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Elongational Experiments on Polymer Melts and Their Assessment

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Abstract. Regarding the literature, steady-state values of the elongational viscosity are not widely documented and it is still an open question, whether the time-dependent elongational viscosity of strain-hardening polymeric materials runs through a maximum as a function of time before it reaches its steady state. For the assessment of molecular theories reliable experimental data are essential, however. From a survey of extensional experiments at constant elongational rates it becomes very probable that an extended stationary state of elongational exists and that maxima of the tensile stresses or even overshoot phenomena are due to non-uniform deformations of the samples. This conclusion is supported by creep experiments for which a steady state is reached at comparatively smaller total elongations corresponding to a better uniformity.

Keywords: Polymer melts, Extensional rheology, Experimental devices, Steady-state elongational viscosity, Theories, Uniformity of deformation.

PACS: 83.80.Sg, 83.85.Cg, 83.85.Rx, 83.85.Tz

INTRODUCTION

Starting in the nineteen seventies elongational experiments on polymer melts have gained a lot of interest for two reasons. Firstly, some aspects of processing operations containing a great deal of extensional deformation cannot be understood by shear rheology, only. Secondly, one important criterion for the validity of constitutive equations and the generality of the underlying molecular models is their ability to describe the facets of the elongational behaviour.

The most remarkable feature of extensional flow is the significant increase of the elongational viscosity with time or strain, respectively, which can be found for particular polymeric materials. The so-called strain hardening is dependent on the molecular structure of a material. It was shown to be an important factor for the uniformity of the wall thickness of films and thermoformed beakers, for example [1]. This feature can be made plausible by a “self-healing” effect inherent to strain hardening. Some work has been done on the relationship between strain hardening and molecular structure and, particularly, the role of long-chain branches was elucidated, e.g. [2]. Up to now, only qualitative relationships exist between strain hardening and processing performance and that is the reason why detailed quantitative aspects of the elongational viscosity are not of much relevance from an application point of view. Moreover, the elongation rates occurring during certain processing operations are much higher than those attainable with tensile rheometers.

If molecular models are discussed, however, a detailed knowledge of the elongational properties in dependence on various parameters is essential. Of particular importance are the answers to the questions whether a steady state of viscosity exists and in which way it is reached. The molecular stress function (MFS) theory [3], for example, uses the parameter β which determines the slope of the strain-hardening regime of the elongational viscosity and the parameter $f_{\max}^2$ which is related to its steady-state value. $f_{\max}^2$ is interpreted as the square of the maximum relative stretch of the chain segments and β as the ratio of the number of all entangled chain segments to the number of chain segments stretched. The other way round, from these experimentally determined parameters some conclusions can be drawn with respect to molecular structures within the frame of the model used.

As in many cases the elongational viscosity is only known over a limited range without reaching its plateau value, the parameters are often adapted to the measured part and the steady-state value is attained by extrapolation. Examples for such procedures are represented in [4] on various long-chain branched polystyrenes. A similar route is taken in the case of LDPE exposed to different thermal degradation [5]. In [6] a modified “pom-pom” model for randomly long-chain branched polyethylenes was used to match the elongational viscosities measured for several low density polyethylenes as a function of time. The modified model predicts plateaus at total elongations which could not be reached in the experiments, however, due to the limited total elongation available. These examples demonstrate that elongational measurements on strain-hardening materials up to the steady state are a requirement for the check of models and the reliable determination of the molecular parameters involved.

This obvious conclusion encounters some uncertainties as results from the literature regarding the elongational viscosity at high deformations do not give a consistent picture, even on a qualitative scale. Some authors report on a maximum of the elongational viscosity as a function of time for polyethylenes, e.g. [7], [8] and for polystyrene [9]. In [10] a pronounced overshoot is described before the attainment of a plateau, but results can be found which demonstrate a clear evidence of an extended plateau without any indication of an overshoot, e.g. [11].

Due to this unsatisfactory situation, this paper aims to review experimental results to make a contribution to the question of the existence of a steady state in uniaxial extension of strain-hardening materials and how it is attained.

