

Extensional Viscosity in Uniaxial Extension and Contraction Flow – Comparison of Experimental Methods and Application of the Molecular Stress Function Model

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ABSTRACT

Extensional viscosity of low-density polyethylene was measured in uniaxial extension by Sentmanat Extension Rheometer (SER) and in contraction flow using the Cogswell analysis. The results achieved by SER were compared to the ones obtained by Mündstedt Tensile Rheometer (MTR) and Rheometrics Melt Extensometer (RME). The onset of strain hardening measured by SER was in good agreement with MTR and RME, nevertheless, the measured maximum transitional extensional viscosity values were lower. These were, however, in accordance with the extensional viscosity estimated by Cogswell analysis. The Molecular Stress Function (MSF) model applied to the results was able to describe the onset of strain hardening and the maximum transitional extensional viscosity values.

INTRODUCTION

Extensional flow, although more difficult to produce and measure reliably in laboratory circumstances than shear flow, is of great importance in processing of polymers. In many industrial melt processes the flow is a mixture of both extensional and shear flows. In injection molding, for example, shear flow is traditionally considered as the only significant deformation type. In the mold, indeed, when the part wall thickness is thin and mainly

remains constant, the melt sticks to the wall and shearing is the prevailing flow type¹. However, in abrupt contractions, such as gates, where the melt accelerates due to a rapidly changing cross-section, the elongational flow becomes dominant. Thereby the major part of the junction pressure losses is determined by the extensional deformation². This justifies the importance of examining the effect of elongational flow also in injection molding and correspondingly considering it in injection molding flow simulations as well.

Measuring extensional viscosity accurately is a challenging task, although different experimental set-ups have been developed during the last decades for the purpose. The difficulties arise often in producing purely uniaxial elongation, and especially in achieving steady-state flow. The limiting factor can be, depending on the measurement device, for example onset of flow instabilities or necking and rupture of the sample. Furthermore, the experimental data are often achieved at strain rates below 10 s^{-1} , which can limit their use to the industrial applications. In order to gain experimental data at higher rates one must settle with approximate methods such as melt spinning experiments or contraction flow analyses.³

Given the limitations of different measurement techniques, obtaining extensional data covering a wide range of strain rates accurately using only one test

method is a difficult task. Thus, in order to achieve this, combining different measurement methods having a sufficient accuracy and easy operation would be an attractive choice. Furthermore, a possibility of predicting steady-state extensional viscosity theoretically on a basis of less experiments utilizing a constitutive equation, would offer a great advantage over complicated experimental determination.

We evaluated the extensional viscosity of a low-density polyethylene (LDPE) in uniaxial extension by Sentmanat Extension Rheometer (SER), and in contraction flow by Cogswell method in order to find out if the uniaxial extensional experiments could be combined with an apparent method like contraction flow analysis, to characterize the extensional flow in a wide range of strain rates. Moreover, we revisited the applicability of the Molecular Stress Function (MSF) model^{4,5} for estimating the extensional viscosity on the basis of experimental data.

THEORY AND CALCULATION

Uniaxial extension

Sentmanat Extension Rheometer Universal Testing Platform has two drums that rotate to the opposing directions, while thin metal clips prevent slipping of the sample mounted on them. The torque M resulting from the force of tangential stretching of the sample between the rotating drums is recorded by the torque transducer of the rheometer:

$$M = 2RF(t) \quad (1)$$

where F represents the force and R the drum radius, 5.155 mm. It should be mentioned, that the frictional force is usually less than 2 % of the stretching force owing to the precision bearings and gears of the SER device, thus its contribution to the torque can be considered negligible⁶. The Hencky

strain rate at constant drum rotating speed Ω is:

$$\dot{\epsilon}_H = \frac{2\Omega R}{L_0} \quad (2)$$

L_0 being the initial length of the stretching zone, that is, the gage length between the fixing clips, 12.72 mm. The transient extensional viscosity can be calculated as

$$\eta_E^+ = \frac{\sigma_T}{\dot{\epsilon}_H} = \frac{M - M_{offset}}{2R\dot{\epsilon}_H A(T) \exp[-\dot{\epsilon}_H t]} \quad (3)$$

where the term

$$A(T) = A_0 \left(\frac{\rho_S}{\rho_M(T)} \right)^{2/3} \quad (4)$$

takes account of the thermal expansion, thus changing dimensions of the sample, upon melting (ρ_S = sample density at solid state and $\rho_M(T)$ = melt density at temperature T). A_0 is the initial cross-sectional area of the sample. M_{offset} is a pre-set torque which can be applied prior to the actual test phase in order to avoid the gravitational slack of the sample due to melting.⁶

