



Extensional viscosity of polyolefin's and polystyrene

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ABSTRACT

Extensional viscosity of a series of polyolefin's with varying architecture and composition and anionic polymerized polystyrenes have been analyzed using a new melt extensional fixture (EVF) for the ARES rheometer. This fixture can perform uniaxial extension measurements up to a Hencky strain of 4 and elongation rates as high as 30 s^{-1} ; the maximum temperature is 350°C . The EVF profits from the separation of motor and transducer in the ARES rheometer and allows very sensitive force measurements, free of inertia and friction contributions. The sample size of $18 \times 10 \times 0.8 \text{ mm}$ is ideal for characterizing R&D products usually available only in very small quantities. Results for the standard LDPE Lupolen 1810H obtained on the ARES-EVF are in excellent agreement with those from the RME and the original Meissner rotating clamp rheometer.

The elongation viscosity obtained from measurements on polyethylene is discussed as a function of the degree of long chain branching. Two narrow distributed polystyrenes with different molecular weight and their binary blends were tested also. Whereas the two pure components show very little strain hardening, do the blends exhibit a pronounced strain hardening with increasing rate.

INTRODUCTION

Although Trouton was conducting elongation measurements on pitch and shoemakers wax at the beginning of last century /1/, elongation flows of highly viscous materials, became subject to further investigations only in the late sixties with the growth

of the plastics industry. The first rheometers build were based on the same concept, Trouton used more than half a century before: - clamping a rod like sample at both ends and pull it apart (fixed clamps) /2, 3/. This technique will be referred to as "constant volume" technique. In order to eliminate sagging and flow under gravity of the free polymer melt strand during the measurement, the sample is supported by silicone oil, matched to the sample's density. A major issue of the fixed clamp technique is necking at the clamps and the finite total strain, which is given by the size of the instrument.

In the 70th, Meissner /4/ replaced the fixed clamps with rotary clamps, mounted at a fixed distance in an oil bath. The sample is extended while the material is expelled out off the test section with two pairs of rollers (rotary clamps). The advantage of this technique is: 1 - the maximum elongation is not a function of the instrument size anymore and 2 - end effects are eliminated because the necking is continuously removed from the measuring zone. This technique is referred to as "constant length" technique. However the rotary clamps introduce another problem - slip - that means, the velocity of the rotating clamp is not fully transferred onto the sample and the true elongation rate is lower than the command rate. A calibration or independent measurement of the rate is needed.

Elongation measurements with the instruments available at the time were difficult and time consuming. The costs for operation were prohibitive for industrial applications.

In the early 90th Makosco /5/ came up with a very simple device to do elongation measurements on polymer melts; the windup fixture, an accessory for

the rotational rheometer. The wind up fixture was designed to operate without a supporting medium (oil or air). The actuator of the rheometer applies a constant elongation rate, while winding up the sample around a cylinder mounted on the motor axis at constant rotation speed and the force is measured with the torque transducer. The advantage of this approach: - fast and inexpensive. The disadvantage: - only one side of the sample is elongated and the other end is fixed to the transducer conventionally, which forces the stagnation point into the necking zone of the fixed clamp.

Sentmanat /6/ in the late 90th merged the rotary clamp and wind-up technique. He miniaturized the rotary clamps and replaced the rotary clamps with two single rotating cylinders – a sort of wind up fixture, winding up the sample on both sides. This approach corrected the main issues of the wind-up fixture, however unfortunately has one disadvantage – the force measurement is not decoupled from the driving mechanism of the cylinders and as such, the force transducer has to be calibrated for the friction of the gears and cylinder bearings – which reduced the available torque range of the instrument.

The new elongation fixture /7/ described in the following corrects this problem – the force measurement system is fully decoupled from the motor and the full torque range and sensitivity of the transducer is accessible to measure the force, while the sample is extended on both ends equally.

