Evaluation of A New Extensional Rheometer

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Abstract

The performance of a new extensional rheometer, the Sentamanat Extensional Rheometer (SER), was evaluated by measuring the properties of two metallocene polyethylenes having low levels of long- chain branching. The SER is a fixture that can be installed within the heating chamber of a standard, strain-controlled rotational rheometer. The fixture consists of a pair of mechanically coupled drums, between which the sample is stretched to generate a uniform deformation. A measurement can be made in a few minutes, and only a small amount of polymer is required. Measurements at several rates up to 20 s^{-1} were performed, and both materials show marked strain–rate thickening. The results were compared with those measured using a Münstedt rheometer, and the agreement was satisfactory.

Introduction

Extensional flow behavior is of importance in plastics processing and in polymer science. Industrial forming processes such as film blowing and extrusion coating involve large, rapid stretching deformations. And in polymer science, extensional properties are very sensitive to long chain branching[1,2] and are useful for the evaluation of molecular theories[3,4].

However, extensional flow measurements are much more difficult to carry out than shear measurements. The most problematic aspects of extensional flow studies are supporting the sample and applying a tensile force without introducing strong end effects. In most instruments the sample is supported by an oil bath, but this is a troublesome feature, and Meissner proposed the use of a bed of pressurized gas. One approach to the sample "clamping" problem is to use an adhesive to fix the ends of the sample to metal supports, but deformation is suppressed near the ends. Another approach is to use a "rotary clamp" consisting of a set of coupled gears at one or both ends of the sample. However, if only one set of gears is used, the extensional rate nearest the fixed end is non-uniform; the maximum Hencky strain rate is limited to 1 s^{-1}. Meissner's[5] dual rotary clamp rheometer and the improved version making use of metal conveyor belts by Meissner and Hostettler[6] overcome the problem of nonuniform deformation and allow larger total strains. However, it is necessary to use a video camera to record the movement of the sample to evaluate the true strain rate. The maximum Hencky strain rate is still limited to 1 s^{-1}. Connelly *et al.*[7] and Padmanabhan *et al.*[8] modified a rotational rheometer by fixing one end of the sample to a stationary post and winding up the other end using the rheometer motor. While the nonuniformity of the extension rate is an issue in these designs due to the fixed end, it was reported that strain rates up to 10 s^{-1} could be generated.

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Sentmanat[9] recently described a new instrument, the Sentmanat Extensional Rheometer, which also makes use of a standard rotational rheometer. The rheometer consists of master and slave windup drums coupled via intermeshing gears, as shown in Fig. 1. The master drum is rotated at an angular speed Ω by the motor of the rotational rheometer, while the gear system drives the slave drum at the same speed in the opposite direction. These counter-rotating drums uniformly stretch the sample over the unsupported length, L_0. Therefore, the total deformation is not limited. The uniformity of the deformation has been examined by Sentmanat[10] using a video technique. The tensile force in the sample F is transformed into a torque T that is detected by the torque transducer in the rotational rheometer. Sentmanat[10] demonstrated that the actual strain rate is equal to the nominal value $R\Omega/2L_0$. This design can be operated at both high strains (Hencky strain of 4 per drum revolution) and high strain rates (up to 20 s^{-1}). The fixture can be accommodated within the oven of a rotational rheometer, which allows measurements over a wide range of temperatures.

The SER was used to make measurements at several strain rates on two metallocene polyethylenes having low levels of long-chain branching. The tensile stress growth coefficients were compared with those measured by a Münstedt rheometer at the University of Erlangen[11]. The linear viscoelastic responses of the two samples were calculated from the steady shear data and compared to the SER results. It was found that at the low rates or at short times, the SER data were close to the linear viscoelastic envelope. At the high extensional rates, both samples deviated from the linear envelope and showed strong strain-rate thickening.

