PN002

The ARES-EVF: Option for Measuring Extensional Viscosity of Polymer Melts

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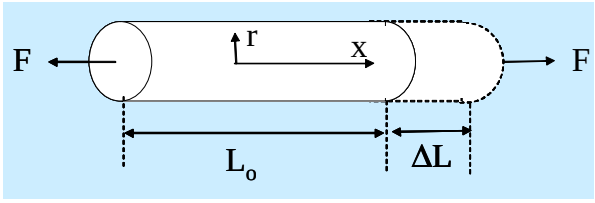
INTRODUCTION

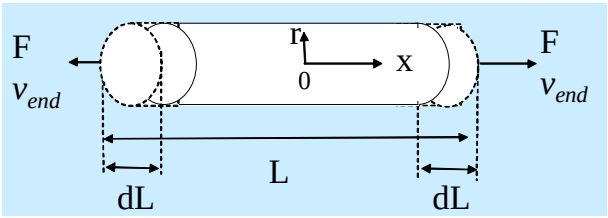
The roots of extensional rheometry are to be found at the very beginning of the 20th century. It was Trouton, who when experimenting with pitch and shoemaker's wax, subjected these materials to "torsion" and "traction" deformations. He discovered through his ingenious experiments, that the uniaxial extension viscosity is three times the shear viscosity."….A variety of pitch which gave by traction method λ=4.3 x 10^{10} poise was found by torsion method to have a viscosity μ=1.4 x 10^{10} poise… F.T. Trouton (1906)"/1/

Despite these early experiments, the developments in elongational rheometry were few until the end of the sixties. In 1955 Bueche /2/ reported on elongation measurements performed with PMMA. Karam et al./3/, Ballman /4/ and Cogswell /5/ in 1969 published results on PS, obtained on home built elongation rheometers. The exciting phase in elongation rheometry started in 1969 with Meissner /6/ and Vinogradov et al./7/. Whereas all experimental approaches up to this date were based on pulling a rod like sample apart by the ends, Meissner introduced a novel idea, which changed the field of elongation rheometry. He replaced the moving clamps with fixed mounted rotating clamps. The sample is held between two pairs of rotating spur gears pulling the sample and expelling the material from the fixed test section. The advantage of this technique is – first, the total elongation is not limited by the apparatus size and second, by expelling the sample out of the test section, necking or end effects at the clamps are removed continuously. The concept introduced by Meissner is also used in the Extensional Viscosity Fixture (EVF) introduced later in this presentation.



$$\varepsilon_C = \Delta L / L_o = \lambda - 1$$

Figure 1: Cauchy or engineering strain

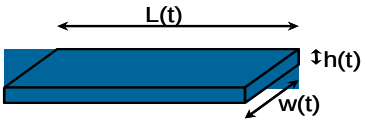


$$v_x = \dot{\varepsilon} x \quad L(t) = L_o e^{\dot{\varepsilon} t}$$

$$\varepsilon_H(t) = \dot{\varepsilon} t = \ln L(t) / L_o$$

Figure 2: Hencky strain and Hencky rate

Why are elongation experiments important and why has so much effort been put into the design and manufacturing of elongational rheometers, while rheological measurements in shear using rotational rheometers are so much easier to perform? The number one reason is that extensional deformations play a significant role in many processing operations. Fiber spinning, film blowing, blow molding, thermoforming etc. are essentially dominated by extensional flow. Most process flows however are mixed flows, such as converging regions in dies, or coating processes. In many processes extensional flows are essential. Extensional material functions are needed to model the flow and since extensional flows are strong



$$L_o w_o h_o = L_o A_o = const. \quad \text{(incompressible)}$$

$$\Rightarrow A(t) = A_o e^{-\dot{\varepsilon}_o t} \text{ and } h(t) = h_o e^{-\frac{1}{2}\dot{\varepsilon}_o t}$$

$$\Rightarrow \sigma_E(t) = \frac{F(t)}{A(t)} = \frac{F(t)}{A_o} e^{\dot{\varepsilon}_o t} \text{ and } \eta_E(t) = \frac{\sigma_E(t)}{\dot{\varepsilon}_o}$$

Figure 3: Elongational stress and viscosity in an uniaxial elongation experiment

flows, consi/derably orienting molecules, asymmetric particles or the dispersed phase in blends, the final product properties are strongly effected. The second reason to perform elongational measurements is related to the sensitivity of these flows to molecular structure, such as branching. The elongational viscosity at large strains is more sensitive to variations in long chain branching than the linear viscoelastic shear properties. The third reason is academic. Since elongation properties differ so much from shear properties, the elongation experiments are ideal to test constitutive equations and flow models.

