# A New Tool for Measuring Extensional Viscosity

Peter Hodder and Aly Franck

TA Instruments Ltd., Fleming Way, Crawley, West Sussex RH10 9NB, U.K.
www.tainstruments.com

ABSTRACT

A fitting has been developed to allow the extensional viscosity of polymers to be determined on TA Instruments' ARES rotational rheometer, over a range of strain rates. The operation of this fitting is described, and results are presented for various polymers including LDPE and HDPE.

## INTRODUCTION

The roots of extensional (or elongational) 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 a viscosity of $4.3 \times 10^{10}$ poise was found by torsion method to have a viscosity of $1.4 \times 10^{10}$ poise[1].

Despite these early experiments, the developments in extensional rheometry were few until the end of the sixties. Karam et al.[2], Ballman[3] and Cogswell[4], published results on polystryrene, obtained on home built extensional rheometers. The exciting phase in extensional rheometry started in 1969 led by the work of Meissner[5]. 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 extensional 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 extension 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.

Much effort been put into the design and manufacturing of extensional rheometers, despite rheological measurements in shear using rotational rheometers being much easier to perform. The main reason for this 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 flows, considerably orienting molecules, asymmetric particles or the dispersed phase in blends, the final product properties are strongly affected. The second reason to

perform extensional measurements is related to the sensitivity of these flows to molecular structure, such as branching. The extensional 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 extensional properties differ so much from shear properties, the extensional experiments are ideal to test constitutive equations and flow models.

THE HENCKY STRAIN

The most common extensional measurement is the engineering strain or Cauchy strain, $\varepsilon_C$, defined as the increase in length $\Delta L$ divided by the initial length $L_0$. The Cauchy strain is a deformation measure valid for small deformations. For large deformations ($\Delta L > L_0$), the Cauchy strain is replaced by the Hencky strain, $\varepsilon_H = \ln (L/L_0)$ The Hencky strain rate is then $(1/L).dL/dt$.

In a constant rate experiment (two ends of the test piece, usually a cylindrical rod, moving apart at the same speed), the particle in the centre of the rod has a velocity of zero and the particle velocity increases with the distance, along the axis of extension, from the centre. The rotating clamp technique deforms the material at constant Hencky rate by expelling the material at a fixed distance $x = L_0/2$ from the sample center with a constant velocity $v_x$ applied by the rotating clamps. In a traditional extensional 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 $L_0$ to the final length $L_f$, leads to an exponential increase of the sample length over time $L(t) = L_0 \exp[(d\varepsilon_H/dt)t]$, a motion which presents some engineering difficulties.

The extensional viscosity $\eta_E$ is defined as the stress divided by the extension rate. The stress is the force divided by the surface area normal to the direction of deformation. For an incompressible material, the volume is conserved and the surface area must therefore decrease exponentially as $A(t) = A_0 \exp\{(d\varepsilon_H/dt)t\}$ with the sample length increasing while the experiment proceeds.

THE ARES-EVF

The ARES-EVF patent pending design 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 (Fig. 1). 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.

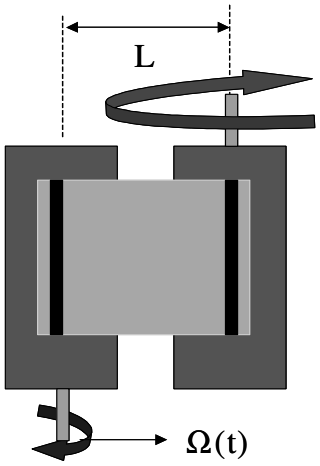


Figure 1: the eccentric drum rotates around the fixed drum while spinning around its own axis

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. The ARES transducer measures a torque. The

force at the sample can be easily calculated from the ratio of measured torque and cylinder radius. The strain rate applied is the velocity at the cylinder, divided by the sample length $L_0$ which is equivalent to the separation of the centre axes of the two cylinders. The velocity is given by the product of the angular rotation speed $\Omega(t)$ and the cylinder radius, R. Since the sample is extended 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.