EXPERIMENTAL DEVICES

Pioneering experimental work on the elongational behaviour of polymer melts was performed by Meissner. His device is presented in [12] and [13]. The cylindrical polymer sample of several hundred mm in length is drawn by two pairs of toothed wheels which counter-rotate to each other. The pulling force is measured by a special transducer mounted to the driving unit. The sample floats on a silicone oil bath which compensates its gravity and acts as the heat transferring medium. Stretching ratios up to 400 could be realised which correspond to Hencky strains up to 6. By cutting the sample into pieces of equal lengths at any state of deformation, the uniformity of

deformation can be checked by weighing and the recoverable portion of the total elongation can be determined after annealing.

To overcome the disadvantages of the tedious preparation of the long uniform samples and the relative large amount of material needed, Meissner developed a rheometer the principle of which is described in [14]. It became the base of the commercialized rheometer called RME. The rectangular sheet floats on a cushion of a preheated inert gas provided by a flat metal frit, i.e. the oil bath is avoided. The rotating clamp technique is preserved, but another type of clamp is used. The toothed wheels of the former design are replaced by metal conveyor belts. A video device allows the optical control of the sample surface and its geometrical change during deformation. By cutting the sample its retraction and following from that the recoverable elongation can be determined. However, this procedure requires some care in order to allow an unhindered recovery.

The role of a work horse in the field of extensional rheometry has been taken over by a design developed by Sentmanat (SMR) [15]. A polymer sheet is clamped to two drums which counter-rotate to each other driven by the shaft of the “master drum”, the rotation of which is transferred to the “slave drum” by intermeshing gears. From the torque exerted on the “master drum” the tangential force acting on the sample can be determined. This device gets its popularity from the fact that it can be built into the housings of commercial rotational rheometers making use of their existing heating chamber, driving unit, and torque sensor.

Several rheometer manufacturers offer this equipment commercially. It has proven its performance in the field of routine measurements but its contribution to fundamental research has to be regarded very critical for several reasons. The one is that sagging of the samples cannot be avoided even for the geometries chosen, as a supporting medium is not applied. This effect is particularly pronounced in the case of samples with low viscosities. It reduces its versatility for measurements at high temperatures which, in principle, could easily be achieved by making use of the heating ovens of commercial rheometers. Another deficiency may arise from a too high friction of the bearings and the intermeshing gears which negatively affects the measurement of the torque acting on the sample. Furthermore, the uniformity of the sample deformation cannot be checked which is very important, however, for a reliable determination of the elongation rate and the tensile stress and, therewith, the elongational viscosity. Measurements of the recovery of the sample are not possible due to the principal design of the device.

For measurements up to high elongations, the use of a filament stretching rheometer (FSR) is propagated [16]. Its basic elements are two plates to which the cylindrical sample is fastened. The lower one is fixed and the upper one driven in a way that the diameter in the middle of the sample decreases exponentially with time in order to keep up a constant Hencky strain rate. They are placed in a temperature controlled oven with glass covered slits allowing the measurement of the sample diameter by a laser device. The exerting force is registered by a load cell mounted to the lower plate. The upper plate and the laser are driven by the same motor. Using an appropriate gear, the laser is moved at half the velocity of the upper plate which results in a position just in the middle between the two plates. If the symmetry of the sample is preserved during the experiment, then the elongational viscosity at the given

constant elongation rate can be determined from a local measurement. The small aspect ratios of the specimens used are favourable to achieve high Hencky strains, but they are prone to problems regarding the fastening of the specimens to the clamps and the uniformity of deformation. Visualisations of the sample geometries are not reported in the literature. Principally, the FSR is not suitable to determine the recoverable elongation.

Based on the idea of a vertically suspended sample first realized by Cogswell [17], Münstedt developed a versatile instrument [8], [18] which has been used to characterise the elongational properties of a great number of polymeric materials, particularly, in dependence on their molecular structure. For such kind of investigations the rheometer is particularly suited as comparably small amounts of samples are needed and, therefore, the elongational behaviour of polymer materials can be investigated which are available on a laboratory scale, only. As cylindrical samples are used, they can comfortably be prepared by extrusion through appropriate capillaries. Typical samples have diameters of around 5 mm and lengths between 10 and 25 mm.