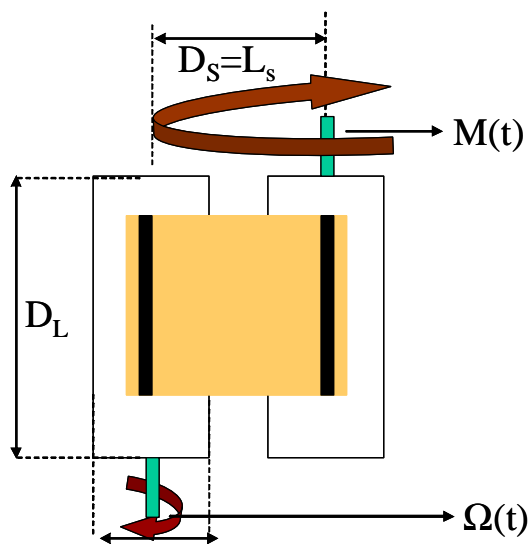


Figure 1: EVF operation principle

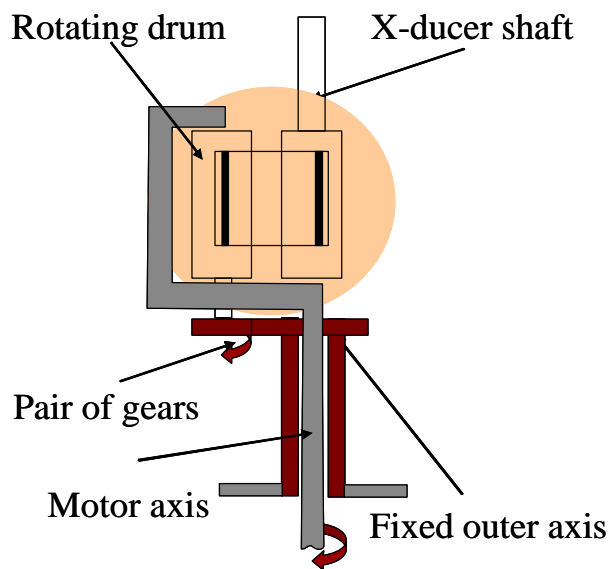


Figure 2: Schematical drawing of the EVF

EXPERIMENTAL

The extensional viscosity fixture EVF is based on the „constant length” design and elongates a high viscosity polymer melt sample at constant Hencky rate when mounted on a rotational rheometer with separate torque transducer. Two single cylinders are used to wind up the sample (figure 1). While one cylinder is fixed and connected to the transducer to measure the force, is the other cylinder connected to the motor which performs two different movements in order to wind up the sample on both drums. The first is a rotation around its own axis to wind up the sample; the second is a rotation around the axis of the stationary cylinder at the transducer winding up the sample on the second cylinder. Since the motor cylinder, during one revolution around the transducer cylinder performs one revolution around its own axis, the sample is wound up equally on the two cylinders. Rotating the two drums at the same speed around their own axis gives the same result. The advantage of the new technique: the force measurement is decoupled from the motor motion and no friction contributions need to be corrected for.

The schematical representation of the EVF is shown in figure 2. The stationary cylinder is aligned with the transducer axis and the force is calculated from the measured torque divided by the radius of the cylinder. The motor cylinder is mounted eccentric onto the motor shaft at a distance (center to center of the two cylinders) of 12,7mm. A rigid hollow shaft

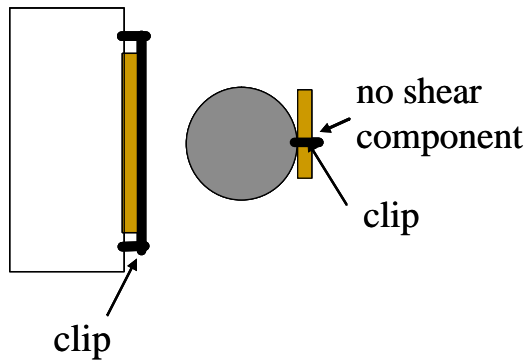


Figure 3: Illustration of the mounting of the sample clips

which ends as a spur gear at the top, mounted over the motor shaft spins the motor cylinder around its own axis while the motor rotates the whole manifold around the transducer cylinder. The clearance between the cylinders is 2.4 mm. The dimensions are chosen such that the fixture fits into the air convection oven, while optimizing maximum strain and sample size.

