Crystallization of a High-Performance Semi-Crystalline Polymer: PEEK

Claire Strasser and Senol Gezgin

Introduction

In the molten state, the polymer chains of a semi-crystalline polymer are in a disordered state. During cooling, some of them rearrange to form ordered regions and crystallize. In addition to this crystalline phase, a semi-crystalline polymer also contains an amorphous phase without an ordered molecular structure (see figure 1). Cooling does not lead to crystallization of this phase, but to a transitions from a soft to a hard brittle state. This transition is called the glass transition.

Different methods can characterize the crystallization and glass transition of polymers, providing a variety of valuable information.

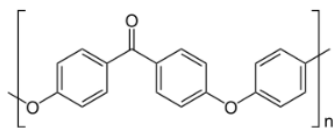A typical method for analyzing thermal transitions is Differential Scanning Calorimetry (DSC). It provides information about the glass transition, phase transformations like crystallization/melting or solid-solid phase transitions and degree of crystallinity, etc. Its ease-of-use and ability to automate measurement steps have made it a popular and widely used technique.

Crystallization and glass transition have a significant influence on the mechanical properties of a product. Another method for determining these parameters is rheology. A measurement using a rotational rheometer provides information on the rheological changes that occur as a semi-crystalline polymer cools from the melt into the glassy state.

In the following, the cooling behavior of polyether ether ketone (PEEK) (see chemical structure in figure 2) is determined using the DSC 303 *Caliris®* and Kinexus rotational rheometer.
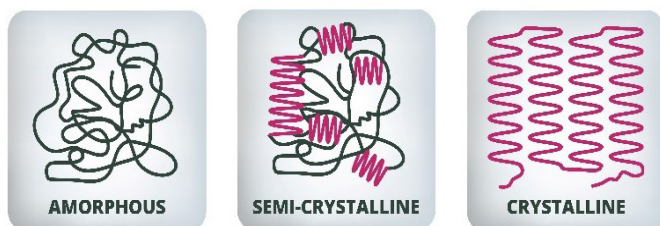
1 A semi-crystalline polymer is made of an amorphous, disordered phase and an ordered, crystalline region.

2 Chemical structure of PEEK (polyether ether ketone); source: polysciences.com.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Phone: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

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Measurement Parameters

The PEEK sample was heated to above its melting temperature. After an isothermal phase, the polymer was cooled down at a controlled cooling rate. The standard cooling rates of the respective methods were used, i.e., 10 K/min for the DSC 300 *Caliris®* and 2 K/min for the Kinexus rotational rheometer. Table 1 summarizes the measurement conditions.

DSC 303 *Caliris®*: Crystallization Behavior

Figure 3 displays the resulting curve of the DSC measurement performed on PEEK. The exothermal peak beginning at 305°C (endset temperature) is due to the crystallization of PEEK. The step in the DSC curve with midpoint at 146°C is the glass transition.

Table 1	Measurement parameters	
Instrument	DSC 300 *Caliris®*	Kinexus HTC Prime
Crucible	*Concavus* (aluminum)	-
Sample mass	9.80 mg	-
Temperature program	370° to 30°C	400°C to 40°C
Cooling rate	10 K/min	2 K/min
Atmosphere	Nitrogen (40 ml/min)	NItrogen (1 ml/min)
Geometry	-	PP8 (plate-plate, diameter: 8 mm)
Gap	-	1 mm
Shear strain	-	Within linear-viscoelastic range (LVER)
Frequency	-	1 Hz
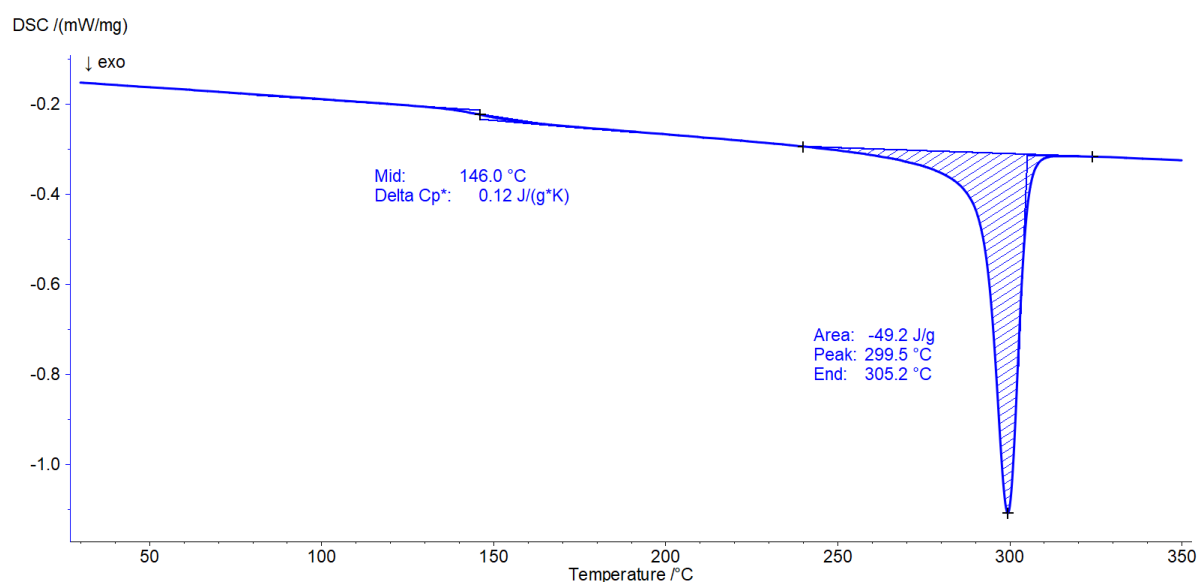
3 Cooling curve of the DSC measurement on PEEK from 350°C to room temperature