The sample is suspended perpendicular in a silicone oil bath of a density adapted to that of the polymer melt. The one end is fixed to the force transducer the other to the pulling device. Besides compensating the weight of the sample by buoyancy, the oil serves as the heat transferring medium. Sophisticated drive and control units allow a wide variety of experimental modes. Besides stressing and creep experiments, retardation and relaxation measurements can be performed. The steady-state recoverable strain may elegantly be determined by setting the stress to zero and waiting till the equilibrium of the sample retraction is reached. The uniformity of the sample deformation can be visualised in-situ using optical devices [19]. By lowering the vessel, the sample can be frozen at various states of elongation for further outside characterisations.

EXPERIMENTAL RESULTS

Stressing Experiments

In Figure 1 extensional experiments on a LDPE named IUPAC A at two different constant elongational rates are presented. Its thorough molecular and rheological characterisations are documented in [20]. The measurements were performed with the Meissner type of oil-bath rheometer. The initial lengths of the rod-like samples used for the measurements presented in Figure 1 were 650 mm. They were elongated up to a stretching ratio of 400 which corresponds to a Hencky strain of 6. The uniformity of the sample deformation was determined by cutting the stretched strand into pieces of the same lengths and weighing the various cuts obtained. For a more descriptive comparability, the diameters of the strands before cutting are calculated from their weight assuming a cylindrical shape. At the elongational rate of $\dot{\epsilon}_0 = 0.03 \text{ s}^{-1}$ and the temperature of 150°C , for example, the diameters of ten cuts along the stretched sample deviate from each other by maximal 2% up to $\epsilon_H = 5$ and by 5% at $\epsilon_H = 6$ [11].

These relatively small differences stand for an excellent uniformity of the samples whose data are presented in Figure 1.

FIGURE 1. Stress-strain curves of a LDPE (IUPAC A) at two constant Hencky elongational rates $\dot{\varepsilon}_0$ [11]. The different symbols mark experiments on various samples. λ is the stretching ratio.

The stress increases as a function of elongation and reaches a pronounced plateau for $\varepsilon_H > 4$ which extends to the highest measured elongations of $\varepsilon_H \approx 6$. The different symbols mark various samples and demonstrate the satisfactory reproducibility of the measurements, particularly, if one takes the large stretching ratio of 400 into account.

A real steady state in extension should not only be reflected by viscous, but by elastic properties, too. With the Meissner oil-bath rheometer the recoverable strain ε_r as a measure of the elasticity of a material can be obtained from the total recovery of the cuts taken at any state of stretching. The recoverable strain is defined as

$$\varepsilon_r = \ln l/l_r \quad (1)$$

with l being the length between two pairs of scissors and l_r that after cutting and total recovery. Averaging over ten cuts obtained from one stretched sample provides experimentally well verified data.

In Figure 2 the recoverable strains of specimens deformed at $\dot{\varepsilon}_0 = 0.1 \text{ s}^{-1}$ up to various elongations are plotted together with the corresponding curves for the stresses. Each symbol of the curve of the recoverable strain stands for one stretched sample. A plateau of the recoverable strain ε_{rs} is reached around a Hencky strain of 3.5 which goes along with that of the stress adding another experimental evidence to the existence of a steady state.

FIGURE 2. Tensile stress σ and recoverable strain ε_r as functions of the total strain ε_H for stressing experiments at $\dot{\varepsilon}_0 = 0.1 \text{ s}^{-1}$ on the LDPE IUPAC A [22].

With an improved version of the rheometer used for the measurements presented in the Figures 1 and 2, elongations up to $\varepsilon_H = 7$ could be reached for samples of a LDPE very similar to IUPAC A. Flat maxima of the tensile stress and the recoverable strain are reported [21] which occur at Hencky strains between 5 and 6, i.e. just close to the highest extensions of the experiments in the two figures above for the same elongational rates of $\dot{\varepsilon}_0 = 0.1 \text{ s}^{-1}$ and $\dot{\varepsilon}_0 = 0.03 \text{ s}^{-1}$. Although the measured data accounted for a maximum, only, an overshoot was described theoretically by adapting the data to the MFS theory [23].