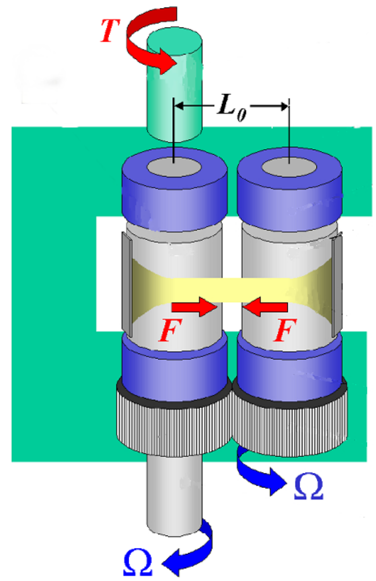

Figure 1: Fixture of the SER rheometer (from Ref. 9)

Experimental

Materials

Two high-density metallocene polyethylenes with low levels of branching, HDB6 and HDB7, were studied[11]. The weight- and number-average molecular weights of HDB6 were 70,000 g/mol and 25,000 g/mol, while for HDB7 these values were 67,000 g/mol and 17,000 g/mol. The molecular weight distributions were determined by triple-detector GPC. For HDB6 and HDB7, the branching levels were 0.19 and 0.33 branch points per 1000 carbons respectively, which were measured by ^{13}C nuclear magnetic resonance. The polymers and the molecular structure characterizations were provided by The Dow Chemical Company.

Sample preparation

To obtain reliable data, it is necessary to ensure that samples are dimensionally and materially homogeneous. Samples were molded using a Carver Press. Two buffer plates made of stainless steel with mirror smooth surface were used to avoid defects at the sample surfaces. The mold has dimensions of 180mm $\times$ 180mm $\times$ 0.5mm and is also made of stainless steel. A layer of polyester film was placed between the buffer plate and the mold. Samples were molded at 150^{o}C at 15 tons force for 30 minutes. Cooling water was used to bring the press to room temperature, while holding the force constant. The sample was then removed from the press and allowed to relax overnight. The samples molded using the above procedure are flat plaques having a uniform thickness. A dual blade cutter is used to cut test specimens having a width of 6.4 mm and a length of 12.7 mm. The thickness and the width of each sample were measured at room temperature with an accuracy of 0.0001" using a precision micrometer.

The cross-sectional dimensions at 150^{o}C were calculated from those measured at room temperature by taking the thermal expansion into account using Eq. 1:

$$\frac{A}{A_0} = \left(\frac{\rho_0}{\rho}\right)^{\frac{2}{3}} \qquad (1)$$

where A and ρ are the cross-sectional area and density of the sample at 150^{o}C, and A_0 and ρ_0 are the cross-sectional area and density of the sample at room temperature respectively. In using Eq. 1, we assume that the thermal expansions are the same in all three directions. The thermal expansion in the length results in a slight initial lag in the deformation response, which can be accounted for with a small time offset.

Procedures

The SER was mounted on the upper fixtures of a Rheometric Scientific (now TA Instruments) ARES rheometer. When the temperature of the oven is stabilized, tweezers are used to mount the sample using clamps on the drums. The oven is now closed, after which it takes about three minutes for the temperature to restabilize. The duration of an experiment at a high strain rate (>1 s^{-1}) is usually less than 2 minutes. Due to the short experimental time, it is not necessary to use a nitrogen atmosphere.

Results and discussion

Figures 1 and 2 show the stress growth coefficients at several Hencky strain rates at 150^{o}C for HDB6 and HDB7. The results are compared with the linear viscoelastic function $3\eta^{+}(t)$ measured at a shear rate of 0.005 s^{-1} using a cone-plate geometry in the ARES. We can see that for a strain rate of 1 s^{-1} of HDB6 the SER data fall on the linear envelope curve. Short-time results at the other strain rates also agree well with the linear viscoelastic behavior. This indicates that the extensional behavior at low strain rates or short times of the samples is linear, the linear behavior is independent of the kinetics of the deformation, and the measurements of SER are the true characterizations of the extensional properties of the sample.