THE ELONGATION STRAIN RATE (HENCKY STRAIN)

The most common elongation measurement is the engineering strain or Cauchy strain, defined as the increase in length ΔL divided by the initial length L_o (Figure 1). The Cauchy strain is a deformation measure valid for small deformations. For large deformations ($\Delta L >> L_o$), the Cauchy strain is replaced by the Hencky strain. The Hencky rate is related to the velocity of a particle along the deformation axis $v_x=(d\varepsilon_H/dt)x$ (Figure 2). In a constant rate experiment (two ends moving at the same speed), the particle in the center of the rod has a velocity zero and the particle velocity increases with the distance from the center. The rotating clamp technique deforms the material at constant Hencky rate by expelling the material at a fixed distance $x=L_o/2$ from the sample center with a constant velocity v_x applied by the rotating clamps. In a traditional elongation experiment, with the sample volume constant, the sample ends must therefore move at a speed $v_{end}=(L/2)d\varepsilon_H/dt$. Integrating from L_o to the final length L_f, leads to an exponential increase of the sample length over time $L(t)=L_o\exp[(d\varepsilon_H/dt)t]$. The final strain thus can be expressed as $\varepsilon_H=\ln[L_f/L_o]$.

The elongation viscosity η_E is defined as the stress divided by the elongation rate. The stress is the force divided by the surface area normal to the direction of deformation. For an in-compressible material, the volume is conserved and the surface area must decrease exponentially as $A(t)=A_o\exp\{(d\varepsilon_H/dt)t\}$ with the sample length increasing (Figure 3) while the experiment proceeds.

THE ARES-EVF

The EVF concept

The ARES-EVF design (patent pending) is based on the original Meissner concept and elongates the sample within a confined space by expelling the sample with rotary clamps. Instead of the rotary clamps, two cylinders are used to wind up the sample; one cylinder is rotating, the other measuring the force. In order to wind up the sample equally on both sides, the rotating cylinder moves on a circular orbit around the force measuring cylinder while rotating around its own axis at the same time (Figure 4). Since the force measuring cylinder is fixed in space it can be directly coupled with the torque transducer of the ARES. All the motion of the rotating cylinder is generated by the ARES actuator. As such the force measurement is decoupled from all the moving parts and consequently friction and inertia contributions are not affecting the material response, namely the force signal.

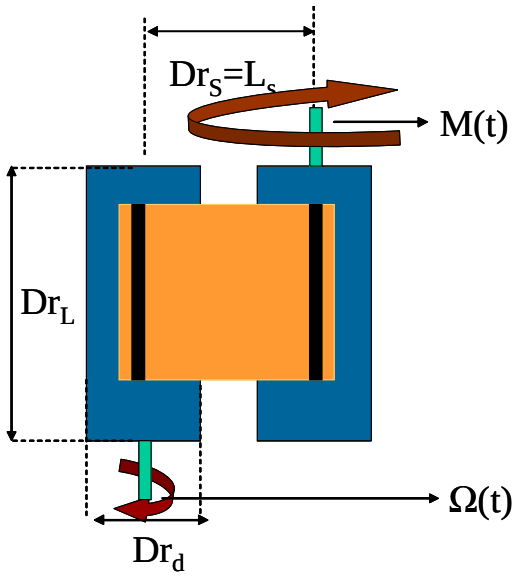


Figure 4: The eccentric drum rotates around the fixed drum while spinning around its own axis

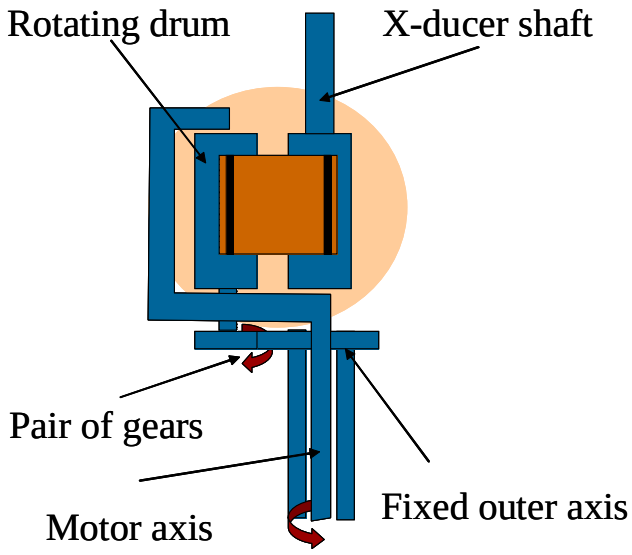


Figure 5: Schematic of the EVF (ExtensionalViscosity Fixture)

