Optimizing Injection Molding Parameters of HDPE by Means of DSC and Kinetics Neo

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Introduction

Injection molding is the primary process in the polymer industry for producing parts of a defined shape. The molten polymer is injected into a relatively cold mold cavity where it is rapidly cooled. The temperature of the mold directly influences the crystallization rate and thus the properties of the final product, so it must be perfectly defined. To this end, the use of a DSC for isothermal crystallization tests, where the behavior of a polymer in the mold is simulated, is a real gain in time.

Fast Cooling and Stabilization

For isothermal crystallization tests, a DSC must fulfill two requirements. The sample must be cooled very quickly to prevent the start of crystallization during cooling. In addition, the temperature must be stabilized at the specified crystallization temperature without any under- or overshooting. Particularly a temperature undershot can lead to the premature start of crystallization. Some polymers such as polyolefins crystallize very fast. Only a few seconds at a temperature slightly below the target temperature can unintentionally start crystallization.

Thanks to the low thermal mass of its furnace, the P-Module of the DSC 300 *Caliris*® achieves very fast heating and cooling rates as well as excellent temperature control during subsequent isothermal segments.

In this example, isothermal crystallization tests were carried out on a high-density polyethylene with the NETZSCH DSC 300 *Caliris*®. After heating to 230°C, i.e., to a temperature higher than the melting temperature of HDPE (High Density Polyethylen), followed by a 5-minute isothermal segment, the samples were cooled down at a high cooling rate to three different crystallization temperatures. Table 1 details the measurement conditions.

Table 1 Conditions for the isothermal crystallization tests

Device	DSC 300 *Caliris*® with P-Module		
Crucible	*Concavus*® (aluminum), pierced lid		
Sample mass	5.55 mg	5.68 mg	5.58 mg
Temperature range	230°C to temperature of crystallization		
Temperature of crystallization	122.5°C	123.0°C	123.5°C
Nominal cooling rate	200 K/min		
Atmosphere	Nitrogen (40 ml/min)		

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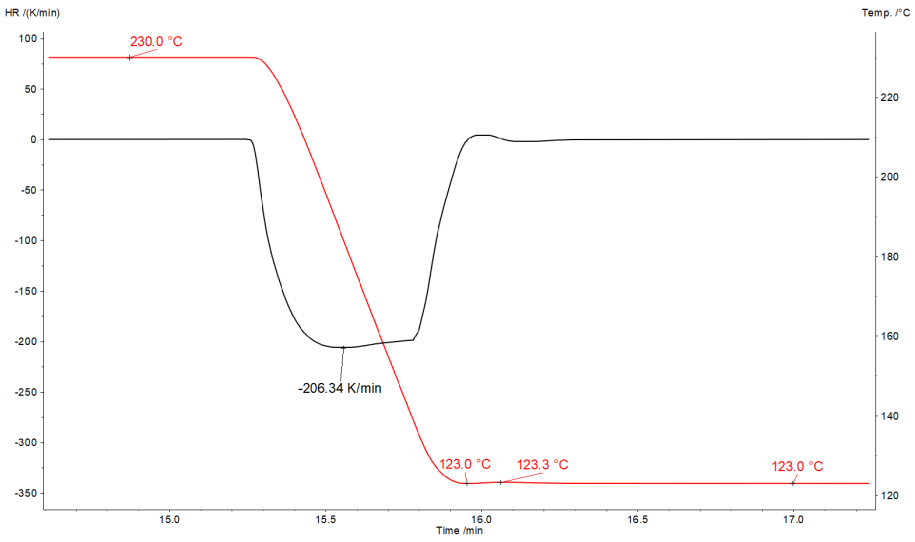
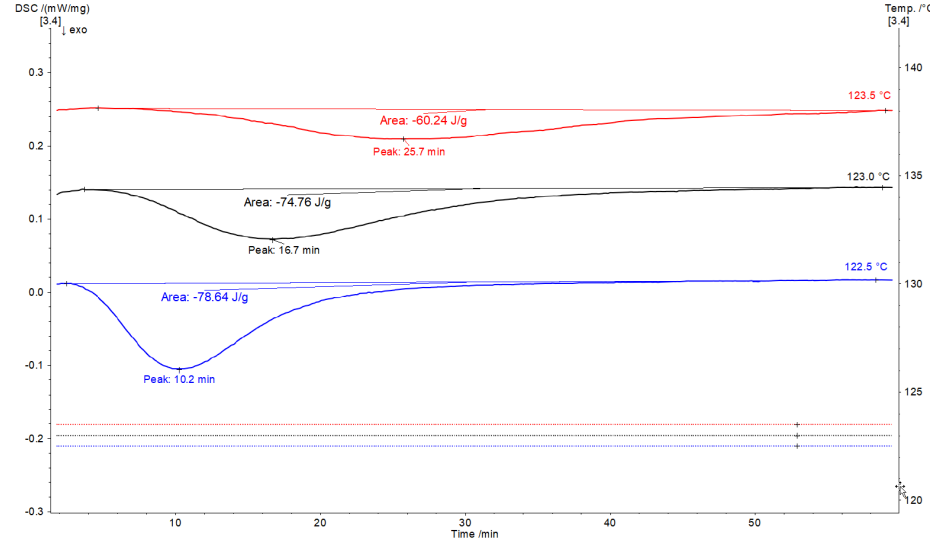
Measurement Results

