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Teodor Burghilea, Zdenek Stary. Homogeneity of deformation states during extensional measurements of polymer melts: an important issue revisited. CFM 2011 - 20ème Congrès Français de Mécanique, Aug 2011, Besançon, France. hal-03421293

HAL Id: hal-03421293

<https://hal.science/hal-03421293>

Submitted on 9 Nov 2021

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Homogeneity of deformation states during extensional measurements of polymer melts: an important issue revisited

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Résumé:

Nous étudions la relation entre le phénomène d'overshoot de la viscosité extensionnelle d'un polyéthylène basse densité (LDPE) fondu et l'uniformité géométrique de l'échantillon en fonction de la déformation. Par des mesures intégrales de la viscosité transitoire effectuées dans des conditions identiques sur des échantillons avec différents rapports d'aspect initial, une dépendance systématique du phénomène d'overshoot de la viscosité en fonction des rapports d'aspect initial est démontrée. La visualisation directe de l'échantillon en extension autour du point d'overshoot révèle la formation des cols secondaires autour du point médian de l'échantillon. La relation entre l'homogénéité de l'échantillon et son ratio d'aspect initial est également précisée.

Abstract:

We focus on the relation between a viscosity overshoot phenomenon during uniaxial extension of a low-density polyethylene (LDPE) melt and the geometric uniformity of the sample under deformation. By integral measurements of the transient elongational viscosity performed in identical conditions on samples with various initial aspect ratios, a systematic dependence of the viscosity overshoot phenomenon on the initial aspect ratios is found. Direct visualization of the sample under extension around the overshoot point reveals the formation of secondary necks around the midpoint of the sample. The relation between the sample homogeneity and its initial aspect ratio is also clarified.

Keywords: polymer melts, extensional viscosity, oil-bath rheometer, homogeneity of deformation states

1 Introduction

The transient and steady state elongational properties of polymer melts and polymer blends have particularly interested both theoreticians [1, 2] and experimentalists [3, 4]. Several techniques to measure the extensional properties of polymer melts have been proposed: the Rheometrics Melt Extensometer (RME) by Meissner, [5], the supporting oil-bath design by Münstedt, [6], the Sentmanat extensional rheometer (SER), [7] and the Filament Stretching Rheometer (FISER) [8].

For each of the approaches listed above, there exist, however, practical challenges in reliably assessing the extensional properties of polymeric materials. One of them is related to the fact that such measurements are extremely sensitive to the geometric homogeneity of the sample under deformation. Although this concern is now nearly four decades old, [9], a quantitative investigation of the impact of geometric inhomogeneities on the measurements of the transient extensional viscosity is, to our best knowledge, still missing. Only very recently the true danger of sample non-uniformity during elongation has been made explicit, by measuring locally both the stresses and the strains and showing that in the case of strongly geometrically non-uniform samples the classical extensional measurements become completely unreliable, [10]. In [10] it has been demonstrated by combined traditional integral viscosity measurements and local viscosity measurements based on in-situ local measurements of the sample diameter that geometric non-uniformities of the sample

under elongation typically result in unreliable viscosity data. Moreover, it has been shown that even initially homogeneous (perfectly cylindrical) samples lose their uniformity at high enough Hencky strains and thus, the impact of sample non-homogeneity on the viscosity measurements is always an issue to worry about during extensional tests.

Since the early days of extensional rheometry it has been observed that some strain hardening materials under uniaxial extension display a clear maximum in the transient extensional viscosity right before (typically within less than a Hencky strain unit) the physical rupture of the sample occurs, [11 - 14]. There is only one experimental paper we are aware of [15], which also presents an extended (over several Hencky strain units prior to the physical rupture of the sample) plateau after the stress maximum. During the experiments presented in [15] the geometric uniformity of the sample has been locally monitored by means of a laser sheet which images a (presumably) small portion of the sample around its middle, measures in situ the mid-point diameter of the sample and passes this information to a feedback loop which maintains a constant rate of deformation at the mid-point of the sample (this procedure is explained in detail in Bach et al. (2003)). However, we are not aware of any experimental study in which the homogeneity of the deformation states is assessed via real time video imaging of the entire sample under deformation and ultimately connected to the behaviour of the transient elongational viscosity. A local maximum in the tensile stress (transient elongational viscosity), followed or not by a plateau, has been coined as "viscosity overshoot".