The test sample has a rectangular shape and is attached to the cylinder with two small clips (figure 3). The purpose of the clips is twofold: 1) holding the solid sample during loading and 2) transferring the cylinder velocity equally on both sides of the sample, thus eliminating any shear contributions at the clamp i.e. eliminating slip. Note: adhesion of the sample to the cylinder surface is assumed.

The experimental procedure will be discussed, based on the uncorrected force trace in figure 4. The test specimen expands, once loaded into the rheometer due to the density change during melting - the sample buckles and therefore needs to be straightened before starting the proper experiment. This is critical in order to obtain good test start up results.

A typical experiment consists of the following steps:

- After loading and temperature equilibrium, the motor is rotated by an angle sufficient to straighten the sample and compensate for the sample expansion. The sample expansion is determined from the density difference of the sample at loading and at test temperature. During the pre-stretch, a force is applied to the sample (in addition to expanding, the sample will also shrink due to internal stresses).

- A relaxation step allowing the force to decay to

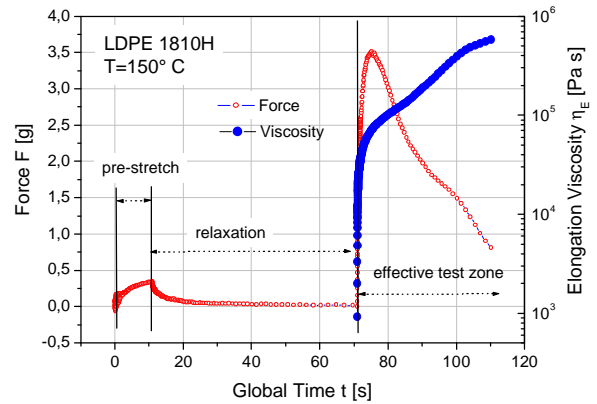


Figure 4: Test procedure including pre-stretching, relaxation, step rate test and final relaxation

zero.

- The third step is the elongation test itself. At a constant rotation speed, the motor deforms the sample at a constant Hencky rate.

- After the test is completed, an optional relaxation zone can be added. This relaxation zone is useful to check the test performance and to detect eventual transducer drifts. This is recommended, as the force decays exponentially during the experiment and small drifts generate large errors in the viscosity towards the end of the experiment.

The desired material response is the force as a function of time collected during the 3rd step of the test procedure. The force grows as the stress builds up at the start, then goes through a maximum (Figure 5). Due to the exponential decrease of the cross-section of the sample the force decreases continuously towards the end of the test. The sample stress is increasing strongly at the beginning and then

