

# Nakamura Model for Polymer Crystallization Kinetics During Cooling

Dr. Elena Moukhina, Research & Development, and Dr. Stefan Schmölder, Applications Laboratory

## Introduction

Thermoplastic polymers are polymers which become moldable at a certain elevated temperature. In this state, they can be molded and upon cooling, the polymer solidifies and stays in the desired shape.

For example, in the production of PET bottles, firstly the PET preform is manufactured by an injection molding process, and then PET preforms are expanded with compressed air to the bottle shape. During injection molding, thermoplastic polymers are quickly cooled down from the melt temperature to the temperature of the mold, which is typically between 20°C and 120°C. In the case of semi-crystalline polymers, crystallization starts at temperatures below the melt temperature, and the crystallization rate depends on the degree of supercooling.

On the other hand, semi-crystalline polymers also exhibit glass transitions at lower temperatures. As soon as the glass transition temperature is reached, the polymer is in the glassy state. Then no more crystallization will occur, even with high supercooling.

## Crystallization under High Cooling Rates

Therefore, it is very important to know what the crystallization rate is, what fraction of the polymer becomes crystalline, and what fraction is in the glassy state at low temperatures. During the injection molding process, it is possible for cooling rates to be so high that crystallization cannot be measured with a conventional DSC. In such cases, the Kinetics Neo software can be used for predicting the crystallization process. The crystallization rate of polymers depends on two parameters: the current degree of crystallization,  $\alpha$ , and the temperature,  $T$ .

$$\text{Crystallization rate} = f(\alpha) \cdot K(T) \quad (1)$$

The first part of Equation (1),  $f(\alpha)$ , depends on the degree of crystallization. In this case, the Avrami equation (nucleation type with dimension  $n$ ) was considered:

$$f(\alpha) = n \cdot (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{\frac{n-1}{n}} \quad (2)$$

The second part of Equation (1),  $K(T)$ , is the reaction constant at the temperature  $T$ . It has a non-Arrhenius dependence on temperature.

In the simplest case of isothermal crystallization, the function  $K(T)$  is a constant value, and crystallization is described just by the Avrami equation. But for crystallization during cooling, we must take into account that the crystallization rate depends on the current temperature with respect to the temperatures of melting and glass transition. Above the melting temperature, the material is in a liquid phase and no crystallization takes place. If the material temperature is below the glass transition temperature, the material is in the glassy state, where the polymer chain motion is so slow that no further crystallization occurs.

If the reaction constant  $K(T)$  at the temperature  $T$  is known, then – based on Equations (1) and (2) for the cooling rate  $\beta$  – it is easy to obtain the Nakamura equation for the degree of crystallization  $\alpha$ :

$$\alpha(T) = 1 - \exp\left\{-\left[\frac{1}{\beta} \int_{T(0)}^{T(t)} K(T) dT\right]^n\right\} \quad (3)$$

DIN EN ISO 11357-7:2015-12 uses this Nakamura equation for the kinetic analysis of non-isothermal crystallization during cooling.

For the analytical dependence of  $K(T)$ , the Hoffman-Lauritzen theory can be used:

$$K(T) = A \cdot \exp\left(\frac{-U}{R(T-T_\infty)}\right) \exp\left(\frac{K_G}{T\Delta T f}\right) \quad (4)$$

with

$A$ : pre-exponential factor

$U$ : activation energy of segmental jump in polymers; this parameter has a universal value of 6.3 kJ/mol

$T_\infty = T_g - 30$ : temperature at which crystallization transport is finished; this temperature is 30 K below the glass transition temperature  $T_g$ .

$K_G$ : kinetic parameter for nucleation

$\Delta T = T_m - T$ : undercooling from the equilibrium melting point  $T_m$

$f = 2T/(T_m + T)$ : correction factor.

The melting temperature  $T_m$  and glass transition temperature  $T_g$  are usually known, but could be adjusted a bit during optimization. Other parameters like  $K_G$ ,  $A$ , and  $n$  will be found by the Kinetics Neo software.