The temperature profile of the cooling to 123.0°C demonstrates the excellent stability of the temperature during the isothermal segment after the targeted crystallization temperature was reached (figure 1).

Figure 2 presents the resulting DSC curves for the isothermal segments at 122.5°C, 123.0°C and 123.5°C. Due to the fast stabilization of the temperature at the specified value, the initial effect on the DSC curve caused by the segment change from cooling to isothermal is low enough to allow separation from the thermal effects occurring at its beginning. The exothermal peak detected during the isothermal segment of the three measurements can be attributed to the crystallization of polyethylene. As expected, the crystallization enthalpy (peak area) increases as the temperature of the isothermal segment decreases, indicating a higher degree of crystallinity in the final product. Also, the slope of the peak is steeper with decreasing isothermal temperature, so the peak minimum is reached faster. This signifies a faster crystallization.



1 Temperature profile of the cooling run to 123°C



2 Isothermal crystallization of HDPE at 3 different temperatures

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From DSC Measurements to the Kinetics of Crystallization: Kinetics Neo

The dependence of the crystallization peak on the temperature allows for the use of DSC curves for a kinetics analysis of the crystallization process. For this, the Kinetics Neo software was used. It can assign each individual step different reaction types with kinetic parameters of their own, such as activation energy, order of reaction, and pre-exponential factor.

The rate of chemical reaction for each crystallization step, j, can be written as the product of two functions, where the first function, $f_j(e_j,p_j)$, depends on the concentrations of the reactant (e_j) and product (p_j). The second function, $K_j(T)$, depends on temperature [1].

$$\text{Crystallization rate} = f_j(e_j,p_j) \cdot K_j(T)$$

e_j – concentration of non-crystallized material

p_j – concentration of product (crystallized material)

Here, a one-step reaction was selected for the crystallization kinetics. Crystallization model by Sbirrazzuoli [2] uses the Nakamura dependence K(T) und Sestak-Berggren dependence on concentrations f(e,p):

$$f(e,p) = e^n \cdot p^m \cdot [-\ln(e)]^q$$

n: order of reaction

m: order of autocatalysis

q: order of Logarithmic term

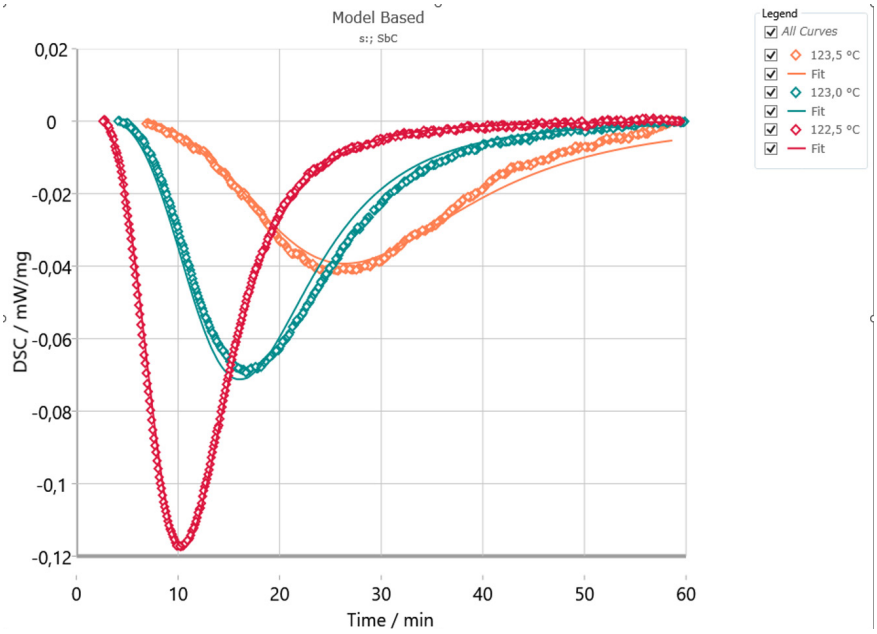
Use of this model requires knowledge of the glass transition and melting temperature of the sample, even if the software will be optimizing the value of the melting temperature. The kinetics evaluation will then be valid across the entire temperature range between those two temperatures.