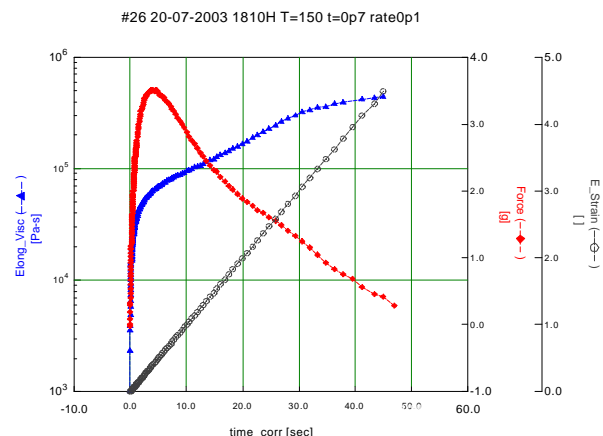


Figure 5: Typical force curve for a branched polyethylene

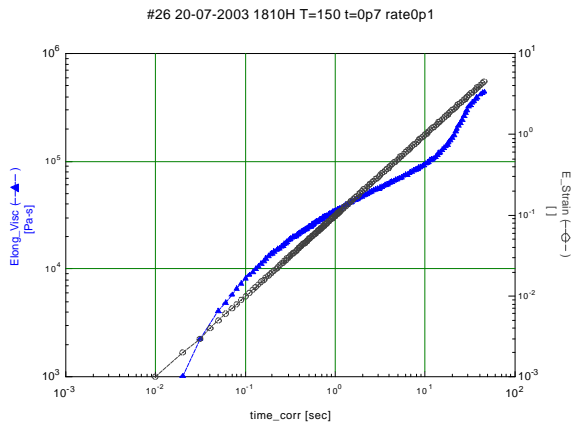


Figure 6: Time dependent viscosity corresponding to the force trace in figure 5

levels of to a steady state. Typical for a branched polyethylene is the bump in the decaying force curve, which translates into a second strong increase in the stress curve, referred to as strain hardening.

Figure 6 shows the viscosity as a function of time in a double logarithmic plot. The strain hardening effect, represented by the viscosity increase after 10 s at a Hencky rate of 0.1 s⁻¹ is very pronounced and typical for the LDPE used in this experiment.

INSTRUMENT VALIDATION

In order to validate the EVF, a series of tests has been performed with the well characterized Lupolen 1810H. Data for this material are available for the first generation of the Meissner rheometer using silicone oil as a sample support medium and the RME*, a commercial rheometer based on the

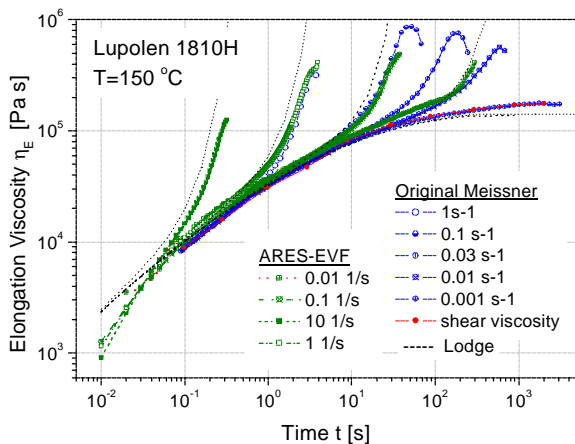


Figure 7: Results for LDPE 1810H comparing EVF and RME

* Extensional rheometer commercialized by Rheometric Scientific until 2003

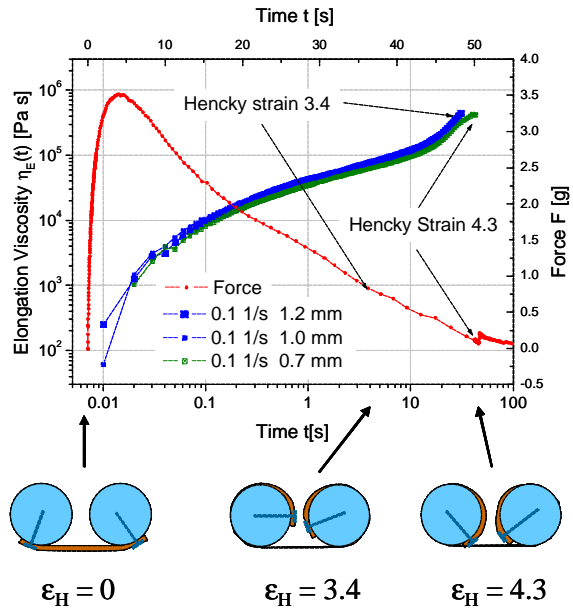


Figure 8: Data reproducibility. Results were obtained using different ratios of sample width to thickness

Meissner design, using air to support the sample. As can be seen in figure 7, excellent agreement has been obtained over the range of rates investigated. Slight differences are seen at lower rates at high elongations. Tests at 10 s⁻¹ were not possible on the Meissner unit and the RME. The EVF can easily generate data up to 30 s⁻¹. On the other hand, is the EVF limited by a lower maximum strain.