# Crystallization Kinetics

## Example of Crystallization Prediction: Polyethylene Terephthalate (PET)

Within a crystallization experiment, six measurements (figure 1) were carried out with the DSC 204 **F1 Phoenix**® at cooling rates from 1 K/min to 10 K/min. Each crystallization peak has a different crystallization enthalpy ranging from 2.5 J/g at 10 K/min to 38.4 J/g at 1 K/min due to incomplete crystallization for higher cooling rates.

For the analysis, the following known values for the glass transition temperature and for the melting temperature are taken:

$$T_g = 70^{\circ}\text{C to } 80^{\circ}\text{C}; T_m = 240^{\circ}\text{C to } 260^{\circ}\text{C}.$$

Figure 2 presents the Nakamura model; here, the experimental values are presented as rhombuses and the simulated curves in solid lines. Calculation of the simulated curves is carried out according to the Nakamura model.

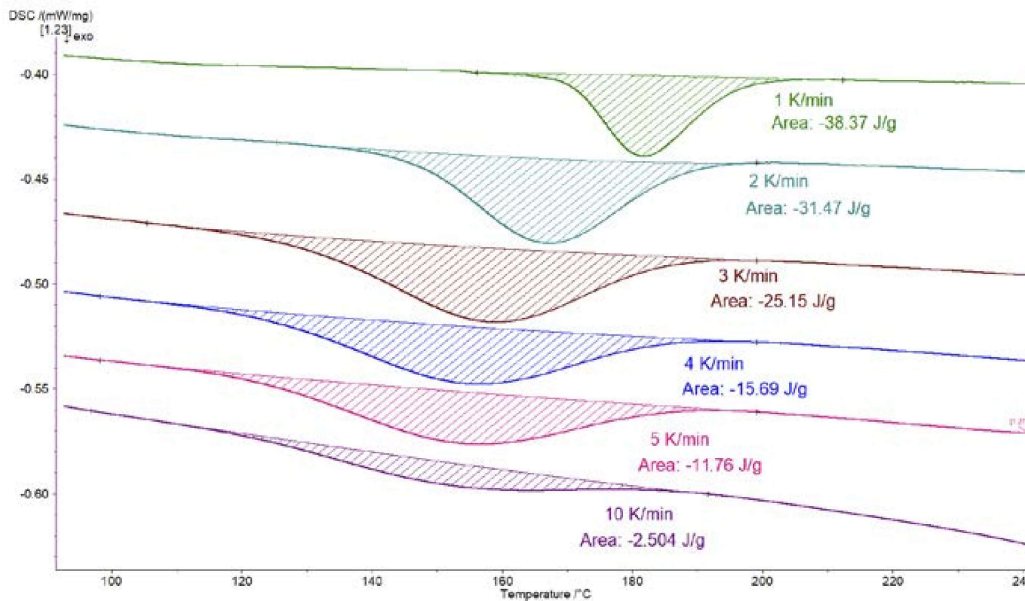


Fig. 1. Crystallization curves for polyethylene terephthalate (PET) measured at cooling rates from 1 to 10 K/min

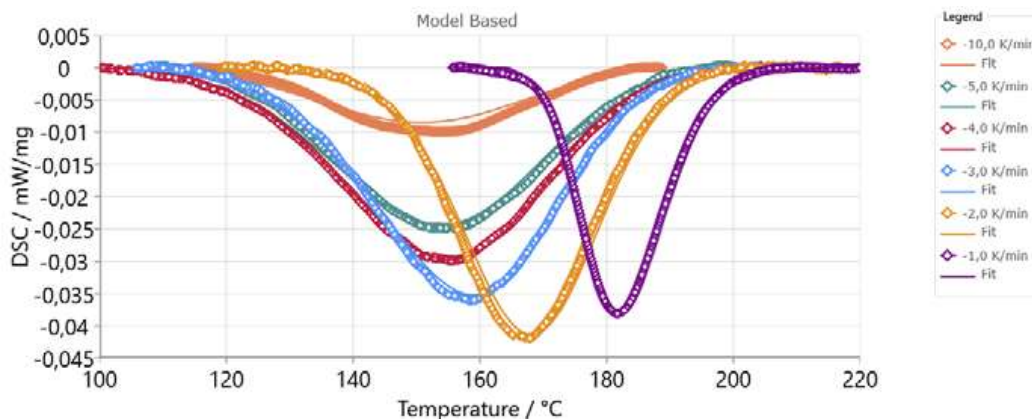


Fig. 2. Experiment and model according to Nakamura for non-isothermal crystallization during cooling