The ARES transducer measures a torque. The force at the sample can be easily calculated from the measured torque divided by the cylinder radius. The strain rate applied is the velocity at the cylinder, divided by the sample length L_o which is equivalent to the separation of the center axes of the two cylinders. The velocity is given by the product of the angular rotation speed $\Omega(t)$ and the cylinder radius $Dr_d/2$. Since the sample is elongated at both ends, the Hencky rate applied by the actuator is the product of angular rotation speed and cylinder diameter divided by the distance of the two cylinders.

Figure 6: EVF installed on the ARES rheometer

The EVF design

A schematic of the Extensional Viscosity fixture (EVF) is given in Figure 5. Motor and transducer axis are aligned, and the rotating drum is mounted eccentric at a distance (center to center) of 12.7 mm. In order to rotate thedrum, a fixed hollow shaft, ending as a spur gear at the top, is mounted around the motor shaft to the ARES frame. As the eccentric mounted drum is orbiting around the transducer drum, the spur gear drives the rotation around its own axis. The EVF is designed to fit into the standard ARES oven. The diameter of each drum is 10.3 mm and the clearance between the drums is 2.4 mm. Figure 6 shows the EVF option, installed on the ARES rheometer.

$$\frac{Stiffness_{EVF}}{Stiffness_{RME}} = \frac{K_{\sigma RME} K_{\gamma EVF}}{K_{\sigma EVF} K_{\gamma RME}} = 1.3x10^6$$

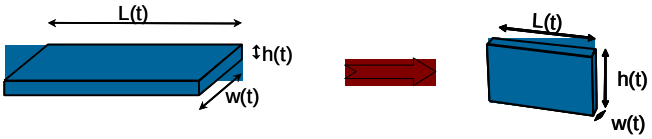


Figure 7: Sample stiffness in the RME and the ARES-EVF

Since the cylindrical drums are mounted vertically, the sample is also loaded vertically onto the drums and attached with two tiny clips.

Sample support a must or not necessary?

The RME (Rheometric Melt Elongation rheometer) and the original Meissner elongation rheometer used a support medium to prevent the molten sample from sagging. The sample was floating on oil or on air during the experiment. In the RME, the belt carriers, which apply the elongation deformation to the sample are mounted horizontally. The rectangular shaped sample consequently is in an horizontal position. On the EVF, the samples are mounted vertically and the sample length L_o is reduced from 40 mm (RME) to 12.7mm (EVF). These two changes increase the effective stiffness increase of a sample by a factor

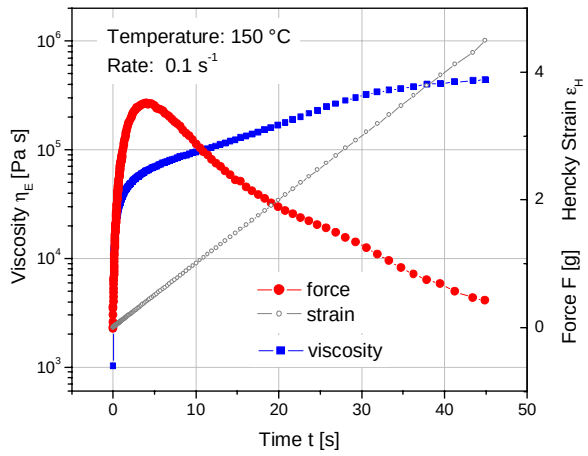


Figure 8: Recorded force during an elongation experiment at constant Hencky rate (Lupolen 1810H)

of 1 million (Figure 7). This is a key advantage of the EVF because materials with a shear viscosity above 1000 Pa s do not significantly sag under the gravity force during loading and testing. Due to the small sample size required for the EVF and the fast heating rate of the ARES oven, the waiting time after loading the sample is less than 3 minutes, thus preventing creep in the sample.

EXPERIMENTAL

Force and stress results

The response of the material to a constant deformation rate is the stress. During the experiment the reactive force at the transducer is measured as a function of time or deformation. In a typical force curve, shown in Figure 8, the force grows from zero as the stress builds up in the sample with time. After a short period, the force goes through a maximum and decreases from then on continuously more or less exponentially. The reason for the force decrease is the exponentially decreasing cross section of the sample with increasing total deformation. The corresponding viscosity, the ratio of force F and sample cross section A(t) divided by the rate increases strongly at the start up and then levels off to a steady state. (see Figure 8).

