

Characterizing long-chain branching in polyethylene with extensional rheology

Authors: Jan Philip Plog, Fabian Meyer and Ulrich Schulz

Key words

Extensional viscosity, SER tool, polyethylene, branching

Introduction

Polyethylene is a partly crystalline thermoplastic polymer frequently used for packaging such as plastic bags or films. Polyethylene exists in different structural types that differ mainly in terms of their branching structure. The degree of branching along the main chain determines the mechanical properties significantly, since the degree of crystallization, amongst others, depends strongly on it. The branching structure can also affect the melt viscosity of a polyethylene usually leading to higher values for materials with more long side chains.

Polyethylene melts are usually characterized by means of small amplitude oscillatory shear (SAOS), as this mode of deformation can be applied easily on a rotational rheometer like the Thermo Scientific™ HAAKE™ MARS™ instruments. However, many technical processes such as blow molding or fiber spinning are dominated by extensional rather than shear deformation.

Thus measuring the extensional behavior of a polymer melt yields important information not only for optimizing processing steps, but also for establishing structure property relationships. This information is usually not available from the results of SAOS or steady shear measurements. Experiments with extensional deformation are needed together with SAOS and steady shear to obtain a complete picture of a sample rheological behavior.

One of the main goals of extensional testing is to probe for the strain hardening behavior, or in other words the increase of the extensional viscosity in dependence of the applied extensional strain rate. This strain hardening is mainly dominated by long-chain branching, where a higher



Figure 1: Controlled Temperature Chamber (CTC) of the HAAKE MARS Rheometer with the SER tool.

degree of branching usually leads to a more pronounced increase in extensional viscosity.

In this application note the results of extensional tests performed on a highly branched low density polyethylene (LDPE) and a weakly branched high density polyethylene (HDPE) are presented and discussed. Furthermore details of the measurement procedure are provided.

Methods and materials

To characterize the extensional behavior of two differently branched polyethylene samples the HAAKE MARS rotational Rheometer was used together with the SER (Sentmanat Extensional Rheometer) tool for extensional testing of films. The testing principle of the SER tool is based on two counter rotating drums to which a rectangular specimen is attached by a clamping mechanism [1]. As both drums rotate with the same speed in inverse directions, the deformation field applied is a purely uniaxial one. More information about the SER tool for the HAAKE MARS Rheometers can be found in Reference [2]. Figure 1 shows the SER tool mounted to a HAAKE MARS Rheometer. For temperature control the rheometer was equipped with a controlled tests chamber (CTC) which combines forced convection and heat radiation techniques and therefore enables fast temperature changes and a homogeneous temperature distribution within the chamber. More information about the CTC can be found in Reference [3].

All tests were performed at a temperature of 150 °C. The temperature was measured with a Pt100 sensor that is located close to the sample. The melting process and the general state of the sample can be monitored visually via two glass windows in the respective CTC halves.

Before one can start with the extensional experiments, it is important to determine the internal friction of the SER tool itself with a rotational test procedure. Details about the exact setup of the calibration procedure can be found in the SER tool instruction manual. The so determined torque needs to be subtracted from the torque signal during the experiment to obtain correct results. This is achieved by implementing this torque in the torque correction factor of the SER in the Device Manager of the Thermo Scientific™ HAAKE™ RheoWin™ Software. The polyethylene specimens were deformed with the SER tool at different extensional rates. To do this, the sample has to be attached carefully to the drums of the SER tool using a clamp mechanism. The test itself was then conducted with HAAKE RheoWin Software via the routine that can be seen in Figure 2. After the sample has reached 150 °C and the temperature was held constant for 5 minutes, the sample was pre-stretched at a constant stress (153 Pa for LDPE) for 10 seconds to counteract any gravitation induced sagging as well as ensure that the gearbox of the SER tool is in a pre-stressed state at the beginning of the test. In the actual extensional experiment (element 4 in Figure 2) the drums rotated at a defined strain rate until the deflection angle reached a value of 230 °. At higher deflection angle

the clamps may touch if the tested specimen exceeds a certain thickness. The experiments were conducted at strain rates of 0.01 s⁻¹, 0.05 s⁻¹, 0.1 s⁻¹, 0.5 s⁻¹, 1.0 s⁻¹ and 5.0 s⁻¹.

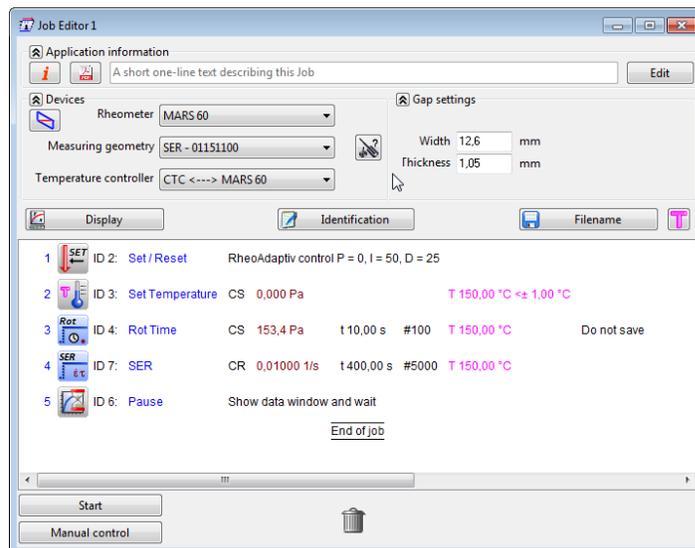


Figure 2: Measuring routine to characterize the extensional behavior of Polyethylene, comprised of the following elements: 1. RheoAdaptiv-Control, 2. Temperature control, 3. Pre-stretch of the sample, 4. Extensional test.