The uniformity of the stretched sample was checked by weighing the cuts of the elongated sample, 50 mm in length each. It was found to be within the range of the samples in Figure 1. Assessing the experimental challenges related with such high elongations it should be realised that $\varepsilon_H = 6$ corresponds to a stretching ratio of about 400 and $\varepsilon_H = 7$ to that of about 1100 resulting in decreases of the diameters of cylindrical samples by the factor 20 or 33, respectively. An initial diameter of typically 6 mm, for example, changes into a filament of some few hundred microns. plateau, i.e. an overshoot, is reported in [10]. The results were obtained with the so-called filament stretching rheometer (FSR) on a LDPE of a branching structure similar to that of the samples described before, but of a higher molar mass (Lupolen 1840 D). The total elongations reached Hencky strains between 6 and 7. Although based on a local measurement of the elongational rate in the middle of the sample, the uniformity of the deformation does play a role, too, as the symmetry has to be preserved in order to keep up a constant elongational rate during the experiment. This condition represents an experimental challenge as a sagging of the sample during elongation may occur due to the absence of a supporting medium. Additionally, the

requirements with respect to a good temperature constancy along the length of the elongated filament are high. A discussion of these essential issues cannot be found, however, in the corresponding literature and observations documenting the sample deformation are not given anywhere.

Maxima of the elongational viscosity, but without a following plateau are reported in [19] for a LDPE of the same type as characterised in [10]. As Figure 3 shows they are found at total Hencky strains of about 3 for the three elongational rates applied. The measurements were performed with the MTR. Using an optical device, a consistence between the maximum of the viscosity and the formation of necks along the sample could be found [19]. It is obvious that necks give rise to a decrease of the force measured and following from that of the stress calculated under the assumption of a uniform sample deformation. This finding clearly relates the maximum to an experimental deficiency and gives a hint that the interpretations of a maximum and an overshoot, respectively, by molecular theories found in the literature may be based on an experimental artefact.

FIGURE 3. Elongational viscosities of the LDPE Lupolen 1840 D at various elongational rates and $T = 140^{\circ}\text{C}$ [19]. The initial sample length was $L_0 = 5$ mm.

A first hint that the maximum of the elongational viscosity may be due to a non-uniform sample deformation was already given in [8]. The experiments with two versions of Meissner's oil-bath rheometer show that if a steady state of elongation exists for the LDPE IUPAC A it may occur at Hencky strains of around 5. Measurements at this degree of extension are very challenging, of course. Neither for the elongational viscosity nor for the recoverable strain an overshoot was found as a function of time, however.

The assessment of the viscosity maxima obtained by using the experimental devices presented in [7], [8] and [10] has to take into account the following experimental facts:

For materials with a pronounced increase of the elongational viscosity as a function of time or strain, respectively, large Hencky strains are necessary in a stressing experiment to reach the steady state.

At large extensions, samples are prone to non-uniform deformations which are the more significant the smaller the initial aspect ratio. Such effects are particularly pronounced in the case of a fixed clamping. Therefore, a check of the sample uniformity during elongation is a precondition for measurements of high reliability.

Experiments with constant elongational rates based on local measurements of the sample diameter rely on the observance of symmetry which is difficult to preserve, in principle, if the effect of gravity is not excluded.

Besides the viscosity, elasticity should be measured in order to prove the existence of a steady state. This quantity can reliably be determined by the Meissner oil-bath rheometer and the MTR, only.

The oil-bath rheometer by Meissner comes closest to all these requirements. However, its handling is elaborate and needs special hardware and sophisticated skills which are not available any more.

Creep Experiments

An interesting contribution to an answer to the question of the existence of a steady state in elongational flow can be obtained from creep experiments, as they reach stationarity at smaller extensions than stressing tests. Since a sample gets the less prone to non-uniformity the lower the degree of deformation, creep tests are the method of choice if steady-state properties are investigated. However, they present an experimental challenge insofar as an accurate control of the tensile force over a wide range is necessary in order to preserve constant stresses up to high elongations at which the cross sections of a sample become small. The MTR is the only instrument which has proven a reliable performance in the creep mode up to now [8].

A creep experiment on a long-chain branched polypropylene is shown in Figure 4. The upper graph demonstrates the constancy of the stress of 1000 Pa over the duration of the experiment. The short-termed spikes are due to the electronic control device and do not have any influence on the experimental performance. The elongation increases as a function of time and reaches a constant slope which corresponds to an elongational rate of $\dot{\epsilon}_0 = 0.002 \text{ s}^{-1}$. As it is seen from the elongational rate, the steady state stretches over a rather long period of time corresponding to a range of Hencky strain between 2.5 and 3.8.