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Kinexus Rotational Rheometer: Stiffness

Figures 4 and 5 depict the typical curves resulting from the temperature sweep performed on PEEK.

The Melt State

Providing no reaction occurs, the complex shear viscosity (figure 4) increases with decreasing temperature. This is the expected influence of temperature on stiffness in the absence of a physical or chemical process, as the mobility of polymer chains increases during heating.

The melt state is also characterized by domination of G" over G´ (figure 5). In other words, at this temperature, the "liquid-like" properties have more influence on the deformation behavior of PEEK than the "solid-like" properties. The polymer flows for the timescale of the applied frequency, even if it still features strong elastic properties (phase angle value closer to the value 45° than to 90°).
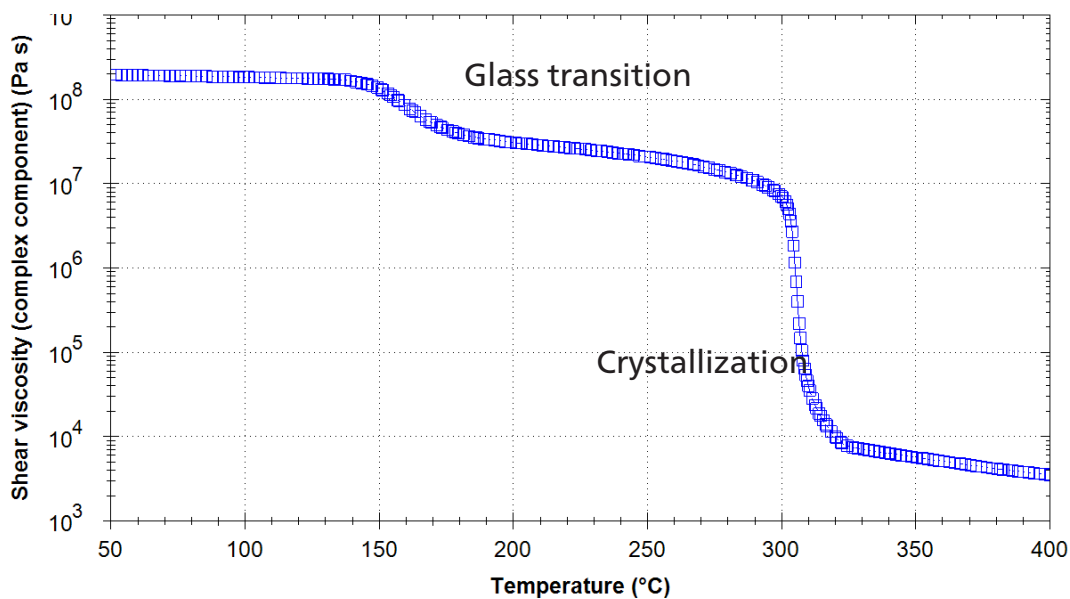
4 PEEK during cooling at 2 K/min. Complex shear viscosity.
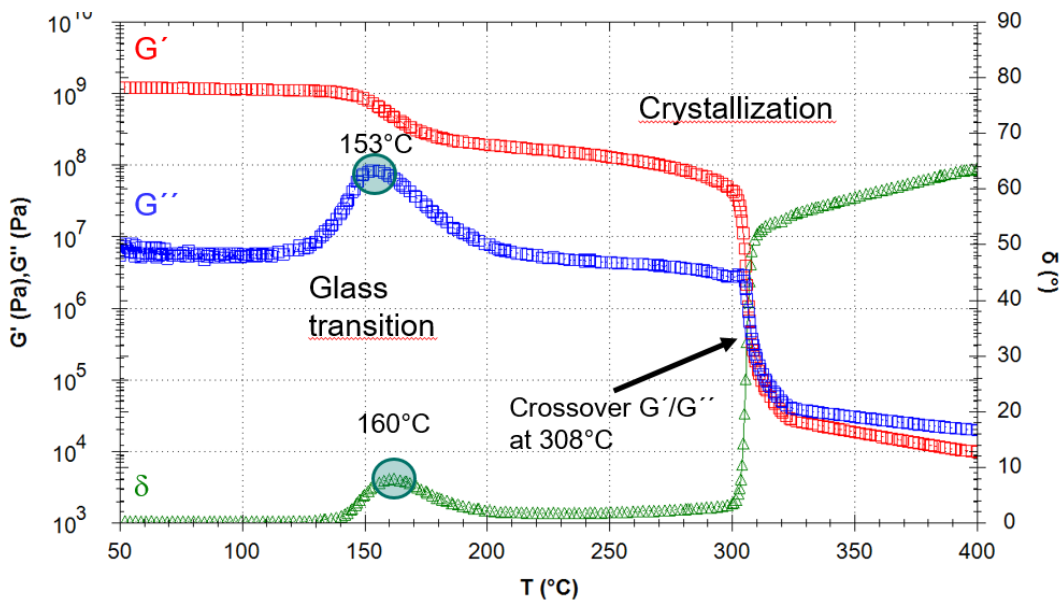
5 PEEK during cooling at 2 K/min. Elastic (red) and viscous (blue) shear moduli, phase angle (green).

