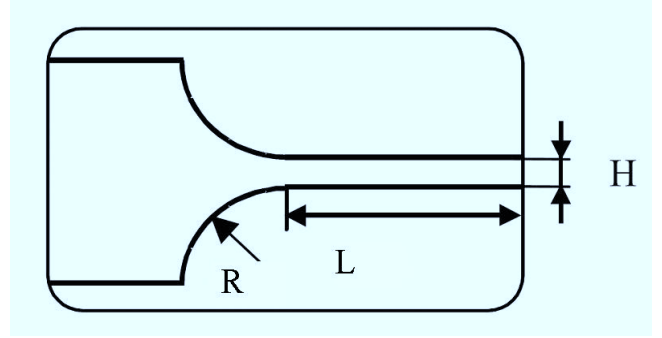


Fig. 3. Flow cell geometry used for flow-induced birefringence and laser-Doppler velocimetry experiments, dimensions are: $R = 8.5$ mm, $L = 20.75$ mm and $H = 1$ mm.

The measured velocity field was then interpolated on any point of the axis and a value of the elongational rate could have been deduced.

4.3 Model predictions in planar contraction flow

Velocity measurements were then used as entry data to solve the constitutive model and birefringence measurements were used for comparison of first principal stress difference model predictions on the flow symmetry axis. The comparison is shown in Figure 4. It appeared that the model was able to quantitatively predict transient planar elongation stresses for non-homogeneous strain rates. Predictions were then rather good in this regime, compared to what was obtained in our previous study [15] using a different model [5], without the need to adjust the set of nonlinear parameters. The slightly poor quantitative prediction at very low flow rates can be attributed to the fact that either 3D effects (for both velocity and stress fields) can occur for such low flow rates [21, 22], or to the fact that a tighter coupling between modes [23] were not considered here.

5 Conclusion

The molecular-based model of Dhole et al. [1] was identified in a simple multimode version and shown to be predictive for polydisperse polystyrene in both steady shear flows and more complex flows characterized by a strong, non-homogeneous planar extensional contraction flow. The pertinence of this constitutive equation is proven by the fact that no adjustment of nonlinear parameters proposed by Dhole et al. was needed to predict flow types for a polystyrene melt that were both different from the ones studied by Dhole et al.

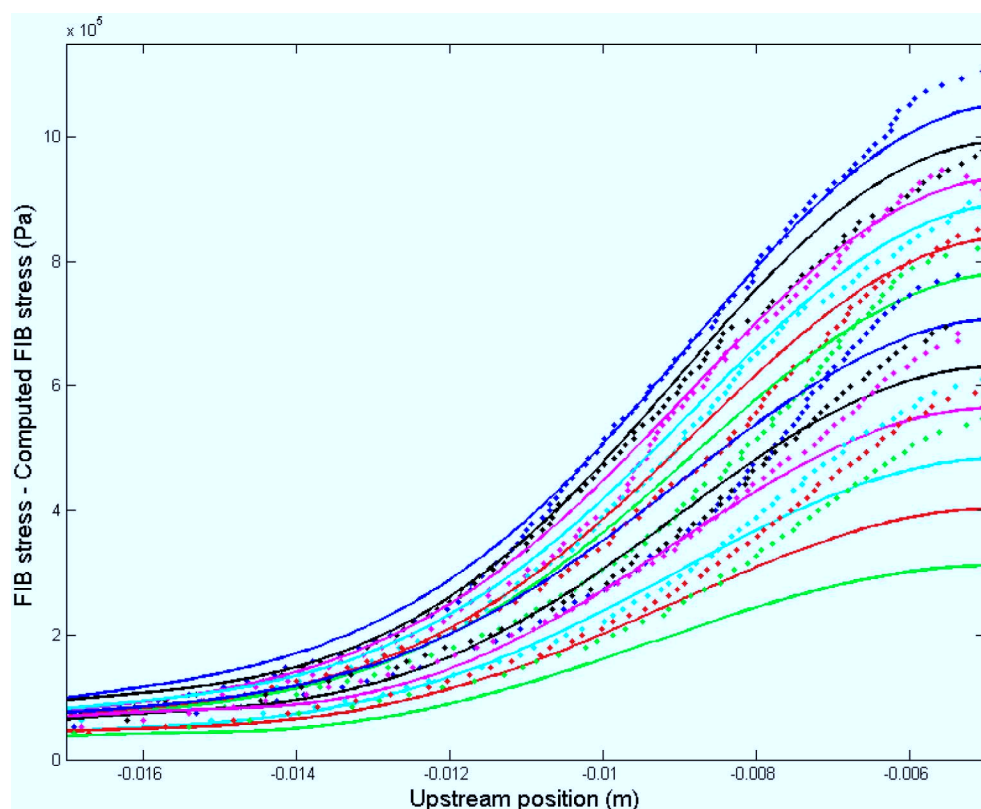


Fig. 4. Comparison between experimental birefringence (o) and model prediction (–) in planar contraction for various flow rates (from bottom to top): 0.15 g.s^{-1} , 0.20 g.s^{-1} , 0.25 g.s^{-1} , 0.30 g.s^{-1} , 0.35 g.s^{-1} , 0.40 g.s^{-1} , 0.45 g.s^{-1} , 0.50 g.s^{-1} , 0.55 g.s^{-1} , 0.60 g.s^{-1} , 0.65 g.s^{-1} , 0.70 g.s^{-1} , a good agreement between measurement and prediction was obtained on most of the measured positions and flow rates.

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