Effective strain rate, minimum and maximum values

A key feature of the rotating clamp concept is the prevention of sample necking at the clamp by continuously removing it out of the measuring zone. This ensures a nice, uniform rectangular sample shape throughout the experiment with minimum boundary effects. This feature is essential when reducing the sample size to a minimum like in the EVF. The polymer melt sample adheres to the drum at test temperature. For a sample thickness of less then 0.8 mm, the variation of the sample velocity at the drum due to the variation of the radius (sample thickness changes) is negligible. As such, the nominal elongation rate varies very little with the average rate applied during the experiment. In order to verify this “non slip” condition, a section of known length can be cut from the remaining sample strand at the end of the test. From the weight and the density at test temperature, an average sample cross section can be determined and subsequently an average Hencky elongation rate. Although the theoretical upper limit in elongation rate for the ARES at 100 rad/s is 81 s^{-1}, 10 s^{-1} is the practical limit; a Hencky strain of 5 will be reached in 0.5 s and reliable force data are obtained from 100 ms on. The ARES is capable of making measurements at extremely low elongation rates, and coupled with a sensitive force rebalance transducer, a wide range of practical elongation rates can be realized.

Reproducibility and maximum strain

Figure 9 shows three experiments performed at a rate of 0.1 s^{-1} on the reference material Lupolen 1810H at 150° C. All tests were done with different sample thickness ranging from 0.7 to 1.2 mm. The viscosity curves overlay, proving excellent

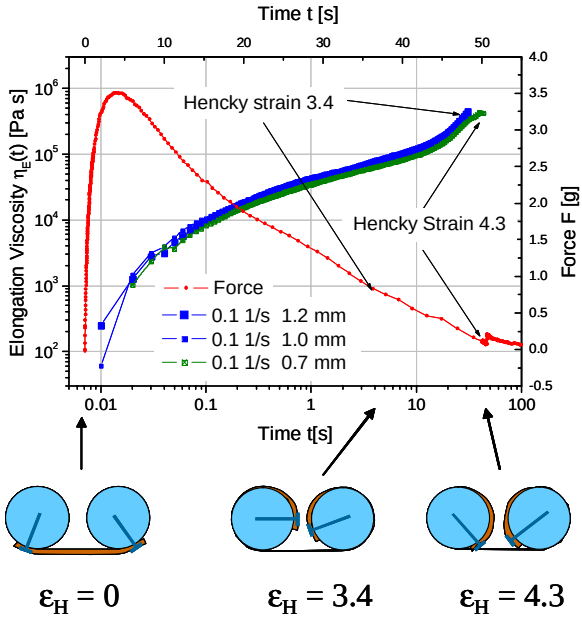


Figure 9: Reproducibility of 3 consecutive tests. The maximum strain depends on the initial sample thickness

reproducibility. During a measurement on the EVF, the sample wraps around both the fixed and rotating drums. After one revolution, the sample will wind up on top of itself and the force signal becomes unusable. A maximum elongation ε_H of 4.3 can be obtained with a sample thickness of 0.7. Samples with thickness >1 mm can be tested to a Hencky strain ε_H of 3.4 only, because the sample at the clips of both drums will come into contact after 3/4 of a revolution (Figure 9). For one experiment in figure 9 the viscosity curve can be observed to level off due to non-uniform sample deformations at $\varepsilon_H = 4$.

Comparison with Lupolen 1810H

In order to validate the EVF, a series of tests was performed on the reference Lupolen 1810H. The EVF data were compared to the data originally published by Meissner and Raible/8/. As can be seen in Figure 10, excellent agreement was obtained for results at 0.1 s^{-1}. Slight differences between the EVF and Meissner data can be seen at lower rates and high elongations. These deviations may be attributed to sample preparation. More important to note is that the EVF can generate data at a rate of 10 s^{-1}, where neither the Meissner unit nor the RME could.