As a continuation of our initial study [10], we focus here on the relation between the geometric uniformity of a low-density polyethylene (LDPE) sample under extension and the emergence of the viscosity overshoot phenomenon.

2 Experimental setup and methods

The experimental setup is an improved version of the system implemented in [10] and it is illustrated schematically in Fig. 1 (a).

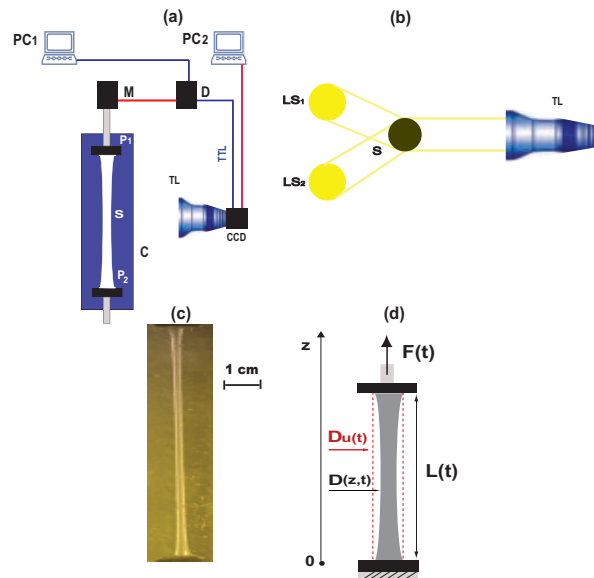


Figure 1: (a) Schematic view of the experimental apparatus: **C** - oil bath, **P₁** and **P₂** - top and bottom plates of the rheometer, **S** - the sample under investigation, **M** - AC servo motor, **D** - the control drive of the rheometer, **PC_{1,2}** - personal computers, **TL** - telecentric lens, **CCD** - video camera. (b) Sample illumination and imaging: **LS₁** and **LS₂** - linear light sources (c) Example of a telecentric sample image corresponding to a Hencky strain $\epsilon_H = 2.7$. The field of view was actually larger but the image has been cropped for clarity reasons. (d) Principle of the local measurements of the extensional viscosity. The vertical dotted lines represent the contour of an ideal uniform sample.

It consists of a traditional oil-bath rheometer to which a real time imaging system has been added. The sample under extension is uniformly illuminated from behind by two linear neon lamps $LS_{1,2}$ and visualized by a **CCD** camera through a high definition telecentric lens, Fig. 1(b). The use of a telecentric with the entrance pupil located at infinity was motivated by the need of acquiring the uniform brightness and distortion free images. Such an image is exemplified in Fig. 1(c). The image acquisition process is synchronized with oil-bath rheometer via a **TTL** signal generated by the rheometer's driving unit **D**.

The material used in this study is low-density polyethylene (LDPE) from Lyondell Bassel with the trade name Lupolen 1840 D. LDPE 1840 D has a branched molecular structure which has been systematically characterized by Nordmaier and co-workers, [16-17]. It has a broad molar mass distribution with a rather large molar mass, M_w , and a pronounced high molar mass tail. Due to the broadly distributed molar mass and the degree of chain branching, the maximum relaxation time of the material, λ , is quite high. It is calculated as $\lambda = Je_0 \cdot \eta_0$, where Je_0 and η_0 are the steady state recoverable compliance and the zero shear viscosity, respectively. For the LDPE samples used in this study, the maximum relaxation time was $\lambda = 1100s$ at $T=140^\circ C$.

