

# Characterizing long-chain Branching in Polyethylene with Extensional Rheology

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## Introduction

Polyethylene exists in many different structural types; most of those differ in terms of their branching structure. The existence of branches along the main chain determines the materials behavior towards mechanical influences as the degree of crystallization, amongst others, depends strongly on them. Also the density of the material decreases with an increasing amount of branches resulting in a lower melt viscosity.

Polyethylene melts are usually characterized rheologically in small amplitude oscillatory shear (SAOS) as this mode of deformation can be obtained easily on a rotational rheometer like i.e. the Thermo Scientific HAAKE MARS. However, most technical processes like i.e. blow molding are dominated by extensional deformation that interfere uni- or multiaxial with the shear flow field.

Thus testing the extensional behavior of a polymer melt yields important information that cannot be obtained via SAOS. As the rheological circle [1] of material characterization shows, extensional deformation is needed together with SAOS and steady shear to obtain a complete picture of a samples rheological behavior.

One of the main goals of extensional testing is to probe for the strain hardening behavior, or the increase of the extensional viscosity of a certain molecular architecture in dependence of the strain rate. This strain hardening is mainly dominated by long-chain branches, more branches lead to a more pronounced viscosity increase. For i.e. LDPE the extensional viscosity shows a steady increase with increasing strain rate, the maximum can thus be found at the highest available strain rate that can be applied. Strain hardening however does not solely depend on branching but also on molecular weight and its distribution. The impact of high molecular weight fractions however can be monitored at low deformational rates in contrast to the branching influence.

## Experimental

To characterize the extensional behavior of polymer melts and viscoelastic solids the SER (Sentmanat Extensional Rheometer, [www.xinst.com](http://www.xinst.com)) can be used together with the Thermo Scientific HAAKE MARS.

The testing principle is based on stretching the sample on two counter-rotating drums. As both drums rotate with the same speed in inverse directions the deformation field applied is a purely uniaxial one.



Fig. 1: Controlled Temperature Chamber (CTC) of the HAAKE MARS with the SER.

As can be seen in Fig. 1, the SER can be coupled with the controlled stress rheometer HAAKE MARS. The testing temperature of 150 °C was achieved via a forced convection/ radiation hybrid oven (CTC) that allows for very fast temperature changes and a homogenous temperature distribution within the heating chamber. The melting process and the general state of the sample can be monitored visually via two glass windows in the respective oven halves. The temperature is monitored via a PT100 sensor that is situated very close to the sample. Before one can start with the tests it is important to determine the friction of the SER itself in a rotational test. If the friction should be too high (> 30 µNm) it should be checked if the coupling is centered correctly. For calibration, a rotation is commanded that correlates with the rotation of the stretching test. The so determined torque corresponds with the friction of the SER and needs to be detracted from the measurement to obtain correct results. This is achieved via implementing this torque in the torque correction c-factor in the options of the SER in the device manager.

## Results and Discussion

The material was deformed with the SER (see Fig. 2) during the stretching tests. To do this the sample has to be secured onto the drums of the SER with included clamps. The test itself was then conducted in RheoWin via the routine that can be seen in Fig. 3. After the sample has reached 150 °C and the temperature was held constant for 5 minutes the sample was pre-stretched (153 Pa for LDPE) for 10 seconds to counteract the gravitation induced sagging as well as ensure that the gearbox is in a state that the test can begin right away. Afterwards the drums rotate at a given strain rate until the deflection angle reaches a value of 230° (afterwards the clamps would touch). The experiments were conducted at strain rates of 0.01 s<sup>-1</sup>, 0.05 s<sup>-1</sup>, 0.1 s<sup>-1</sup>, 0.5 s<sup>-1</sup>, 1.0 s<sup>-1</sup> and 5.0 s<sup>-1</sup>, however the highest strain rate was not used for the HDPE as no strain hardening would have been monitored there.



