

# Polymer Rheology and Molecular Mass

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## Introduction

Extrusion, injection molding and compression molding are all processes reliant upon a material's viscosity, i.e., its resistance to flow. However, viscosity not only influences the processing, but also the mechanical characteristics of the final product. In particular, molecular mass and viscosity are closely connected.

In the following, three different PEEK materials are classified according to their molecular mass using oscillation measurements on a Kinexus rotational rheometer.

## Measurement Conditions

Frequency measurements were performed on three materials, designated PEEK 1, PEEK 2 and PEEK 3. The strain (or stress) applied to the sample must be low enough to not destroy the sample's structure so that the measurement is performed within the linear-viscoelastic range (LVER). An amplitude sweep serves as a preliminary measurement to determine the LVER limit.

Table 1 depicts the conditions of the amplitude and of the frequency sweeps.

**Table 1** Conditions of the oscillation measurements

	Amplitude Sweep	Frequency Sweep
Device	Kinexus ultra+ with electrically heated chamber	
Geometry	PP25 (plate-plate, diameter: 25 mm)	
Gap	500 µm	500 µm
Temperature	360°C	360°C
Shear strain	1 to 100%	-
Shear stress	-	1,000 Pa (PEEK 1), 500 Pa (PEEK 2 and 3)
Frequency	1 Hz	10 to 0.01 Hz
Atmosphere	Nitrogen (1 l/min)	

### Amplitude Sweep: Determination of the LVER (Linear Visco-Elastic Range)

Figure 1 depicts the curves resulting from the amplitude sweep on PEEK 1 as a function of shear strain. For shear strains up to approx. 30% – corresponding to a shear stress of approx. 10,000 Pa – the elastic shear modulus  $G'$  remains constant, suggesting that the material is located in LVER. The decrease in  $G'$  for higher shear strains is due to the breakdown of the sample's structure. For the following frequency sweep, a shear stress of 1,000 Pa is selected.

### Frequency Sweep

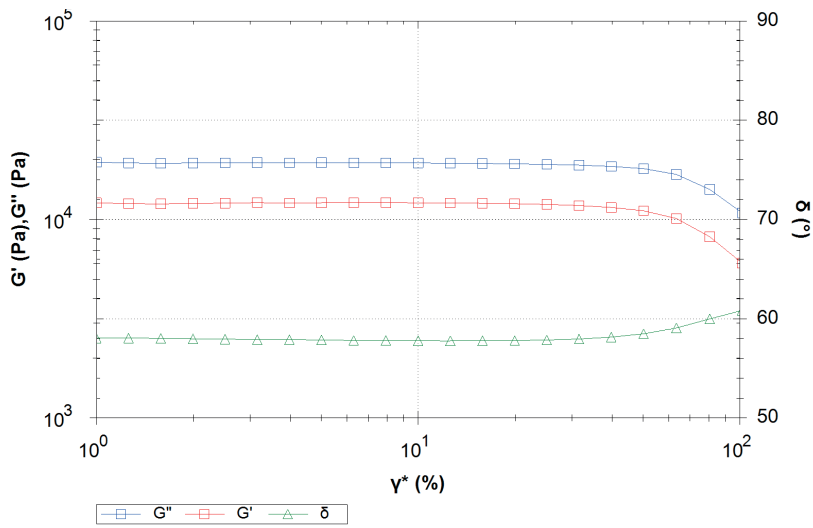
Figure 2 depicts the curves of elastic and loss shear moduli in addition to the phase angle during a frequency

**Some Definitions**

$G^*$ : Complex shear modulus  
 $G'$ : Storage shear modulus, elastic contribution to  $G^*$   
 $G''$ : Loss shear modulus, viscous contribution to  $G^*$   
 $\delta$ : Phase angle

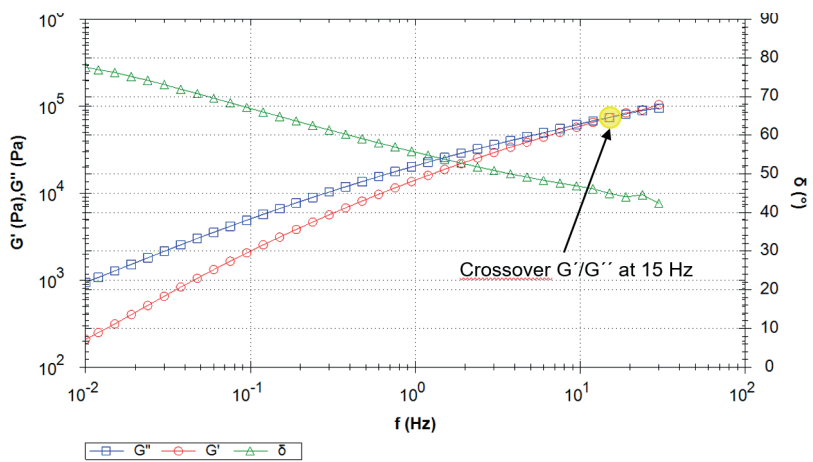
sweep of PEEK material 1. In direction of the lower frequencies, loss shear modulus dominates elastic shear modulus, resulting in a phase angle higher than 45°C.

