

## Rheometers

# Optimizing process conditions and ensuring end product requirements of plastics with rheological analysis

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## Keywords

Polymers, melt, viscoelasticity,  
molecular weight, processing, DMTA,  
extensional testing

## Introduction

Plastics are polymeric materials that are used in a wide range of applications and for a broad variety of consumer products. In order to make these products, polymers are commonly processed at elevated temperatures in a molten state. Understanding how these melts deform and flow is key to knowing how to effectively process and transform them into the end products we readily consume.

Due to their chemical structure and high molecular weight, polymer melts exhibit a complex flow and deformation behavior. They are considered viscoelastic materials, showing both viscous (liquid-like) and elastic (solid-like) properties. A good knowledge of the viscoelastic properties of a polymeric material is essential to optimize formulations and blends as well as to adapt a process to the properties of a given material. The molecular structure as well as the testing or processing conditions of a polymer melt determine which behavior is dominant (viscous or elastic). Too much elasticity can lead to flow anomalies and unwanted effects during many common processing steps.<sup>1</sup> One example is the swelling of a melt stream exiting the narrow die of an extruder. Other examples of flow anomalies caused by elastic properties of polymeric fluids are shown in Figure 1.



Figure 1: Typical flow anomalies of viscoelastic polymer fluids.

Capillary viscometers and melt flow indexers are frequently used to measure the melt viscosity of polymers. However, these instruments will not provide any information about the viscoelastic properties of the tested sample.

Rotational rheometers with the capability to perform rheological tests with small oscillatory mechanical excitations on the other hand, allow for a comprehensive investigation of these properties.

This report is intended to give an overview of the different rheological tests that can be performed with rotational rheometers and explain how the obtained results relate to different processing conditions as well as to the final product properties.

## Rotational vs. oscillatory testing— The Cox-Merz rule

Rheology has proven to be an excellent tool to analyze the mechanical properties of polymers in their different physical states. Various testing methods can be utilized to fully characterize the rheological behavior of polymeric materials. Though rotational steady state shear experiments allow for measuring the non-Newtonian viscosity of dilute and semi-dilute polymer solutions, the preferred testing methods for polymer melts (and solids) utilize the application of an oscillatory shear deformation. This is due to their high elasticity and the consequential occurrence of edge failures when exposed to large deformations in a rotational rheometer. According to the Cox-Merz rule, the complex viscosity ( $|\eta^*|$ ) derived from oscillatory frequency sweep measurements plotted against the angular frequency ( $\omega$ ) is identical to the steady-state shear viscosity from rotational testing plotted against the shear rate.<sup>2</sup> The Cox-Merz rule is an empirical rule that is valid for many polymer melts and polymer solutions. Figure 2 shows the comparison of viscosity data obtained from rheological tests in rotation and in oscillation mode.

Once the end of the Newtonian (zero shear viscosity) plateau is reached and the viscosity starts to decrease, the shear viscosity (red symbols) drops abruptly and no longer displays a continuous, smooth progression. The observed drop is due to sample fracture at the edge of the measuring geometry caused by secondary flow fields.<sup>1</sup> The oscillation frequency sweep (green symbols), on the other hand, provides higher data quality across a broader frequency range.

The improved testing range of the oscillatory frequency sweep is due to the small amplitudes of the imposed oscillatory shear. As a result, performing an oscillatory frequency sweep and applying the Cox-Merz rule is the preferred method for obtaining shear viscosity data for polymeric materials.

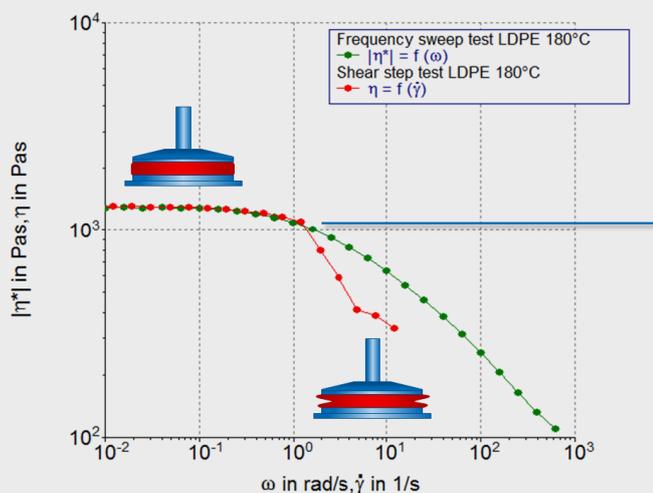


Figure 2: Comparison of viscosity data obtained from a steady state shear (red symbols) and an oscillation frequency sweep test (green symbols).