3 Results

3.1 Observation of a viscosity maximum via integral measurements: aspect ratio dependence

We focus on the experimental observation of a viscosity maximum/overshoot during traditional integral measurements of the transient elongational viscosity on a oil-bath rheometer.

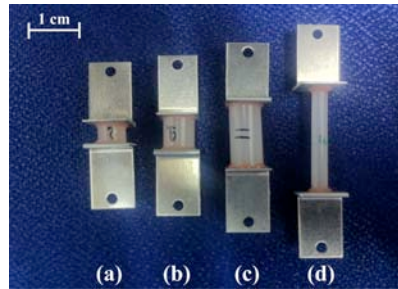


Figure 2: Photographs of several LDPE samples with various initial geometric aspect ratios x_0 used in our experiments: (a) $x_0=0.9$ (b) $x_0=0.7$ (c) $x_0=0.5$ (d) $x_0=0.33$.

A first fundamental question we addressed is the following: “*Is the emergence of a viscosity maximum/overshoot during measurements of the transient elongational viscosity independent of the geometric aspect ratio of the sample under extension*”? To our best understanding, a positive answer to the question above is a necessary condition for the viscosity overshoot phenomenon to reflect a true material property. To address this question, we have conducted extensional tests with samples prepared from the same batch of LDPE and following the same procedure but having different initial aspect ratios, $x_0 = D_0 / L_0$. Here D_0 and L_0 stand for the initial diameter of the sample and its initial length, respectively. Several photographs of such samples taken prior to the extensional measurements are presented in Fig. 2. By varying both the initial length L_0 of the samples and their initial diameter D_0 , 16 values of the initial aspect ratio x_0 ranging between 0.33 and 1.56 have been investigated. In Fig. 3 we present measurements of the transient elongational viscosity for several values of the initial aspect ratio. The elongational viscosity has been defined at an integral scale using the tensile force $F(t)$ as:

$$\eta(t) = \frac{4F(t)}{\pi \dot{\epsilon} D_0^2} \exp\left(2\dot{\epsilon} t\right) \quad (1)$$

The rate of extension used in Eq. (1) has been defined at an integral scale using the actual length¹ of the sample $L(t)$ as $\dot{\epsilon}(t) = L^{-1}(t)dL(t)/dt$.

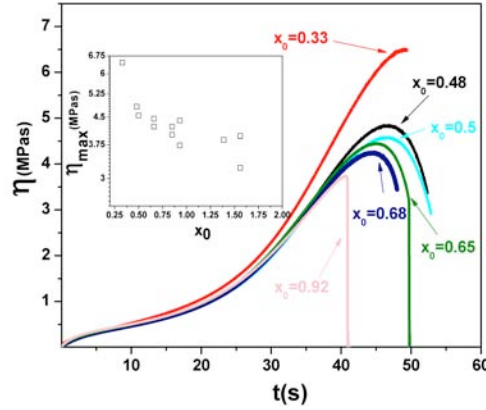


Figure 3: Measurements of the transient elongational viscosity for LDPE samples with different initial aspect ratios x_0 (indicated on the). The temperature is $T=140$ °C and the integral rate of deformation is $\dot{\epsilon}=0.07\text{ s}^{-1}$ for all measurements. The insert presents the dependence of the maximal value of the transient elongational viscosity η_{\max} on the initial aspect ratio of the sample x_0 .