The  $G'$  and  $G''$  curves crossover at a frequency of 15 Hz. Here, the material transitions from a liquid-dominated state, in which the polymer chains have time to disentangle (low frequencies), to a solid-dominated state, where the chains are interlocked and behave like a network (high frequencies).



The **phase angle**  $\delta$  ( $\delta = G''/G'$ ) is a relative measure of the viscous and elastic properties of a material. It ranges from 0° for a fully elastic material to 90° for a fully viscous material.

1 Amplitude sweep of PEEK 1

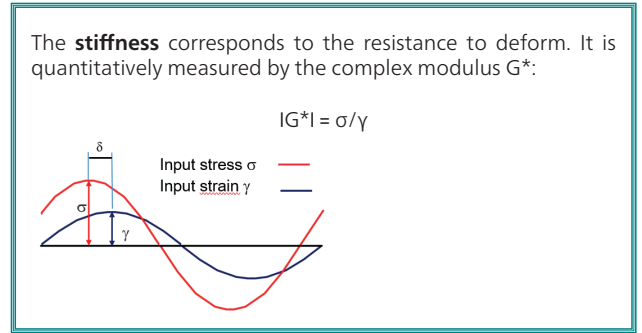


2 Frequency sweep of PEEK 1

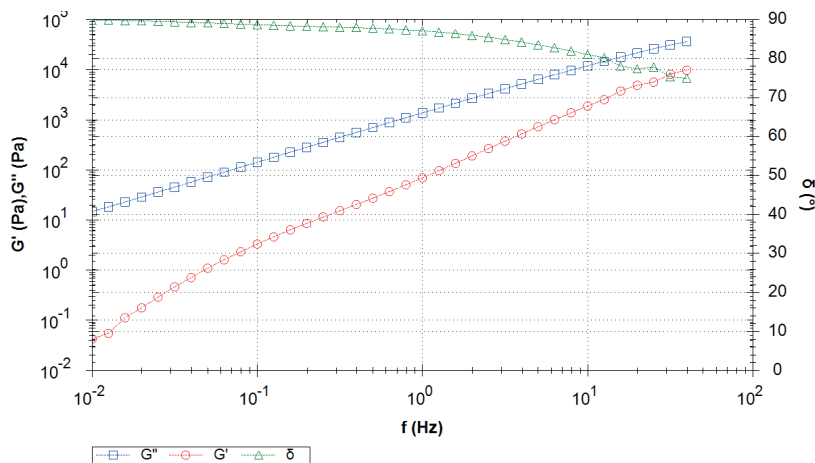
## APPLICATIONNOTE Polymer Rheology and Molecular Mass

Figures 3 and 4 display the frequency sweep of PEEK samples 2 and 3 under the same conditions. The resulting curves of both materials are very similar and differ from the first sample. During the complete measurement, the viscous shear modulus ( $G''$ ) dominates the elastic shear modulus ( $G'$ ), resulting in a phase angle ( $\delta$ ) higher than  $45^\circ$ . In direction of the lower frequencies, the phase angle increases to reach almost its maximum value of  $90^\circ$ . In other words, at low frequencies (or long-time scales), the sample behaves like an almost purely viscous fluid without any elastic properties. No crossover was detected in the measured frequency range, however, it likely exists at higher frequencies because the  $G'$  and  $G''$  curves tend towards each other with increasing frequencies.