## Identifying the linear-viscoelastic range— The amplitude sweep tests

In order to obtain comparable viscosity data from a frequency sweep experiment (as discussed above), the applied sinusoidal oscillatory deformation must be relatively small and within a material's linear viscoelastic range (LVR). In this range, the material's microstructure remains unchanged and as a result, the rheological properties such as the storage and the loss modulus ( $G'$  and  $G''$ , respectively) or the complex viscosity are constant and independent of the applied stress or deformation. Once a critical deformation or stress value is reached, the microstructure of the material begins to change and the rheological parameters start to change.

The linear viscoelastic range of a material is determined by performing an oscillation amplitude sweep test. During this test, which is performed at a constant frequency, the sinusoidal deformation or stress applied by the rheometer is gradually increased. Figure 2 shows the results of an amplitude sweep for LDPE at 190 °C. The end of the linear viscoelastic range of this LDPE melt was calculated automatically by the rheometer software and is equal to a deformation of 55 %. Further tests in oscillation mode, such as frequency, temperature, or time sweep tests, should be performed at a deformation below this critical value (unless the test is intended to be outside the LVR). When a frequency sweep test is performed over a wider frequency range (several orders of magnitude), it is recommended to perform several amplitude sweeps at different frequencies, in order to make sure that the selected deformation remains within the LVR across the entire frequency range.

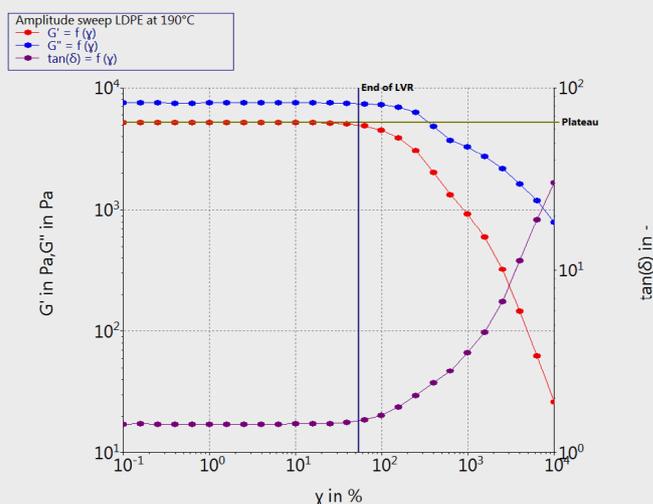


Figure 3: Storage modulus  $G'$ , loss modulus  $G''$  and the complex viscosity  $|\eta^*|$  as a function of the deformation  $\gamma$  for a LDPE melt at 1 Hz and 190°C.

## Viscoelastic fingerprint of a material – The frequency sweep test

The information gained from the rheological tests in oscillation mode is manifold. For instance, shear rate dependent viscosity data derived from oscillatory frequency sweep experiments, together with the utilization of the Cox-Merz rule, allow for quantifying the flow resistance of a material during high shear processing applications such as extrusion or injection molding. The low frequency/shear data (zero shear viscosity,  $\eta_0$ ), on the other hand, can be used to calculate the weight average molecular weight ( $M_w$ ) of a polymer melt according to:

$$\eta_0 = k \cdot M_w^{3.4} \quad (1)$$

The prefactor  $k$  depends on the molecular structure of the polymer.<sup>3</sup> Equation 1 is valid for polymers with a linear chain structure and a molecular weight above a critical value ( $M_c$ ). Figure 4 shows a typical viscosity curve of a polystyrene melt and the corresponding shear rate ranges that occur in common processing applications.