Additionally, the function K(T) includes the parameters U and KG which are optimized by the Kinetics Neo software.

Figure 3 depicts the measurement curves as well as the curves calculated in Kinetics Neo using the kinetics model described above. Table 2 summarizes the parameters of the kinetics. The results show the good accordance between the measured and the calculated results. The coefficient of correlation amounts to 0.996.

Table 2 Parameters of the crystallization kinetics

Reaction type	Sbirrazzuoli crystallization
Nakamuar KG	24.384
Log(PreExp) [Log(1/2)]	2.072
Order of reaction, n	1.286
Order of autocatalysis, m	0.695
Order of logarithmic term, q	0
Melting temperature [°C]	130
Glass transition temperature [°C]	-130
U* [kJ/mol]	6.30



3 Comparison of the measurement curves (symbols) with the calculated curves (continuous lines).

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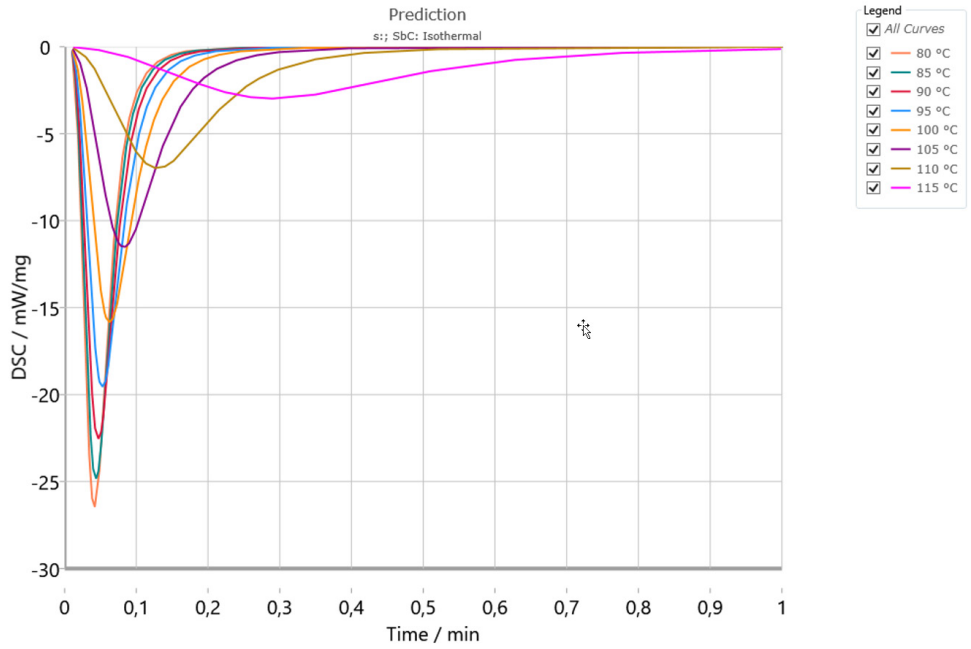

4 Predictions of the crystallization process for different isothermal temperatures.

Based on the results, Kinetics Neo is capable of simulating the reaction for user-specified temperature programs. For example, figure 4 displays the DSC curves obtained for crystallization temperatures between 80°C and 115°C. As expected, the lower the temperature, the faster the reaction. If the material is injected into a small mold at a temperature of 80°C, it will crystallize in a few seconds. If the mold is at 115°C, the polymer will require one minute for complete crystallization.

DSC Tests Accompanying Production for Saving Time and Money

Isothermal crystallization tests can be carried out with the NETZSCH DSC 300 *Caliris*® on polyethylene – a polyolefin known for its fast crystallization. DSC tests are easy to carry out and require only a small sample mass. In particular, isothermal crystallization measurements help determine appropriate processing conditions such as mold temperature and cooling time so that the resulting parts have all the properties required.

Literature

[1] NAKAMURA, K., WATANABE, T., KATAYAMA, K., AMANO, T., Some aspects of non-isothermal crystallization of polymers — Part I: Relationship between crystallization temperature, crystallinity and cooling conditions, Journal of Applied Polymer Science, Vol. 16, pp. 1077-1091, 1972

[2] Vyazovkin S., Sbirrazzuoli N. 2004 Isoconversional Approach to Evaluation of the Hoffman-Lauritzen Parameters (U* and Kg) from the Overall Rates of nonisothermal Crystallization, Macromolecular Rapid Communications, 2004, 25. 733-738.

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