Excellent data reproducibility is achieved with the EVF. Results from experiments with sample thicknesses ranging from 0.7 to 1.2 mm virtually superpose (figure 8). Samples thicker than 0.7mm cannot be tested above $e^H = 3.4$, because the clips come in contact (clearance of the cylinders 2.4mm)

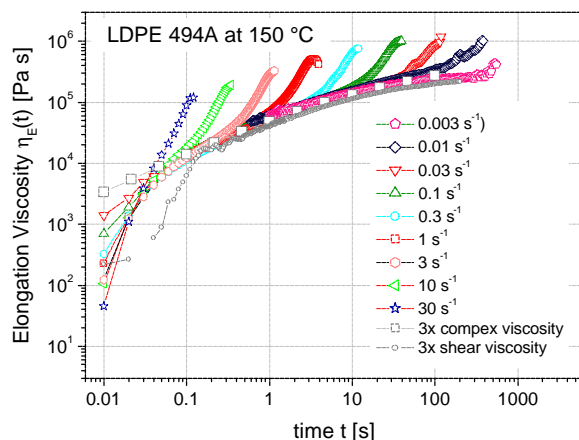


Figure 9: Elongation viscosity for LDPE 494A over a rate range from 0.003 to 30 s⁻¹

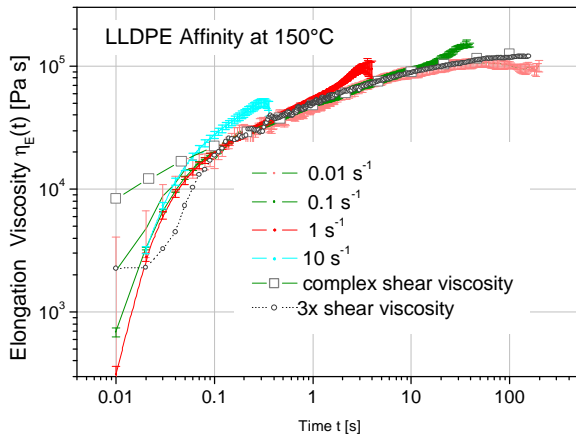


Figure 10: Elongation viscosity for LLDPE Affinity 1880 over a rate range from 0.01 to 10 s⁻¹

after ¾ of a revolution. Experiments with a sample thickness of 0.7mm and below can be evaluated up to $e^H = 4.3$. The theoretical Hencky strain of 5 for one full rotation of the cylinder can not be obtained, because of the offset of the clamps at the start.

RESULTS FOR POLYOLEFIN'S

LDPE 494A and LLDPE Affinity PL 1880 have been the subject of round robin testing in the past. The data obtained with the EVF coincide very well with 3 times the transient shear viscosity and the viscosity extracted from oscillation tests in shear in figure 9 and 10. The LDPE 494A sample was tested over a very wide range from 0.003 to 30 s⁻¹, the LLDPE Affinity 1880 from 0.001 to 10 s⁻¹. The LDPE shows pronounced strain hardening at all rates, whereas the LLDPE exhibits only a small strain hardening effect which seems to disappear at lower rates. The findings from a comparison of the two

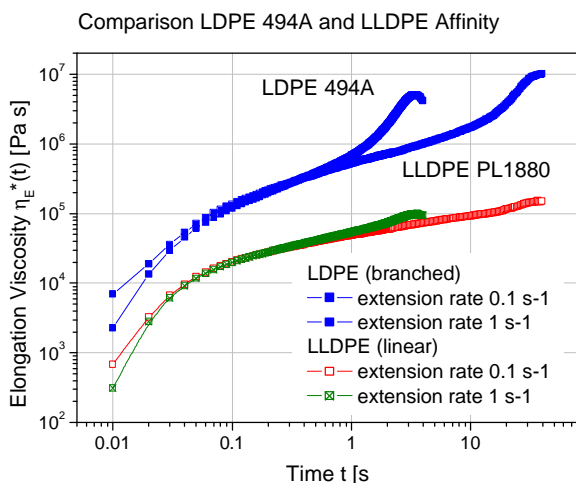


Figure 11: Comparison of LDPE 494A and LLDPE Affinity PL1880

materials are (figure 11): - a higher viscosity for the LDPE 494A and - a strain hardening effect, also much weaker for the LLDPE, appearing at approximately the same strain for the two samples.