The melt density for polyethylene as a function of temperature T (in °C) can be calculated as⁷

$$\rho_M(T) = [1.262 + 9 \cdot 10^{-4}(T - 125)]^{-1} \quad (5)$$

Cogswell method

When the macromolecular fluid flows through a sudden contraction, the center of the flow region is funnel-shaped, whereas, due to the elastic effects, circulating flow vortices are formed at the corners. These vortices dissipate energy, causing an extra pressure drop at the entrance region of the contraction. The contribution of the extensional effects can be calculated according to Cogswell⁸ by deriving it from

the entrance pressure drop, Δp_e , assumed as a sum of pressure drops caused by shear and elongational deformation. This can be presented for a circular symmetry as

$$\eta_e \approx \frac{\sigma}{\dot{\epsilon}} = \frac{9}{32} \frac{(n+1)^2 \Delta p_e^2}{\tau_{wa} \dot{\gamma}_{wa}} \quad (6)$$

where the tension stress is

$$\sigma = \frac{3}{8} \Delta p_e (n+1) \quad (7)$$

and extension rate

$$\dot{\epsilon} = \frac{\tau_{wa} \dot{\gamma}_{wa}}{2\sigma} \quad (8)$$

τ_{wa} is the apparent shear stress at the wall, $\dot{\gamma}_{wa}$ is the apparent shear rate at the wall, and n is the power-law parameter for the shear flow. Although the method is highly empirical involving rough simplifications and assumptions, it has shown, at high strain rates, to give reasonably good agreement with other techniques for measuring extensional viscosity⁹. For Cogswell analysis, the entrance pressure drop has to be determined by performing capillary rheometer measurements using either at least three dies having different length-to-diameter (L/D) ratio, and consequently applying the Bagley correction, or alternatively using one longer die, and an orifice die (die with a nominal length of zero), by which the entrance pressure drop can be directly measured. The maximum strain the melt undergoes at an abrupt contraction of the capillary rheometer can be calculated as

$$\epsilon_{\max} = \ln \left(\frac{A_b}{A_d} \right) \quad (9)$$

where A_b is the cross-sectional area of the cylinder and A_d the cross-sectional area of the die¹⁰.

Modelling

The MSF model^{4,5} is a single tube segment model. The tube diameter a is assumed to be independent of the orientation of tube segments, and to decrease from its equilibrium value a_0 to a value a with increasing deformation (Fig. 1). The extra stress tensor $\underline{\underline{\sigma}}(t)$ of the MSF model is given by a history integral of the form

$$\underline{\underline{\sigma}}(t) = \int_{-\infty}^t m(t-t') f^2 \underline{\underline{S}}_{DE}^{IA}(t, t') dt' \quad (10)$$

$m(t-t')$ being the memory function related to the linear viscoelasticity of the system. The strain measure $\underline{\underline{S}}_{DE}^{IA}$ represents the contribution to the extra stress tensor originated from the affine rotation of the tube segments assuming ‘‘Independent Alignment (IA)’’, and is given by

$$\underline{\underline{S}}_{DE}^{IA}(t, t') \equiv 5 \left\langle \frac{\underline{u}' \underline{u}'}{u'^2} \right\rangle_0 = 5 \underline{\underline{S}}(t, t') \quad (11)$$

with $\underline{\underline{S}} = \underline{\underline{S}}(t, t')$ being the relative second order orientation tensor, $\underline{u}' \underline{u}'$ the dyad of a deformed unit vector $\underline{u}' = \underline{u}'(t, t')$, u' its length and the orientation average over an isotropic distribution of unit vectors⁴, \underline{u} being indicated by $\langle \dots \rangle_0$.

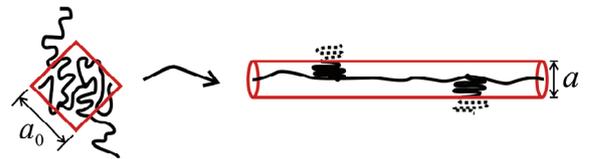


Figure 1. Tube model and the decrease of the tube diameter with increasing deformation.