Fig. 2: SER system

As can be seen in Fig. 4, the linear HDPE does not show any strain hardening, even at lower 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

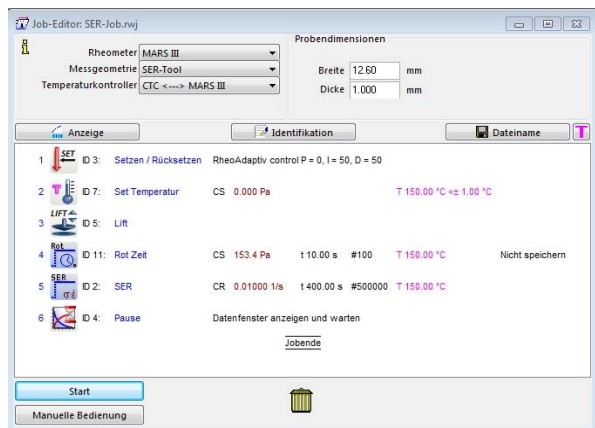


Fig. 3: Measuring routine to characterize the extensional behavior of Polyethylene, comprised of the following elements: 1. RheoAdaptiv-Control, 2. Temperature Control, 3. Lift Control 4. Pre-stretch of the sample, 5. Extensional Test.

can be monitored. In contrast to that the LDPE (see Fig. 5) shows a dramatic strain hardening effect with increasing strain rate as would have been expected due to the degree of branching along the main chain. However, the extensional viscosity itself is lower for a HDPE of the same molecular weight due to decreased coil size in the melt resulting in a lower number entanglements.

The characteristics seen in extensional tests can then be used to model certain processing steps like i.e. blow-molding or foil production. In addition to that, the extensional viscosity can be used for identification and thus for QC applications.

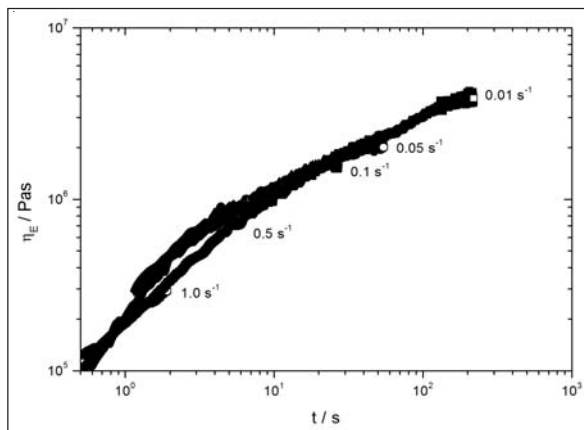


Fig. 4: Extensional viscosity as a function of strain rate for non-branched HDPE.

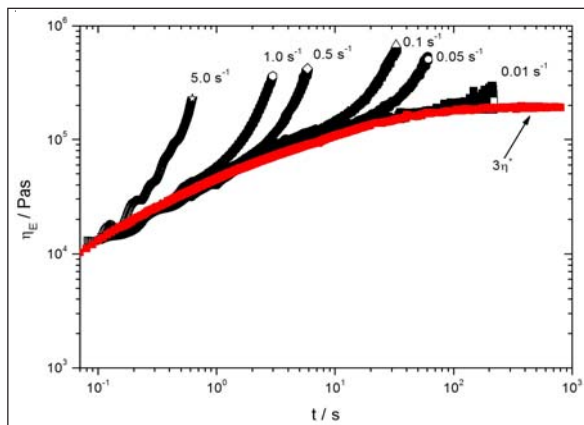


Fig. 5: Extensional viscosity as a function of strain rate for highly branched LDPE.

## References

- [1] "Determination of viscoelastic and rheo-optical material functions of water-soluble cellulose derivatives" (Progress in Polymer Science, Volume 26, Issue 9, November 2001, Pages 1839-1919).
- [2] Thermo Scientific Product information P019-e "SER – Extensional Rheology System for Thermo Scientific HAAKE MARS", Cornelia Küchenmeister, Jint Nijman.

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