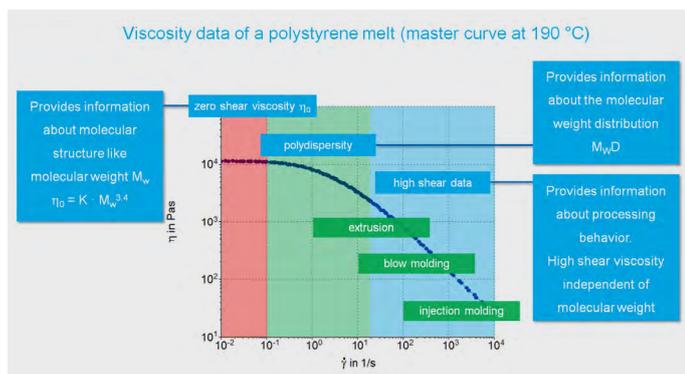


Figure 4: Shear rate depending viscosity of a polystyrene melt and typical applications.

Besides information about the overall flow resistance, frequency sweep data also provides a direct measure of the viscous and elastic properties of a polymer. These are represented by the storage and the loss moduli ( $G'$  and  $G''$ , respectively) measured at different frequencies/time scales. The data reveals the general structure of a material and also provides information of the molecular weight ( $M_w$ ) and the molecular weight distribution (MWD). Repetitive frequency sweep measurements over a narrow frequency range that capture the crossover point can therefore be used to detect thermal degradation causing changes to the MW and MWD. Figure 5 shows how the crossover point (where  $G' = G''$ ) shifts when the MW or the MWD change for an otherwise identical polymer melt.

As already mentioned, flow anomalies caused by the elasticity of polymer melts can lead to poor product quality in polymer processing applications such as extrusion. Figure 6 shows a comparison of storage modulus data as a function of the applied

frequency for polyethylene samples with different Melt Flow Indices (MFI). The three PE samples were processed with a 16 mm parallel twin screw extruder under the same conditions. At the end of the extruder barrel the melts were forced through a vertical rod capillary die with a diameter of 1 mm and an L/D ratio of 10. Die swell of the extrudate was measured with a laser micrometer. A die-swell of 0,5 mm, resulting in a total strand diameter of 1,5 mm, could be found for the PE with the highest MFI (~20) and the lowest molecular weight. As can be seen in Figure 6 the strand came out of the extrusion line as an even strand with no signs of surface defects.

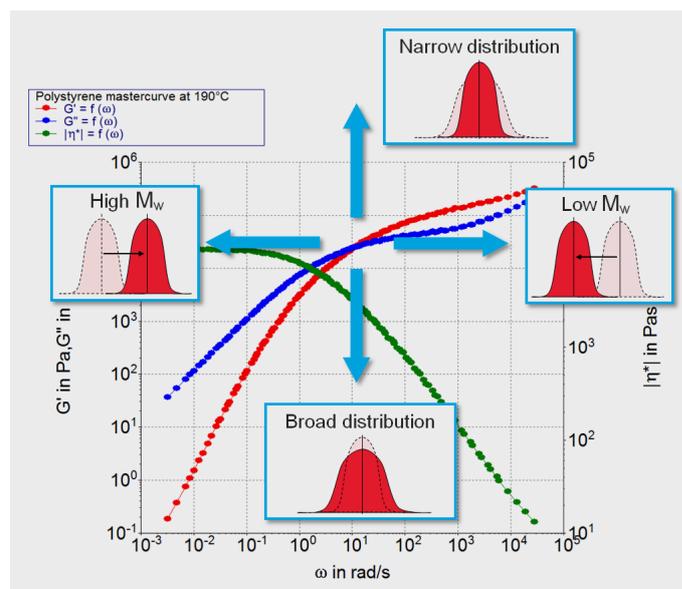


Figure 5: Storage modulus  $G'$ , loss modulus  $G''$  and the complex viscosity  $|\eta^*|$  as a function of the angular frequency  $\omega$  for a polystyrene melt at 190°C.