The square of the relative tension in the chain segment, f^2 , is related to the strain energy stored in the polymeric system, and is determined as a solution of an evolution equation derived from an energy balance argument⁴. For polydisperse branched random polymer melts, considering the change of free energy and the constraint release (CR) term, the evolution equation for f^2 was found to be⁵

$$\frac{\partial f^2}{\partial t} = \frac{\beta f^2}{1 + \frac{\beta - 1}{f^4}} \left[(\underline{\kappa} : \underline{S}) - \frac{CR}{f^2 - 1} \right] \quad (12)$$

with

$$CR = \frac{(f^2 - 1)^2}{f_{\max}^2 - 1} \sqrt{\underline{D}^2 : \underline{S}} + a_2 (f^2 - 1)^2 \sqrt{\underline{W} \underline{D} : \underline{S}} \quad (13)$$

where $\underline{\kappa}$, \underline{D} , and \underline{W} are the velocity gradient, deformation rate, and the vorticity tensors, respectively. The nonlinear parameter β is directly related to the molecular structure of the polymer, f_{\max}^2 represents the maximum stretch to which the molecule can be submitted and a_2 governs the additional dissipation process only occurring in shear flow, due to its rotational character.

EXPERIMENTAL

Sample preparation and measurements in uniaxial extension

Approximately 0.5-0.8 mm thick sheets were pressed by a hot press from the melt homogenized first in a single screw extruder. The pressing temperature, as well as the extrusion temperature and screw rotation speed, was carefully kept low enough to avoid molecular chain scission. Approximately 20 mm long and 10 mm wide sample strips were cut from the pressed sheet and the accurate dimensions of each individual sample were measured.

Extensional viscosity was measured using the SER device in Physica MCR301 rheometer at constant Hencky strain rates 0.01 - 8 s⁻¹ at 170 °C. The sample was attached on the drums as shown in Fig. 2, and as the temperature had reached the set value, the test was commenced. In order to avoid possible error caused due to fixing the sample on the drums, all the tests were run without the fixing clips. Noteworthy is also, that due to the bulky construction of the U-shaped SER frame, the temperature regulation with the device works very slowly: in order to ensure exact testing temperature, a very long pre-tempering time is required. Moreover, for ensuring exact control during the tests, the temperature sensor must be mounted next to the SER frame so that it touches the metal.

A pre-set torque (M_{offset}) of 20 μNm was applied before the actual test phase in order to avoid sample slack, and respectively taken into account in calculation of the true torque as presented in Eq. 3. Additionally, oscillation measurements at 170 °C were made for obtaining the linear viscoelastic spectrum and steady-shear viscosity in rotation was measured for comparison purposes.



Figure 2. SER with an LDPE sample strip mounted on it.

Contraction flow measurements

Capillary measurements at 170 °C were performed by Göttfert Rheograph 6000 capillary rheometer using a round-hole die with a diameter of 1 mm and L/D of 20, and with an orifice die having a diameter of 1 mm. The dies have an abrupt contraction at the entrance, i.e., the entrance angle is 180°. The measured set covered the shear rates 10, 20, 40, 100, 200, 400, 1000 1/s. The rheometer barrel has a diameter of 12 mm thus the contraction ratio $A_b:A_d=144$, and according to Eq. 9, $\epsilon_{\max} \approx 5$.

RESULTS AND DISCUSSION

The transient extensional viscosity measured by SER with MSF model fitting is presented in Fig. 3. The model was able to describe the strain hardening behavior of LDPE with model parameters $f_{\max}^2 = 12.0$ and $\beta = 2.0$ relatively well. The steady-state values predicted by the model are somewhat higher than achieved experimentally and depend on “bending-over” of the extensional viscosity data.

The SER results were compared to results¹¹ achieved earlier using a Mündstedt Tensile Rheometer¹² (MTR) and Rheometrics Melt Extensiometer¹³ (RME). The comparison illustrates that the onset of strain hardening by SER is in very good agreement with that measured by MTR and RME (Fig. 4). On the other hand, the maximum values measured by SER are below the ones measured by MTR and RME. This raises the question, whether or not steady-state flow was achieved in the measurements.