The measurements presented in Fig. 3 indicate that the shape of the transient elongational viscosity curves depends strongly and systematically on the initial aspect ratio of the sample. The measurements presented in Fig. 3 (and all the rest which are not presented in Fig. 3, for clarity reasons) have been performed at the same temperature, $T=140$ °C and at the same rate of extension, $\dot{\epsilon}=0.07\text{ s}^{-1}$. For the smallest initial aspect ratio ($x_0=0.33$) which corresponds to the sample photographed in Fig. 2(d), a monotone increase of the elongational viscosity is observed. Note that in this case, because the measurements on the oil-bath device terminate when the maximum travel distance of the top plate is reached ($L_{\max}=50\text{cm}$), no breakup of the sample was observed. Therefore, we are unable to tell if a maximum of the transient elongational viscosity could be observed for this initial aspect ratio. As the initial aspect ratio of the sample is increased, a viscosity maximum emerges. Unlike in the experiments by Rasmussen et al. [15], no true overshoot behaviour is observed, in the sense that for the data presented in Fig. 3, the viscosity maximum is not followed by a plateau. Upon a further increase of the initial aspect ratio of the sample, a clear trend of the viscosity maximum is observed: the maximum occurs at earlier times t_{\max} and its value, η_{\max} , decreases (see the inset in Fig. 3). One can also note in the inset a decrease of the reproducibility of subsequent measurements with increasing values of the initial aspect ratio.

3.2 Local geometric homogeneity of the sample around the viscosity maximum

To better understand the underlying reasons for the dependence of the experimentally observed dependence of the viscosity maximum on the initial aspect ratio of the sample, we focus on the geometric features of the sample around the moment where the maximum is observed. A sequence of images acquired from the moment the transient elongational viscosity reached a maximum at several later stages of deformation is presented in Fig. 4. It is obvious from the sequence of images presented in Fig. 4 that the sample is

¹ It is important to note that in the case of a geometrically inhomogeneous deformation process where the diameter of the sample is no longer constant along its length (see Fig. 1 c-d) the local rate of deformation defined as $\dot{\epsilon}^*(z,t) = -2\ln[D(z,t)/D_0]$ is not equal to the integral rate of deformation $\dot{\epsilon}$.

geometrically inhomogeneous: its shape is definitely not cylindrical. Besides that, another interesting feature can be observed. Simultaneously with the emergence of a maximum of the transient elongational viscosity, a secondary neck can be observed roughly around the mid-point of the sample.

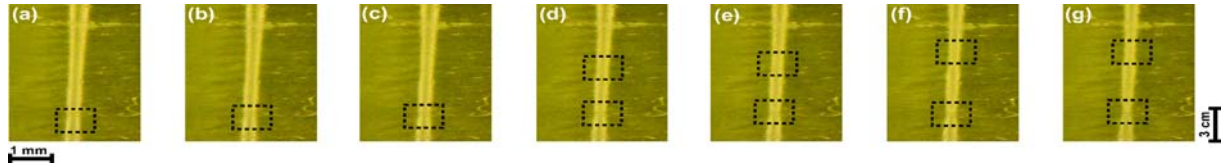


Figure 4: In-situ images of the central part of the sample separated by 1s. The first image corresponds to the point where a maximum of the transient elongational viscosity is observed. The initial aspect ratio of the sample was $x_0=1.6$ and the rate of strain was $\dot{\epsilon} = 0.015 \text{ s}^{-1}$.

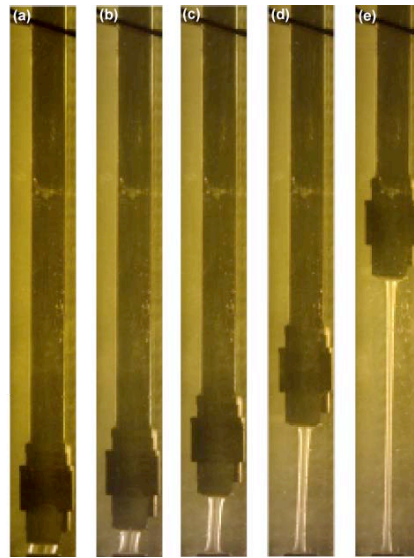


Figure 5: In-situ images of a sample with an initial aspect ratio $x_0=0.8$ at various stages of deformation: (a) $t=0 \text{ s}$ (b) $t=50 \text{ s}$ (c) $t=100 \text{ s}$ (d) $t=150 \text{ s}$ (e) $t=200 \text{ s}$. The last image was acquired right before the emergence of the secondary neck pictured in Fig. 4(a) and the emergence of a maximum of the integral elongational viscosity.