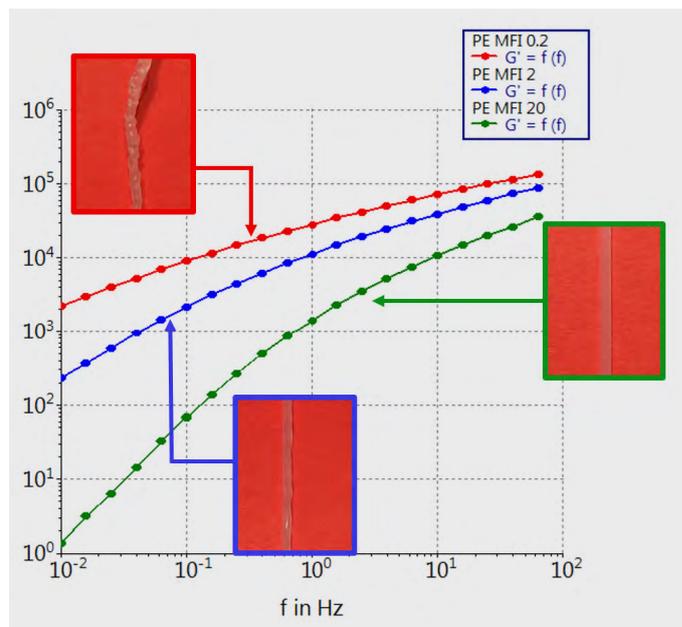


Figure 6: Storage modulus  $G'$  as a function of the angular frequency  $\omega$  for polyethylene melts with different MFI at 190°C. The images show the extrusion strands that were prepared with the melts in a twin screw extrusion process.

The PE sample with the medium MFI (~ 2) already showed an uneven surface structure with a changing diameter. The PE sample with lowest MFI (~ 0.2) and the highest molecular weight showed clear signs of melt fracture under the same extrusion conditions used for the other two samples. When looking at the rheological data, one can see that the three samples clearly differ in terms of their elasticity, as represented by  $G'$ . Especially at the lowest frequency ( $10^{-2}$  Hz), the values in  $G'$  differ in one or more orders of magnitude.

The storage modulus is a very sensitive indicator of the elasticity incorporated by a high molecular weight tail. Figure 7 shows the comparison of the results of three frequency sweeps performed on a low molecular weight LDPE and two blends of the same LDPE with a small weight fraction of a high molecular weight PE. In the low frequency range,  $G'$  shows clear differences for these three melts and even a small fraction of 1 wt% of high molecular weight PE can be detected. These small differences are usually not visible when performing Gel Permeation Chromatography (GPC) or similar techniques to determine the molecular weight distribution. Also the MFI results performed with a capillary viscometer would not reveal any differences between the three samples. The storage modulus data derived from oscillatory frequency sweep experiments is the most sensitive indicator of a high molecular weight tail in a polymer melt. Even small amounts of high molecular weight fraction can already cause flow anomalies that will lead to a poor quality of the final polymer strand. Figure 5 shows rheological data acquired over an angular frequency range from below  $10^{-2}$  rad/s to more than  $10^4$  rad/s. In order to obtain rheological data over such a wide range, more than a single frequency sweep test is necessary. The low and high frequency regions are restricted by either time concerns (duration of a single oscillation) or the rheometer specifications (maximum frequency). The time-temperature superposition principle is then used to overcome these limitations.

## Extending the measuring range— The time-temperature superposition principle

Usually between 2 and 4 orders of magnitude in frequency are covered in a single frequency sweep test. In order to extend the data range beyond the low- and high-end frequencies, the Time-Temperature Superposition (TTS) principle can be applied. TTS uses the fact that temperature and frequency (time) have similar effects on the viscoelastic behavior of polymer melts.<sup>3</sup> As a result, one can perform several frequency sweeps over a smaller range at different temperatures. After selecting one set of data (at one temperature) as a reference, the other results can be shifted towards the reference curve in order to generate a master curve. Using the TTS-principle, it is possible to obtain rheological data over a much wider frequency range compared to a single frequency sweep experiment. TTS works for many polymer melts and polymer blends but usually only over a limited temperature range.<sup>4</sup>

Figure 8a shows the results of several frequency sweep tests performed at different temperatures. The TTS principle was then applied, with 190 °C chosen as a reference temperature. The resulting master curve (Figure 8b) contains viscoelastic data over almost 8 orders of magnitude in frequency. The master curve can be divided in three regions. At low frequencies, the sample is in the terminal region and the polymer melt behaves predominantly viscous. In the terminal region, material behavior is governed by long molecule chain relaxation processes. Also, in the terminal region,  $G'$  and  $G''$  typically have slopes of 2 and 1 in a double logarithmic plot. At medium frequencies, a transition occurs with a crossover between  $G'$  and  $G''$ . The viscoelastic behavior in this range is strongly driven by the molecular weight distribution of the polymer. At the highest frequencies, the sample behaves predominantly elastic, with  $G'$  larger than  $G''$ . Here the polymer's behavior is governed by the fast relaxation motion of the shortest polymer chains.