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Occurance of Crystallization

At 325°C, the slope of the complex shear viscosity curve changes (Figure 4). The complex shear viscosity increases from 7.7E+03 Pa·s at 325°C to 9.0E+06 Pa·s at 295°C, an increase of more than 3 decades in only 30°C! This significant increase is typical for the crystallization of a crystalline or semi-crystalline polymer.

The process also greatly affects the elastic (G') and viscous (G") shear moduli (figure 5). Both curves increase and show the crossover at 308°C. Between crystallization and glass transition, the amorphous phase is in the rubbery plateau. The polymer chains belonging to the amorphous phase are still free to move, while the crystalline phase gives structure to the product.

The higher the degree of crystallinity, the higher the value of the elastic shear modulus. The phase angle lies at 2° to 3°, so that the polymer is now close to a perfect elastic solid.

Glass Transition

The glass transition is reached during further cooling. Stiffness continues to increase but not as significantly as during crystallization (3.0E+07 Pa·s at 200°C to 1.6E+08 Pa·s at 140°C, figure 4).

While the glass transition temperature is usually evaluated by means of the peak temperature, which is typical for the curves of G" and δ (figure 5), cooling over the glass transition is also related with an increase in the G' curve. At temperatures lower than the glass transition temperature, the phase angle decreases again and is close to 0. The polymer is in a glassy, stiff state.

Conclusion

This application example shows how DSC and rotational rheology complement each other. Both methods provide different information describing the crystallization and glass transition of semi-crystalline polymers, thus providing a comprehensive insight into the material behavior during heating and cooling. The typical detected effects are summarized in Tables 2a and 2b.

| Table 2a | Typical effects measured during crystallization and glass transition of a semi-crystalline polymer by means of the DSC 300 *Caliris®* |

	Typical Effect	Evaluation of the effect	Information
Crystallization	Exothermal peak	Endset	Start of crystallization[1]
		Peak maximum	Crystallization temperature
		Peak enthalpy	Related to degree of the crystallinity (normally: evaluation during heating)
Glass transition	Step in heat capacity	Onset/endset	Glass transition start/end[2]
		Midpoint	Glass transition temperature[2]
		Height	Amorphous amount

[1] in accordance with DIN ISO 11357-5:2014
[2] in accordance with DIN ISO 11357-2:2014

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| **Table 2b** | Typical effects measured during crystallization and glass transition of a semi-crystalline polymer by means of the Kinexus rotational rheometer |

Measured curve	Complex shear viscosity	Elastic shear moduus G'	Viscous shear modulus G"	Phase angle δ
Before the crystallization (melt state)	Temperature dependence of stiffness in the liquid state No effect	G' < G" The "liquid-like" properties dominate, the polymer flows		>45°: The lower the value, the more elastic the molten polymer is.
Crystallization process	Strong increase (more than 3 times due to T$_g$). Crystallization start/end	Increase		Decrease from δ > 45° to δ < 45°
Crystallization temperature	Midpoint	Crossover G'/G"		δ = 45°
Between T$_c$ and T$_g$; rubbery plateau	Temperature dependence of the stiffness in the rubbery plateau. No effect.	G' > G" The "solid-like" properties dominate, the crystalline phase gives a structure to the polymer, no flowing.		δ < 45° The lower δ, the stiffer the sample
Glass transition	Increase	Increase	Peak: Glass transition temperature	Peak: Glass transition temperature
After T$_g$: Solid state	Temperature dependence of the stiffness in the solid state	-	-	Minimum value of δ

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