APPLICATION EXAMPLES

LLDPE, HDPE, LDPE

Measuring the extensional viscosity is critical to understand processing behavior of polyolefins Strain hardening is a desired property in film blowing or spinning processes, as it stabilizes the film bubble or the free fiber during the melt

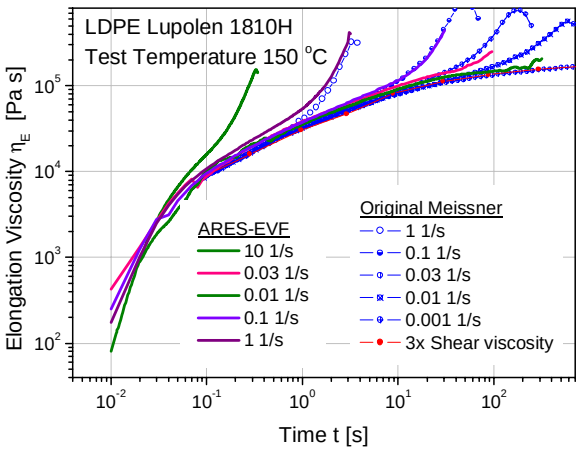


Figure 10: Elongational viscosity of Lupolen 1810H compared with the original Meissner data /8/

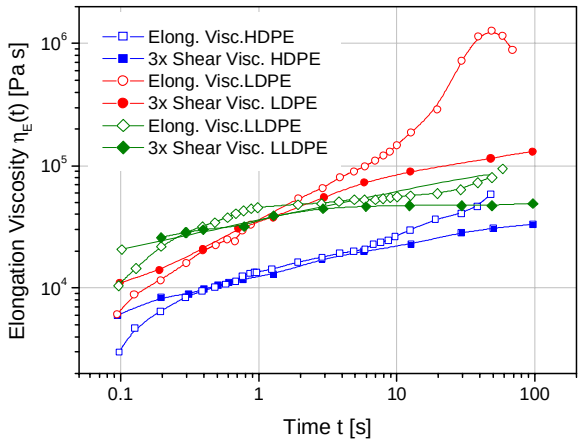


Figure 11: Strain hardening in LDPE, LLDPE and HDPE

elongation phase. High take up speeds are only possible with the right amount of strain hardening to avoid bubble collapsing and fiber breaking. Figure 11 shows the elongation viscosity for different typical representatives of polyethene, LDPE, LLDPE and HDPE. The LDPE sample shows considerable strain hardening at high elongation strain as a result of the high content of long chain branches. The HDPE and LLDPE, with low long chain branching, exhibit very little strain hardening.

Metallocene catalyzed long chain branched PE

Figure 12 shows elongation data of a polyethylene obtained by metallocene catalyse's in the Dow process. For reference LLDPE and LDPE manufactured using the traditional technique are shown also. The metallocene catalyst controls the polymer architecture and thus allows tailoring of the molecular structure and consequently the physical properties to the required needs. The PE synthesized in the metallocene catalized process shows elongational properties with strong strain hardening, the shape of the viscosity curve very similar to the one of the standard LDPE

CONCLUSION AND OUTLOOK

The ARES-EVF is a new melt extensional fixture for the ARES rheometer. It can perform uniaxial extension measurements to a Hencky strain of 4.3, elongation rates up to 10 s^{-1}, to a maximum temperature of 250°C (350°C Optional). The EVF is very easy to operate and combined with the speed of the ARES oven can provide sample throughput

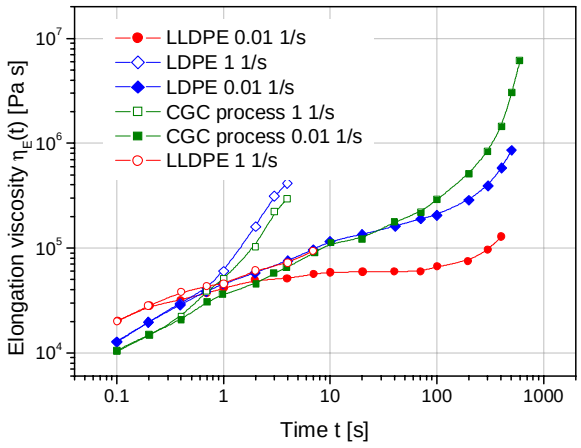


Figure 12: PE manufactured by metallocene catalise's in comparison to LDPE and LLDPE obtained in a traditional manufactured process

of four to five experiments per hour. The data generated on the ARES-EVF show excellent agreement with the RME or the original Meissner rotating clamp rheometer. Although the RME can achieve slightly higher total elongation compared to the EVF, the ARES-EVF is better suited for fast elongation rates not easily accessible on the RME.The new EVF provides for an affordable way to transform any ARES into an even more powerful combined shear and extensional polymer rheology platform.

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