In Fig. 2, the results at a strain rate of 0.5 s^{-1} are below the linear behavior at time around 1s, as the measured torques are very close to the resolution of the torque transducer. For the sample with a lower level of branching, HDB6, the stress growth coefficients cannot be measured at this extensional rate. The torque transducer of our

ARES model is a spring transducer, which has resolution of 2 g cm. This is not a major concern because usually the extensional behavior at high extensional rates is of interest. However, if there is a need to measure the extensional properties at low extensional rates, a more sensitive torque transducer such as force rebalance transducer can meet the requirements and extend the measurements to as low an extensional rate[10] as 0.01 s^{-1}. Increasing the width and thickness of the samples will also increase the torque signals at any given rate and thus allow the measurements at low extensional rates. Compared to HDB6, sample HDB7 shows strain thickening at a relatively low strain rate, 0.5 s^{-1}. We consider the higher level of long-chain branching in HDB7 contribute to this effect.

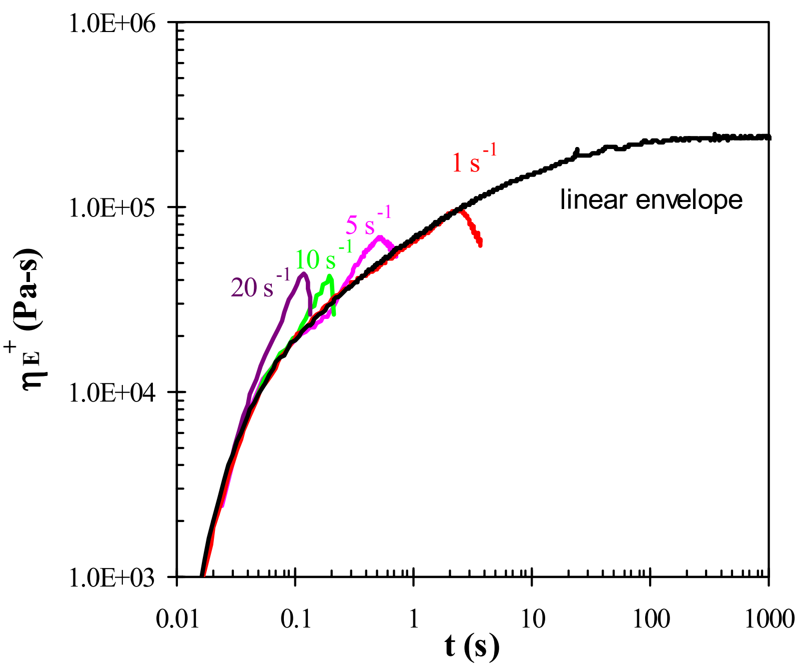

Figure 1: Stress growth coefficients of HDB6 at 150°C at various Hencky strain rates; the linear viscoelastic behavior $3\eta^+$ (linear envelope) obtained from the start-up of steady shear at a strain rate of 0.005 s^{-1}

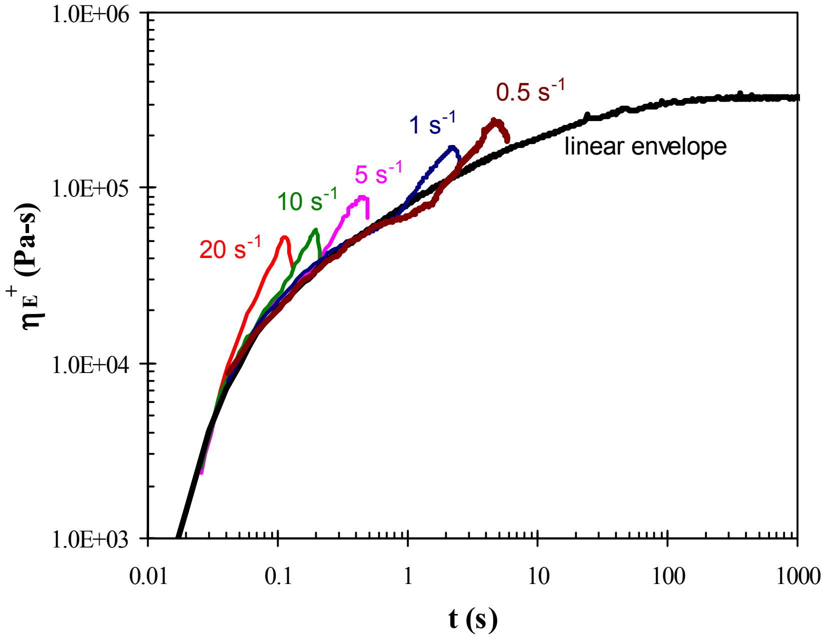

Figure 2: Stress growth coefficients of HDB7 at 150^{o}C at various Hencky strain rates; the linear viscoelastic behavior $3\eta^+$ (linear envelope) obtained from the start-up of steady shear at a strain rate of 0.005 s^{-1}