A series of LLDPE samples with different MI and zero shear viscosity have been tested to investigate eventual correlations with the elongation viscosity. Each elongation experiment was conducted three times. The results are given in figure 12. The error bar represents the standard deviation. The samples C and D with identical MI and zero shear viscosity show the same start-up behavior, but exhibit significant differences in the elongation viscosity at higher elongation. The sample B, with lower MI and slightly higher zero shear viscosity than sample A shows stronger strain hardening. The sample A with the lowest zero shear viscosity and the highest MI

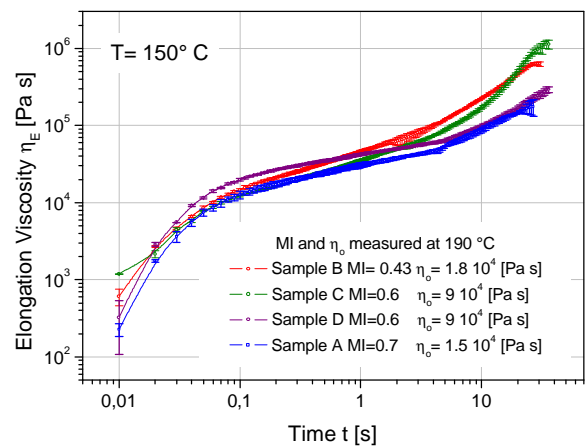


Figure 12: Correlation of the elongation viscosity of several LLDPE with different MI and shear viscosity

has the lowest elongation viscosity at low and high strain. This example demonstrates the ability of the elongation viscosity to discriminate between materials, which cannot be differentiated using standard shear experiments. This difference in elongation viscosity of the LLDPE samples is attributed to differences in the long chain branching (LCB) of the polymers.

To show the sensitivity of elongation measurements to variation in branching, HDPE with slight differences in branching were evaluated in elongation. Figure 13 exhibits the viscosity curves for two types of HDPE, differing only by 2 side chains per 10 000 C of the chain backbone. The material of type 1(batch 1 and 2) has more side chains and shows also a stronger strain hardening effect.

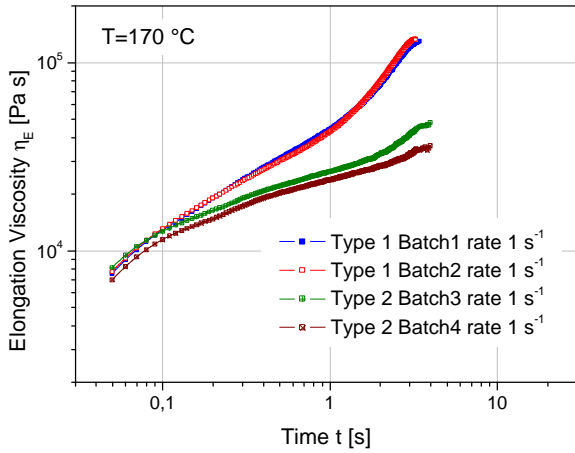


Figure 13: Elongation viscosity of two HDPE, varying by two LCB per 10 000 C

Extensional viscosity is a very sensitive discriminator for polyolefin materials with different degree of branching. Traditional shear tests using rotational or capillary rheometer often are not able to detect these changes, critical to process operations such as film blowing, blow molding, coating, etc.

NARROW DISTRIBUTED PS AND BINARY BLENDS.

Linear, anionically polymerized narrow distributed PS and their binary blends have been tested in elongation. Two different molecular weights, 145000 and 330 000 were chosen. The results are shown in figure 14 and 15 for elongation rates from 0.01 to 10 s⁻¹. The elongation viscosity at low rate superposes quite well with 3 times the shear viscosity and the linear viscoelastic viscosity curve calculated from the complex viscosity. These linear PS samples show hardly any strain hardening. As soon as the elongation viscosity approaches a steady