In the view of this direct experimental observation based on a direct visualization of the sample under deformation, the emergence of a viscosity overshoot as a true material property becomes once more questionable. To understand the relation between the homogeneity of the deformation and the initial aspect ratio of the sample, we compare two sequences of images of the sample under deformation acquired in the same conditions with samples with different initial aspect ratios. If a sample with a large initial aspect ratio is used (the sample is long and thin), the deformation is strongly inhomogeneous (the shape of the sample deviates from a cylindrical one), Fig. 5. For samples with small initial aspect ratios, the deformation is significantly more homogeneous – the shape of the sample is nearly cylindrical, Fig. 6. These visual observations together with the emergence of secondary necks in the case of inhomogeneous deformation of samples with large initial aspect ratio might shed a light on the strong aspect ratio dependence of the transient elongational curves presented in Fig. 3: as the initial aspect ratio is increased, the deformation of the sample becomes increasingly inhomogeneous up to the point where a surface instability (in the form of a secondary neck) emerges (see Fig. 4) which results in a local maximum of the transient elongational viscosity as shown in Fig. 3. This conclusion is consistent with the experiments performed by Münstedt et al on similar LDPE samples on a RME rheometer, [19]. As one can be seen in Fig. 4 of Ref. [19], the measurements of the transient elongational viscosity performed at several various rates of deformation display *no maximum* but a clear plateau which extends over nearly two Hencky strain units. According to our study this can be explained by a very small initial aspect ratio of the samples (in a RME device the distance between the rotating clamps is about 2 m whereas in the oil bath device is limited to 50 cm). According to the trend of the viscosity curves presented Fig. 3 decreasing the initial aspect ratio results in a

broadening and flattening of the viscosity maximum which, once more, makes it questionable.

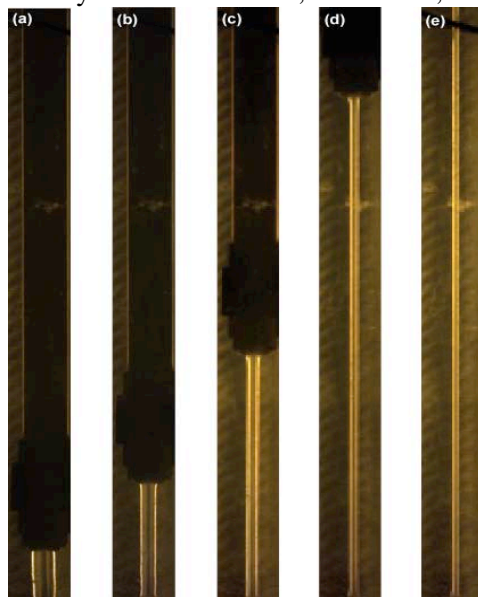


Figure 6: In-situ images of a sample with an initial aspect ratio $x_0=0.33$ at various stages of deformation: (a) $t=0$ s (b) $t=36$ s (c) $t=71$ s (d) $t=106$ s (e) $t=142$ s. No maximum of the transient elongational viscosity has been observed.

4 Conclusions

An experimental investigation of the role of sample's homogeneity during measurements of the transient elongational viscosity of a polymer melt is presented. A local maximum of the transient elongational viscosity depends systematically on the initial aspect ratio of the sample: it is pronounced for large aspect ratios but tends to disappear when the aspect ratio is decreased. We have shown that the emergence of such maximum is associated with a strong inhomogeneity of sample in the form of secondary necks. Samples with smaller initial aspect ratios deform more homogeneously than samples with larger aspect ratios, which explains the aspect ratio dependence of the transient elongational viscosity. In the view of these experimental findings, we conclude that a viscosity maximum emerges merely as an experimental artefact rather than an intrinsic property of the material under extension.

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