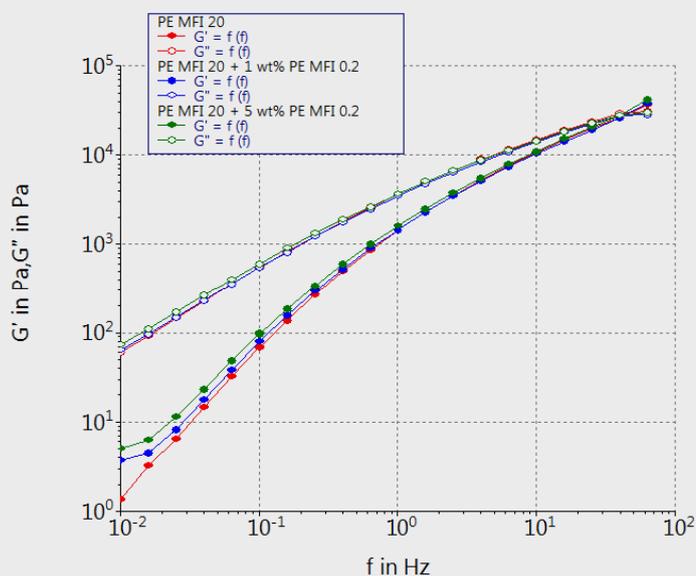


Figure 7: Storage modulus  $G'$  and loss modulus  $G''$  as a function of the angular frequency  $\omega$  for a low molecular weight polyethylene melt and two blends at 190°C.

In addition,  $G'$  and  $G''$  data acquired over a wide frequency range can be used to calculate the molecular weight and molecular weight distribution for many linear thermoplastic homopolymers. In order to perform this calculation, the tested frequency range must include data from the low frequency terminal region up to the end of the high frequency plateau region.

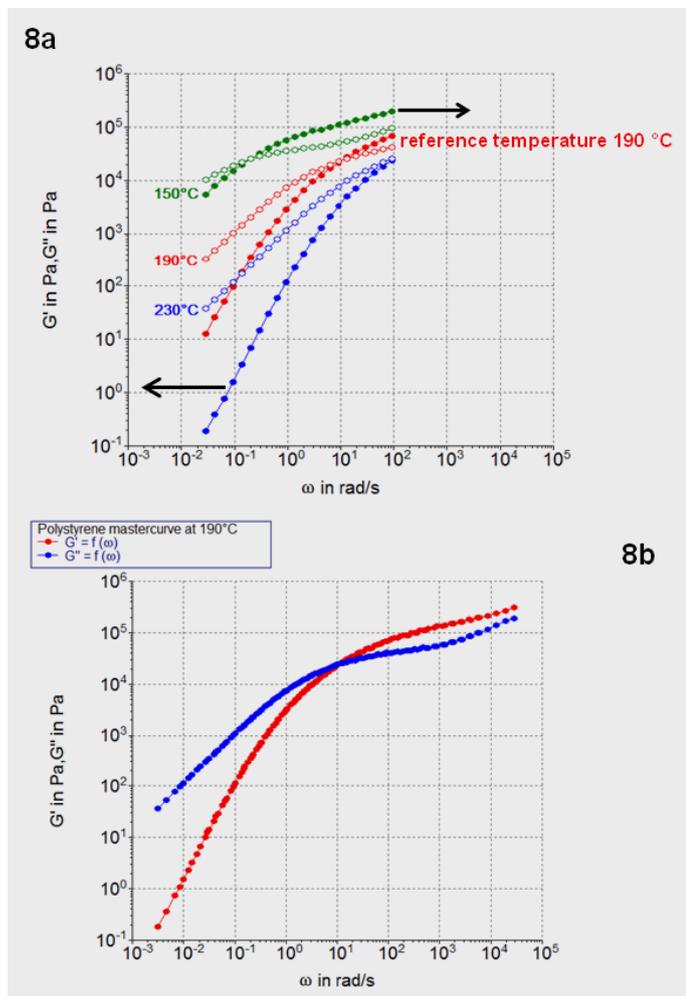


Figure 8: Application of the Time-Temperature-Superposition principle with a polystyrene melt.