The possibility of achieving the steady-state at all in constant strain flow has, a matter of fact, been debated¹⁴, and although the maximum values obtained from transitional tests can be postulated to represent steady-state, this is not necessary the case. The maximum extensional viscosity values from SER tests were taken to represent the “steady-state” and compared

with the values achieved by the Cogswell method (Fig. 5).

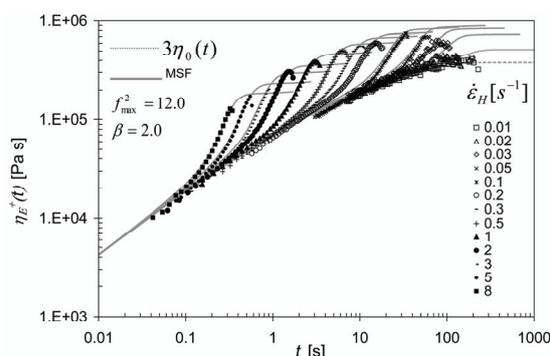


Figure 3. Transient extensional viscosity measured for LDPE by SER and fitting of the MSF model.

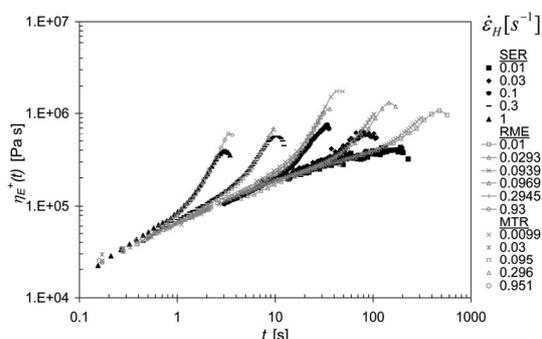


Figure 4. Comparison of the transient extensional viscosity measured for LDPE by SER, RME, and MTR at 170 °C.

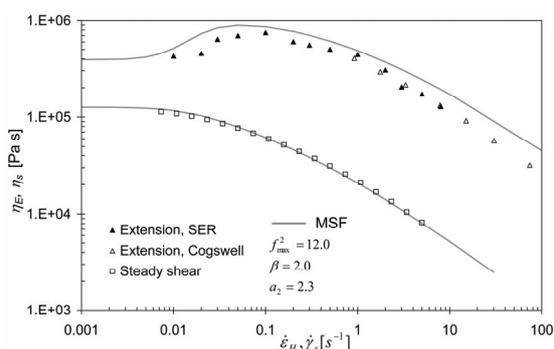


Figure 5. Steady-state extensional and shear viscosities vs. strain rate for LDPE at 170 °C from SER tests, Cogswell analysis, and MSF model fitting.

The overlap appears to be rather good despite - or exactly because of- the fact, that the values from Cogswell method should be considered more as apparent: Flow through a contraction is transient in nature, and not solely a function of strain rate, but also of total strain. In the capillary rheometer with $A_b:A_d=144$, as proposed by Padmanabhan and Macosko¹⁰, the average strain, $\epsilon_{ave}\approx 3$, which approximately equals the ϵ_{max} reached in SER tests. This may partially explain the good correspondence between the results, although the type of deformation the material undergoes in these two measurement methods is quite different.

The MSF model fittings to the steady-state extensional and shear viscosity are also presented in Fig.5. The extensional steady-state model values are achieved from best fit of MSF model to the transient data (Fig. 3), and are somewhat higher than the measured maximum values. The ability of the model to describe the steady-state values is always dependent on the maximum measured transitional values. To the steady-shear viscosity data the model gave a good fit using the value of $a_2=2.3$ for the rotational parameter.

CONCLUSIONS

The transient extensional viscosity measured by SER was in accordance with results achieved by RME and MTR, although the maximum values reached by SER were lower. Furthermore, maximum transient values by SER and the extensional viscosity evaluated from contraction flow by Cogswell analysis were in relatively good correspondence, which may possibly be traced to the equal strain the melt is experiencing in these two test methods. The MSF model was able to describe the strain hardening of the LDPE as well as the "steady-state" extensional viscosity.

For evaluating the rheological behavior of polymers in processing applications, such as for flow simulations in injection molding, where extensional viscosity data over a relatively wide strain-rate range is needed,

using uniaxial extension and contraction flow analysis together could provide relatively accurate and easily measurable data. Moreover, the possibility to fit the MSF model for describing extensional flow behavior can save some experimental efforts.

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