The EVF design

The schematic of the Extensional Viscosity fixture (EVF) is given in Fig. 2.

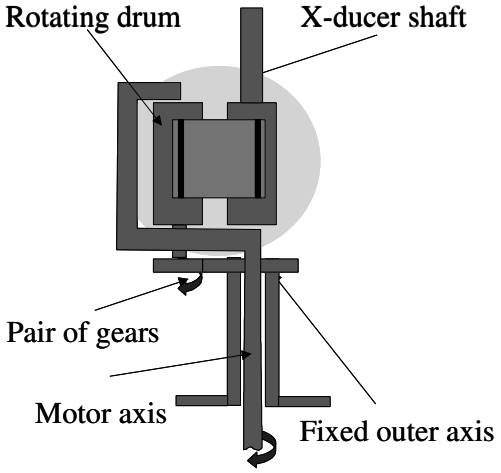


Figure 2: Schematic of the Extensional Viscosity Fixture (EVF).

Motor and transducer axis are aligned, and the rotating drum is mounted eccentric at a distance (centre to centre) of 12.7 mm. In order to induce the spin in the rotating drum, 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 the drums is 10.3 mm and the clearance between the drums is 2.4 mm. Fig. 3 shows the EVF option, installed on the ARES rheometer. Since the cylindrical drums are mounted vertically, the sample is also loaded vertically onto the drums and attached with two tiny clips.


Figure 3: the EVF mounted on the ARES

Sample mounting

The RME (Rheometric Melt Elongational rheometer) and the original Meissner extensional rheometer were using a support medium to prevent the molten sample from sagging. As such the sample was floating on oil or on air during the experiment. In the RME, the belt carriers, which apply the extensional 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 $L_0$ is reduced from 40 mm (RME) to 12.7mm (EVF). These two changes are responsible for a stiffness increase of a sample of the same material at the same temperature of a factor of 1

million. 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

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, 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 stress, the ratio of force F and sample cross section A(t) increases strongly at the start up and then levels off to a steady state.

Range of effective strain rates

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 extensional 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 extensional rate. Although the theoretical upper limit in extension 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 extension rates, and coupled with a sensitive force rebalance transducer, a wide range of practical extension rates can be realized.

Reproducibility and maximum strain

Figure 4 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.

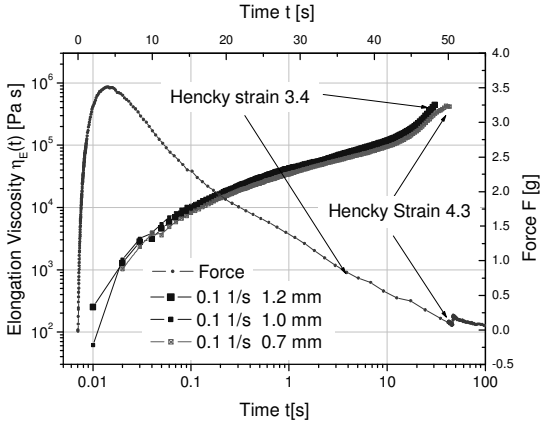


Figure 4: Data for Lupolen 1810, obtained using three different sample sizes

The viscosity curves overlay, proving excellent 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 extension $\varepsilon_H$ 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 $\varepsilon_H$ of 3.4 only, because the sample at the clips of both drums will come into contact after 3/4 of a revolution (Fig. 4). For one experiment in Fig. 4 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[6] As can be seen in Fig. 5, 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 extensions. 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.

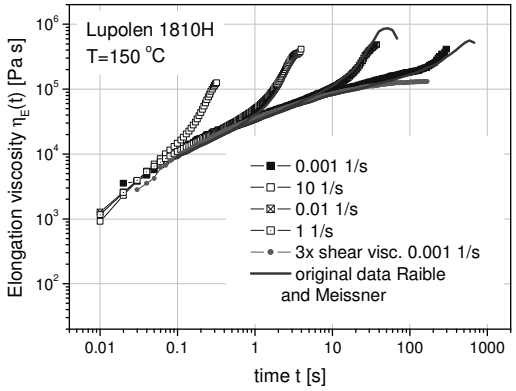


Figure 5: comparison of EVF data with that obtained on the same material using the Meissner apparatus

APPLICATION EXAMPLES

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 extension phase. High take up speeds are only possible with the right amount of strain hardening to avoid bubble collapsing and fiber breaking. Fig. 6 shows the extensional viscosity for different typical representatives of polyethylene, LDPE, LLDPE and HDPE. The LDPE sample shows considerable strain hardening at high extensional 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.