### Investigating the final product properties— Dynamic Mechanical Thermal Analysis

Rotational rheometers can also be utilized to perform Dynamic Mechanical Thermal Analysis (DMTA) on solid, rectangular, or cylindrically shaped polymer specimens. During DMTA testing, a material is exposed to an oscillatory mechanical excitation while the temperature is continuously changed. The obtained data is used to identify characteristic phase transitions, such as the glass transition or the occurrence of melting and/or crystallization within the polymer matrix. In addition, DMTA can be used to determine final product performance and to interrogate relevant application-based properties such as stiffness, brittleness, damping or impact resistance.

Figure 9 shows an example of a DMTA test with a semi-crystalline polyetheretherketone (PEEK) sample, tested from below its glass transition to just below its melting temperature. The test was performed using a special solids clamping tool for

rotational rheometers.<sup>5,6</sup> The rectangular specimen was prepared with a lab scale injection molding system.<sup>7</sup> For rheological testing, the glass transition can be identified using different metrics. The most common metric uses the maximum in the loss modulus  $G''$ , while the initial decrease in the storage modulus  $G'$  or the maximum in the  $\tan\delta$  ( $G''/G'$ ) are also readily used to indicate glass transition. As can be seen in Figure 9, the maximum in  $G''$  is located in the middle of a wider transition range, while the onset of the  $G'$  decrease is near the beginning of the transition and the maximum in  $\tan\delta$  closer to the end of this range.

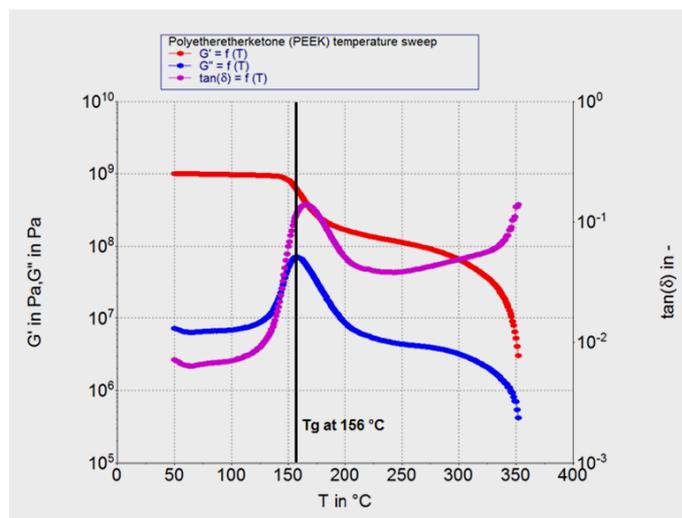


Figure 9: Storage modulus  $G'$ , loss modulus  $G''$  and  $\tan\delta$  as a function of temperature for a polyetheretherketone.

The generalized behavior of a polymeric sample during a temperature sweep test is presented in Figure 10. All semi-crystalline polymers transition from a glassy region at low temperatures to a rubbery plateau and eventually into the melt state at higher temperatures. The height of the step from the glassy region to the rubbery plateau depends on the degree of crystallinity of the polymer. As the degree of crystalline domains inside the polymer increases, the step height between the two regions will decrease.

Low molecular weight polymers do not exhibit a rubbery plateau. Once the glass transition is completed, the material becomes a soft melt and  $G'$  decreases with increasing temperature. Cross-linked polymers do not melt; instead they remain in a rubbery state until thermal decomposition occurs.

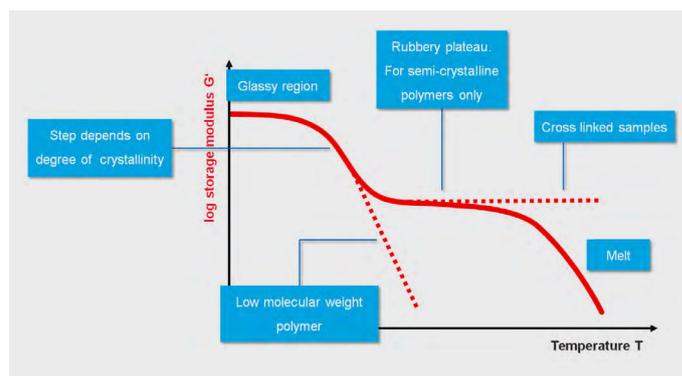


Figure 10: Generalized behavior of polymer sample in a DMTA test.