At high extensional rates, the stress growth coefficients of both polymers deviate from the linear viscoelastic envelope and show marked strain thickening. The deviation occurs at earlier times with the increase of the extensional rate.

Because the maximum Hencky strain rate the Münstedt extensional rheometer can reach is 1 s^{-1}, we only compare the results of HDB7 measured by these two rheometers because they have two overlapping strain rates. The comparison of stress growth coefficients measured by the SER and by the Münstedt extensional rheometer[11] of HDB7 at 150^{o}C is shown in Fig. 3. We observe that the results from the two rheometers superpose very well except that the results at an extensional rate of 0.5 s^{-1} measured by the SER fall below the linear curve at time around 1s. As mentioned previously, this results from the measured torques being close to the resolution of the ARES. The results measured by the Münstedt rheometer ended at earlier times, which is because the total deformation of the instrument is limited.

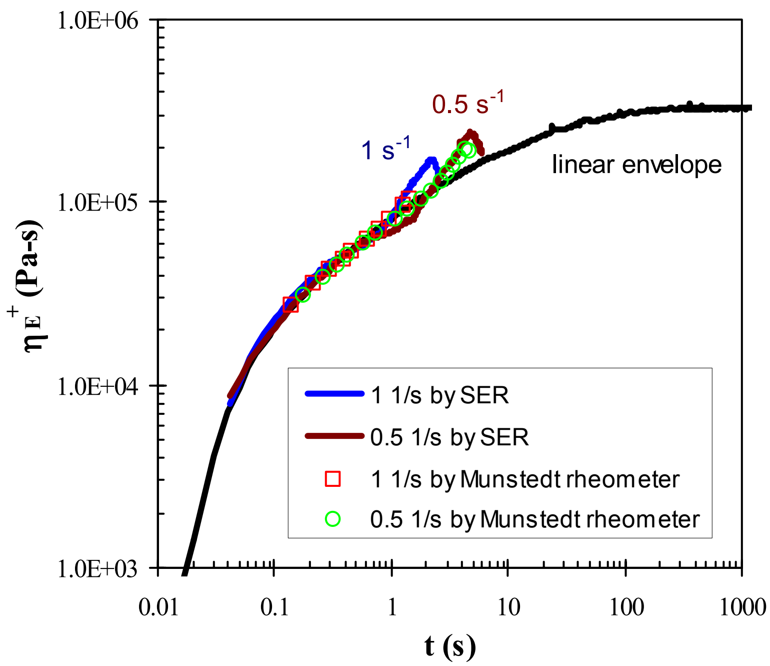

Figure 3: Comparison of stress growth coefficients measured by SER and by Münstedt rheometer for HDB7 at 150^{o}C

Conclusions

A new extensional rheometer (SER) designed by Sentmanat was employed to characterize the extensional properties at constant Hencky strain rates of two metallocene polyethylenes with low levels of long chain branching. Both materials show obvious strain thickening at high strain rates. The rheometer allows fast measurements, which is attractive in industrial polymer characterization. The maximum Hencky strain rate in this report can reach to 20 s^{-1}. The stress growth coefficients at low strain rates or short times agree well with the linear viscoelastic behavior. Good agreement is found in the comparison of the stress growth coefficients measured by the SER and by Münstedt extensional rheometer. The high accessible Hencky strain rate, the unlimited total strain, the short experimental time and the true extensional property characterization of the SER bring a new era of extensional property characterization.

Acknowledgements

The polymers and the molecular structure characterizations were provided by The Dow Chemical Company. The extensional data from the Münstedt extensional rheometer were collected by Enrique J. Torres. The author received valuable advice from Drs. John M. Dealy and Martin L. Sentmanat.

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