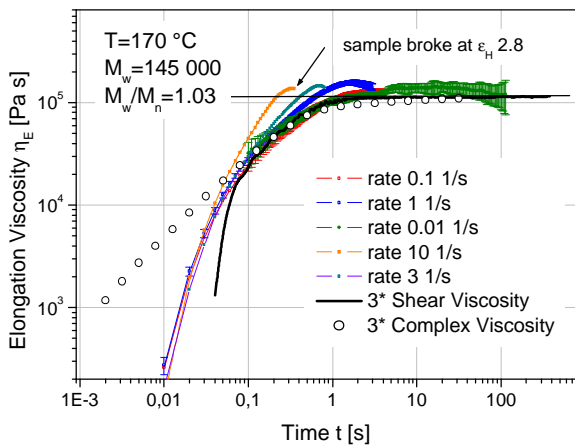


Figure 14: Elongation viscosity of a narrow distributed polystyrene: $M_w = 145000$.

state at low rate, the viscosity drops again. It seems that linear polymer chains are inherently unstable at large elongation as soon as a steady state has been reached. At higher rates, the samples break (shown by the fast drop in viscosity). The sample breaks always at the same strain. The breaking strain is **around** $\epsilon_H = 2.8$ for the sample with $M_w = 1450000$ and 3.1 for the sample with $M_w = 330\ 000$. Breaking

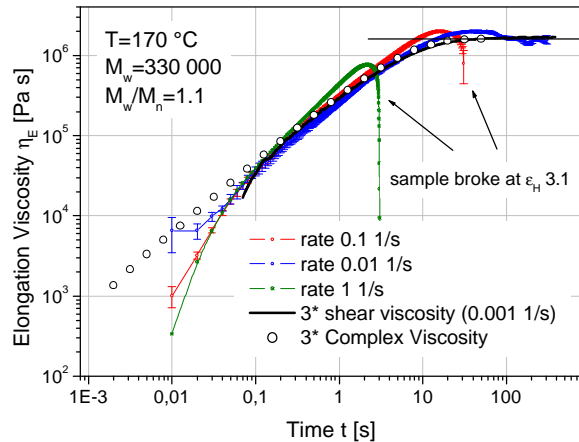


Figure 15: Elongation viscosity of a narrow distributed polystyrene: $M_w = 330000$.

occurs at lower rates with increasing molecular weight and decreasing temperature.

In contrast to the narrow distributed PS, do the binary blends of these same polymers show a pronounced strain hardening. The results of sample PS-145-330-70-30 (70% M_w 145k and 30% M_w 330K), measured over a range of elongation rates

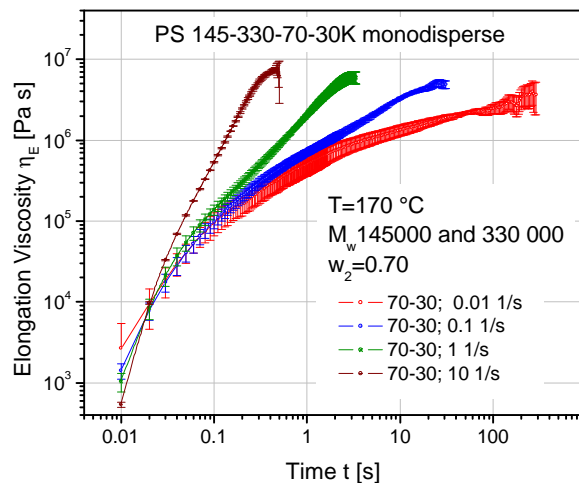


Figure 16: Elongation viscosity of a binary PS blend. Composition: 70% of the component with $M_w = 145\ 000$ and 30% of the component with $M_w = 330\ 000$