# Crystallization Kinetics

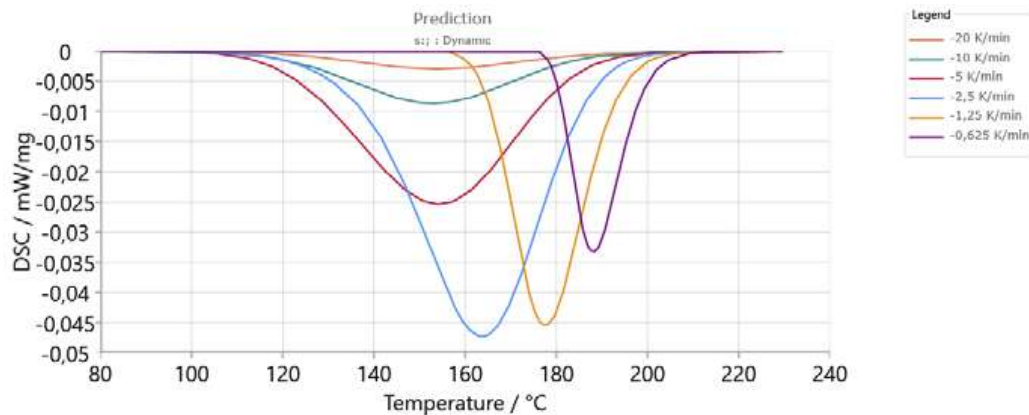


Fig. 3. Prediction of crystallization at fast cooling rates up to 20 K/min. Peak shapes and peak areas are different because of the incomplete crystallization

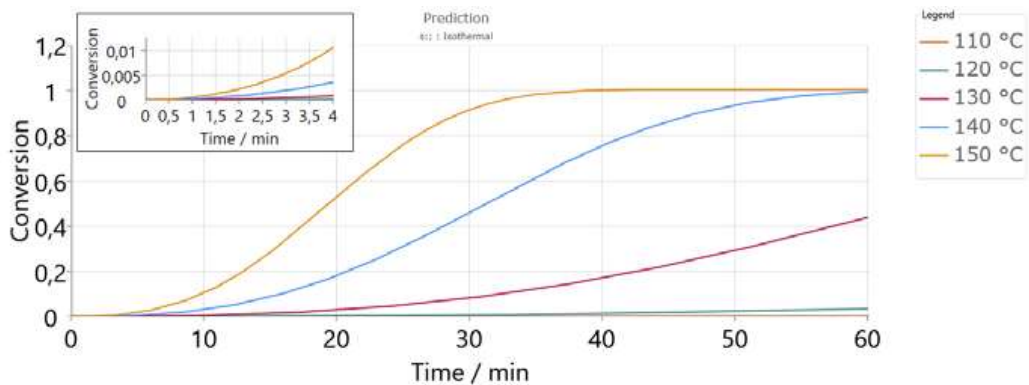


Fig. 4. Isothermal crystallization at temperatures from 110 to 140°C

In figure 3, the prediction of the crystallization process is shown. Crystallization is not complete for fast cooling because of the glass transition. Here, the polymer is partially amorphous. During injection molding, the PET preform undergoes fast cooling to 110°C and then no more crystallization will occur in the glassy state.

For the production of PET bottles, the preforms are heated and expanded with compressed air to the bottle shape (Stretch Blow Molding). Figure 4 shows the simulated crystallization during this process.

One can observe that at temperatures of 110°C to 120°C, no crystallization occurs and the bottles remain in the glassy state and transparent. If the production temperature is too high – e.g., 140°C

– then crystallization starts earlier, and the bottles get turbid.

## Conclusion

Kinetics NEO is a very helpful tool for gaining an understanding of even complex production steps in polymer processing. By knowing the kinetics of the processes, as are shown here for the crystallization process, it is possible to simulate production steps. Instead of carrying out time-consuming experiments, it is possible to simulate different processing conditions in order to draw conclusions, resulting in a more efficient production of polymer parts.