FIGURE 4. Hencky strain ε_H and strain rate $\dot{\varepsilon}_0$ as a function of time in a creep experiment on a long-chained branched polypropylene (LCB-PP) [24]. The upper curve presents the tensile stress. The initial sample length was $L_0 = 10$ mm.

From the results of Figure 4, $\sigma_0/\dot{\varepsilon}(t)$ is determined and plotted as a function of time in Figure 5. This quantity reaches a pronounced stationary state from which a steady-state elongational viscosity of $\mu_s = 5 \cdot 10^5$ Pa.s follows. As can be seen from Figure 5, too, in the stressing experiment performed at the constant strain rate $\dot{\varepsilon}_0 = 0.002 \text{ s}^{-1}$ reached in the creep experiment, a steady state is not attained up to the maximum achievable total strain of $\varepsilon_H = 3.8$, and $\sigma(t)/\dot{\varepsilon}_0 = 3 \cdot 10^5$ Pa.s at this deformation is still distinctly lower than μ_s in the steady state of the creep experiment. Furthermore, the shapes of the two viscosity functions are totally different. The experiments with two different initial sample lengths leading to various maximum elongations are in good agreement. This figure clearly demonstrates that the time-dependencies of the elongational viscosities measured at constant stress or constant elongational rates are different. Of course, the steady-state elongational viscosity is independent of the experimental mode applied.

FIGURE 5. Elongational viscosity μ as a function of time t for a long-chain branched polypropylene at a constant elongation rate of $\dot{\epsilon}_0 = 0.002 \text{ s}^{-1}$ in comparison with $\sigma_0/\dot{\epsilon}$ from the creep experiment in Figure 4 (open circles). The creep test was performed with a constant stress of $\sigma_0 = 10^3 \text{ Pa}$ and a steady-state elongational rate of $\dot{\epsilon}_{\text{stat}} = 0.002 \text{ s}^{-1}$ was attained. The full line describes three times the linear shear viscosity. Two initial sample lengths L_0 were used for the stressing experiments [24].

For the LDPE IUPAC A steady states were reached in creep and stressing experiments as well. The corresponding elongational viscosities are plotted in Figure 6 as a function of the elongational rates. The agreement between the results from the two modes is good. A comparison with the viscosity function in shear demonstrates that the Trouton relationship $\mu_0 = 3\eta_0$ is fulfilled in the linear range adding another experimental evidence for the reliability of the experiments. From the figure it becomes obvious how different viscosity functions in elongation and shear can be.

FIGURE 6. Comparison of the steady-state elongational viscosities μ_{stat} obtained from stressing experiments (full symbols) and creep experiments (open symbols) [22]. The stationary shear viscosity η_{stat} as a function of the shear rate $\dot{\gamma}$ is plotted as a broken line.

CONCLUSIONS

From the experiments presented the probability becomes very high that the elongational viscosity attains a steady state without any maximum or overshoot. It seems likely that the reason for the occurrence of a maximum has to be sought in a non-uniform deformation of the sample. Indeed, for the LDPE Lupolen 1840 D which exhibits pronounced maxima already in the range of deformation attainable with the MTR these maxima could be related to necking within the sample [19]. Detailed investigations on this material in creep and stressing experiments are discussed in [25] and in the presentation by Z. Sary at this conference.

From the results presented follows the requirement that information of the sample uniformity should be available before conclusions on the existence of a maximum or an overshoot of the elongational viscosity are drawn. This demand relates to all extensional rheometers, particularly, if high deformations are applied. Although very obvious, investigations of this kind are not found in the literature. From the experiments shown it is evident that the uniformity of deformation depends on experimental conditions and material properties. In addition, geometrical quantities like diameter and aspect ratio of the samples come into play. Not negligible in this aspect is the way of clamping and a critical review of this influence may be helpful to avoid artefacts. The conditions of uniform deformations make elongational experiments rather demanding. But if not considered and discussed, misleading results can be obtained very easily.

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