Results and discussion

Figure 3 shows the results of several extensional experiments with HDPE performed at different extensional strain rates. The extensional viscosity η_E is plotted versus the experimental time. For comparison the linear viscoelastic response, represented by three times the shear viscosity is also displayed in the same plot. The transient shear viscosity was obtained by rotational experiments using a cone & plate setup. The factor three derives from the Trouton ratio for uniaxial flow [4]. As can be seen in Figure 3, the linear HDPE does not show any deviation from the linear viscoelastic response and therefore no strain hardening, even at highest extensional strain rates. The branches, if any are present, are so small that they don't influence the result, meaning that only the molecular weight effect can be monitored. In contrast to that the LDPE (Figure 4) shows a clear deviation from the linear viscoelastic behavior and dramatic strain hardening effects. The onset of strain hardening is shifted towards longer experimental times with decreasing extensional rate. However, when comparing the results for both polyethylenes, it can also be observed, that the overall extensional viscosity before the onset of strain hardening, is lower for a HDPE of the same molecular weight. This is due to the decreased coil size in the melt, resulting in a lower number of entanglements. The characteristics

seen in extensional tests can be used to model certain processing steps like for instance blow-molding or foil production. In addition to that, the extensional viscosity can be used for sample identification and thus for quality control applications.

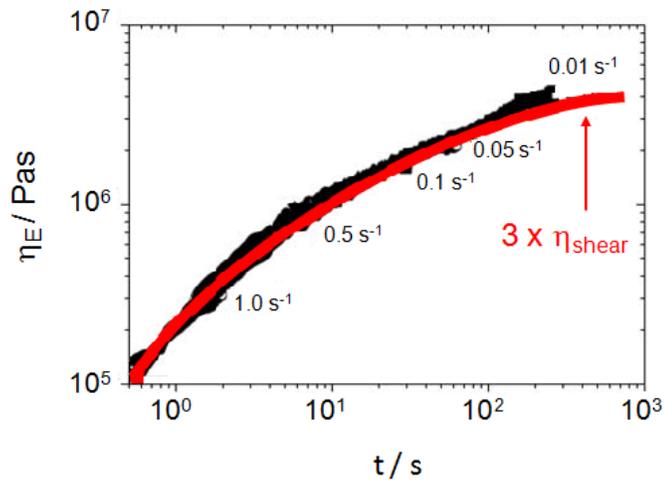


Figure 3: Extensional viscosity as a function of strain rate for non- branched LDPE.

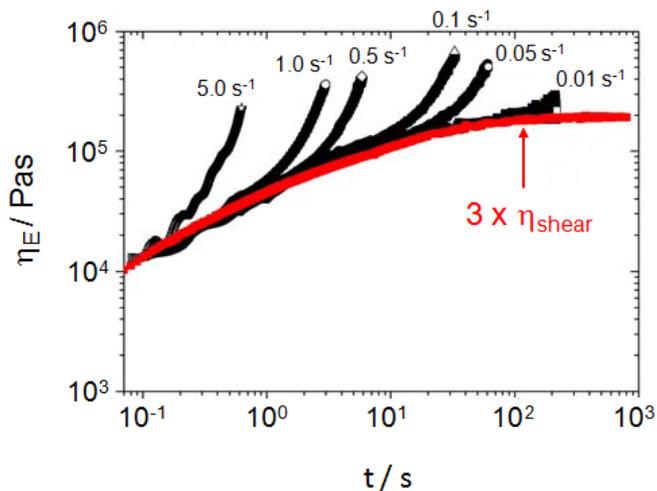


Figure 4: Extensional viscosity as a function of strain rate for highly branched LDPE.

References

1. Sentmanat, M. L., Miniature universal testing platform from extensional melt rheology to solid state deformation behavior, *Reol. Acta*43, 657-669, 2004
2. Küchenmeister-Lehrheuer, C., Meyer F., Sentmanat Extensional Rheometer (SER) for HAAKE MARS, Thermo Scientific Product information P019
3. Küchenmeister-Lehrheuer, C., Meyer F., Controlled Test Chamber (CTC) for HAAKE MARS Rheometers, Thermo Scientific Product information P057
4. Trouton, F.T., On the coefficient of viscous traction and its relation to that of viscosity *Proc. Roy. Soc.*, A77 426-440, 1906

Find out more at thermofisher.com/rheometers