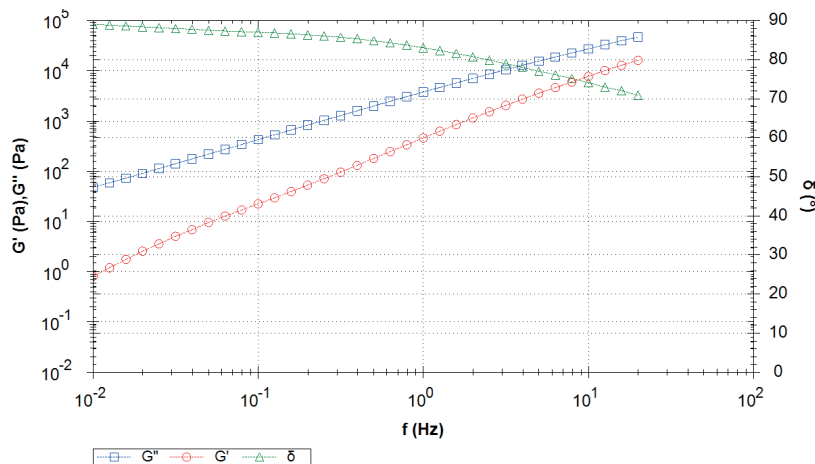
The molecular mass of the polymers is related to the position of the crossover: The lower the frequency of the crossover, the higher the molecular mass.



In this case, PEEK 1 has a higher molecular mass than PEEK 2 and PEEK 3. PEEK 2 and PEEK 3 differ in the values of the elastic shear modulus. It is lower for PEEK 2 than for PEEK 3 in the entire frequency range measured (more than one decade difference at 0.01 Hz). The loss shear modulus of PEEK 2 is also lower than PEEK 3. This results in a higher stiffness for PEEK 3.



3 Frequency sweep of PEEK 2



4 Frequency sweep of PEEK 3

### From the Zero Shear Viscosity Plateau to the Molecular Mass

Figure 5 compares the complex viscosity ( $\eta$ ) of all three samples. The curves of PEEK 1 and PEEK 2 are almost parallel, both reach a Newtonian plateau in the low-frequency range and show a shear-thinning behavior at higher frequencies. The level of the Newtonian plateau is related to the molecular mass of the polymer: The higher the molecular mass, the higher the zero viscosity. [1]

In contrast, the complex viscosity ( $\eta^*$ ) of sample 1 continues to increase with decreasing frequencies and the Newtonian plateau is still not reached at a frequency of 0.01 Hz. Moreover, for the complete frequency range measured, this PEEK material shows higher complex

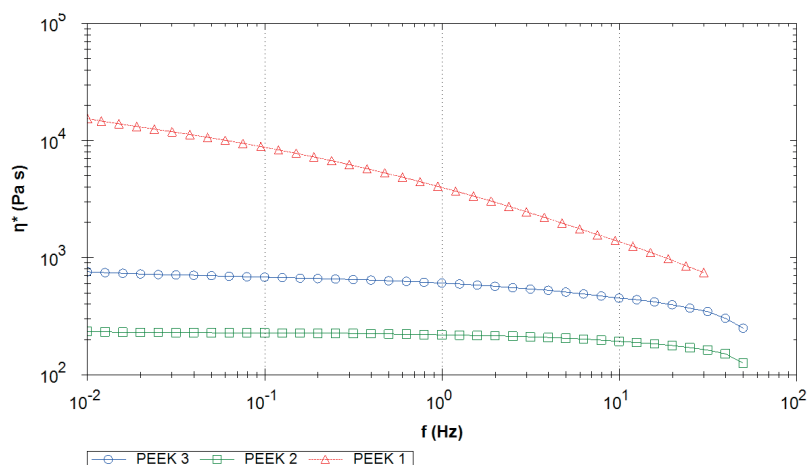
The **complex viscosity  $\eta^*$**  is obtained from the complex stiffness  $G^*$  and the angular frequency  $\omega$ :

$$\eta^* = G^*/\omega$$

It expresses in [Pa·s].

viscosity with more than 1.5 decades difference to sample 2 at 0.01 Hz.

From the level of shear viscosity plateau of all three samples, it can be concluded that PEEK 1 has a higher molecular mass, followed by PEEK 2 and PEEK 3. This confirms the results obtained by the  $G'$  and  $G''$  curves.



5 Comparison of the complex viscosity of the 3 materials.

### Conclusion

The rheological behavior of three PEEK samples were characterized using the Kinexus rotational rheometer. They differ in the value of the zero-shear viscosity plateau of the complex viscosity. This is due to differences in the molecular masses of the materials.

### Literature

[1] Rotational Rheology: Interpretation of Data by Application, Netzsch Application Book, Philip Rolfe, [www.netzsch-thermal-analysis.com](http://www.netzsch-thermal-analysis.com)