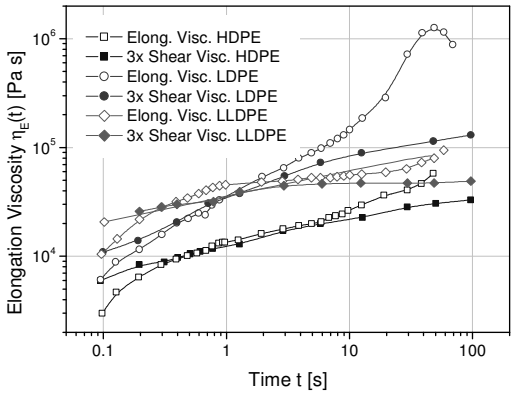


Figure 6: comparison of data for LDPE, LLDPE and HDPE, showing the effect of strain hardening in each

Metallocene catalyzed polyethylene

Fig. 7 shows extensional data of a long chain branched polyethylene obtained by metallocene catalysis in the Dow process. For reference LLDPE and LDPE manufactured with 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 catalysed process shows extensional properties with strong strain hardening, the shape of the viscosity curve very similar to the one of the standard LDPE.

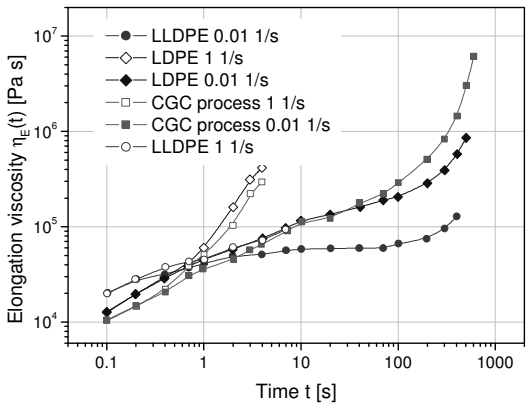


Figure 7: polyethylene manufactured using a metallocene catalyst, compared with LDPE and LLDPE obtained from a traditional manufacturing process.

## 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, extensional rates up to 10 $s^{-1}$, to a maximum temperature of 250°C (350°C Optional). The EVF is straightforward to operate and combined with the speed of the ARES oven can provide sample throughput 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 extension compared to the EVF, the ARES-EVF is better suited for fast extension rates not easily accessible on the RME.

## ACKNOWLEDGEMENTS

The authors would like to thank TA Instruments Ltd., New Castle, Delaware, USA, for permission to publish this work.

## REFERENCES

1. Trouton, F. T. (1906) "On the Coefficient of Viscous Traction and its Relation to that of Viscosity" *Proc. Roy. Soc*., A77, 426-440.

2. Karam , H. J., Hyun, K.S. and Bellinger, J.C. (1969) "Rheological Properties of Molten Polymers" *Trans. Soc. Rheol*. 13, 209-229.

3. Ballman, R.L. (1965) "Extensional Flow of Polystyrene Melt" *Rheologica Acta*, 4, 137-140.

4. Cogswell, F.N. (1969) "Tensile Deformations in Molten Polymers" *Rheologica Acta*, 2, 187-194.

5. Meissner, J. (1968) "Rheometer zur Untersuchung der Deformationmechanischen Eigenschaften von Kunstoffschmelzen Unter Definierter Zugbeanspruchung" *Rheologica Acta*, 8, 78-88.

6. Raible, T., Demarmels, A. and Meissner, J. (1979) "Stress and Recovery Maxima in LDPE Melt Elongation" *Polym. Bull.*, 1, 397-402.