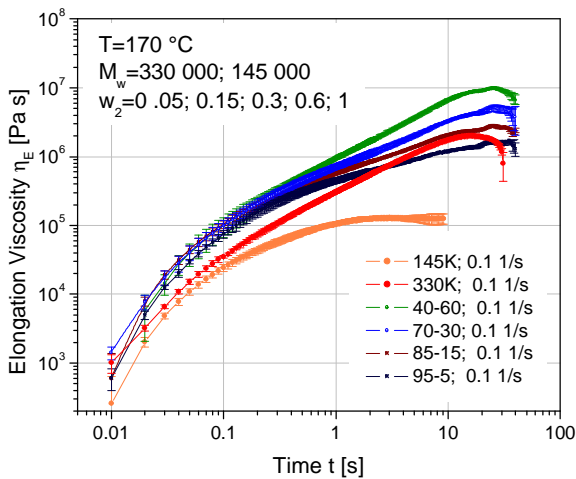


Figure 17: Elongation viscosity a series of blends with different composition of the components with $M_w = 145\ 000$ and $M_w = 330\ 000$

from 0.01 to 10 s⁻¹ are shown in figure 16. The higher the rate, the steeper is the viscosity increase (strain hardening effect). Figure 17 represents the viscosity curve at 0.1 s⁻¹ for a range of mixing ratios from w_2 (weight fraction)= 0.05 to 0.6. The final viscosity is always higher than the maximum viscosity of the lower molecular component. For the weight fractions $w_2=0.05$ the maximum viscosity is lower than the viscosity of the pure higher MW component, for all others the maximum viscosity is higher

METALLOCENE CATALYZED PE

A comb, metallocene catalyzed Polyethylene (CM3) with 1 side chain per 10 000 C in the backbone chain shows significant strain hardening compared to conventional LLDPE (figure 18). The drop of the viscosity at the low rate is due to sample

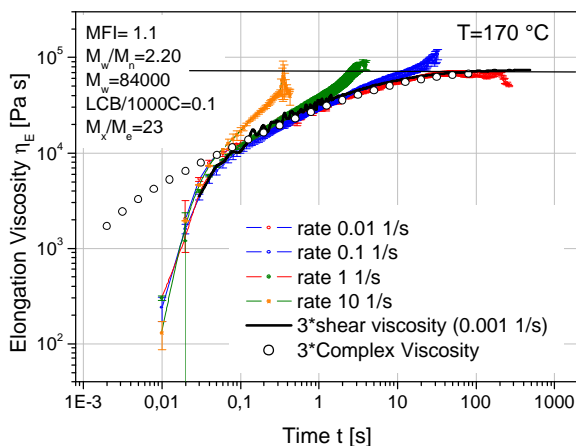


Figure 18: Elongation viscosity of a metallocene catalyzed polyethylene CM3 with 1 LCB per 10 000 C

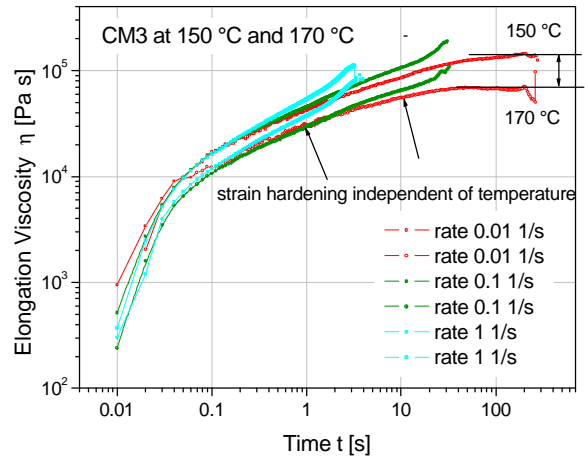


Figure 19: Temperature dependence of the elongation viscosity for the polyethylene CM3.

instability and low force readings. The low rate curve follows 3 times the zero shear viscosity and the complex viscosity.

The CM3 shows medium strain hardening with the strain hardening effect disappearing with lower rate. The PE comb has been tested at 150 and 170 °C (Figure 19). Comparison of the results obtained shows, that the strain hardening onset is temperature independent, however the steady state viscosity decreases with increasing temperature.

CONCLUSION

The EVF is a simple and cost efficient option for the ARES to measure the elongation viscosity of polymer melts. When operated with the ARES rheometer, the force measurement is decoupled from the motor - thus no calibration and torque corrections are necessary. Results on PE S show, that LCB is causing pronounced strain hardening in the elongation viscosity. Also blends of linear polystyrenes, which show no strain effects at all, exhibit strong strain hardening at high elongation rates.

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