## Extensional Testing

Besides rotation and oscillation, extension is the third main type of flow that can be investigated rheologically. Spraying and vessel filling are two examples of processes where extensional flows occur, however they are not very common for polymer melts. Examples of processes where extensional flows occur and that are more closely related to polymer melts are film blowing, injection molding, foam extrusion or fiber spinning. Figure 11 shows the transient extensional viscosity at different extensional deformation rates for two different polyethylene samples. The tests were performed with the Sentmanant Extensional Rheometer (SER) fixture for rotational rheometers.<sup>8</sup> The plot on the top presents the extensional behavior of a non-branched high density polyethylene (HDPE) sample. No strain hardening was observed for this type of material. The plot on the bottom, however, shows the results of the same experiments, performed with a highly branched low density polyethylene (LDPE) sample. For comparison, the red curves show the transient shear viscosities multiplied by three according to the Trouton ratio for uniaxial extension.<sup>9</sup> The shear viscosity data were obtained from rotational step experiments. Unlike the linear HDPE sample, the extensional behavior of the branched LDPE sample differed significantly from the behavior observed in shear flow. During extensional testing, the LDPE sample displayed shear hardening behavior, especially at higher deformation rates. Strain hardening behavior can be beneficial for many polymer processing techniques such as film blowing or fiber spinning. Therefore, having a good understanding of the extensional behavior of a polymeric material is crucial for optimizing its final product properties (behavior that is left uncaptured by standard rotational rheological measurements).

## Conclusion

Understanding the viscoelastic properties of a polymeric material is essential to optimize formulations and blends as well as to adapt a process to the properties of a given material and avoid problems caused by flow anomalies. Rheological tests performed with rotational rheometers can be utilized to investigate the viscoelastic behavior of polymers from the melt-state to the solid-state and everywhere in between. The obtained data can be used not only to optimize processing conditions and the final product performance, but also to establish structure property relationships. This is the reason why rheological tests are commonly used in analytics for polymeric fluids in industry as well as academia.

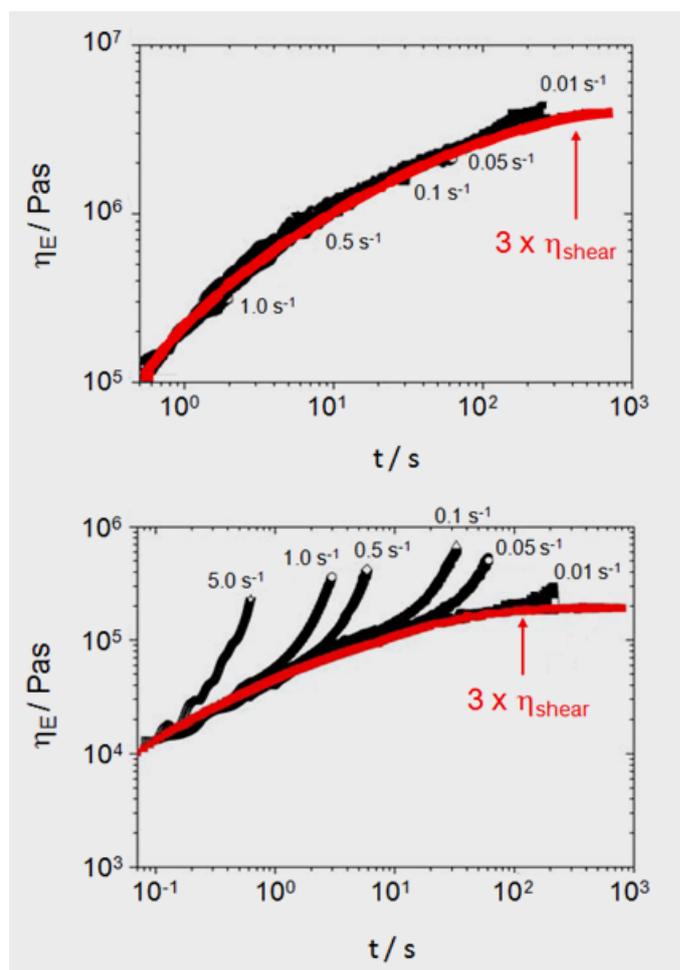


Figure 11. Extensional viscosity as a function of strain rate for a non-branched HDPE (top) and highly branched LDPE (bottom). All tests were performed at 150 °C.

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