

Clever Tool for Short Cooling Times

Systematic Approach to the Selection of Nucleating Agents

The precise prediction of polypropylene's crystallization behavior is of great economic importance. Not only do important processing parameters – such as mold temperature and time, and therefore productivity – depend on it, but so do the mechanical properties of the manufactured product. DSC measurements are helpful in precisely assessing the influence of different nucleating agents.

The most common forming technique for manufacturing polypropylene is injection molding. The polymer melt is filled into a tempered mold cavity, followed by a holding pressure during cooling to compensate for the shrinkage of the polymer due to crystallization prior to

polymer melt, around which the polymer chain can crystallize, forming spherulites [2]. So-called nucleating agents are commonly used as additives because of their influence on the nucleation process, and therefore on crystallinity (i.e., the mechanical properties) of the final product.

finished part: it is stiffer than the product without additives. Moreover, some nucleating agents – the clarifying agents – reduce the spherulite size down to a scale where the visible light is no longer scattered. This leads to decreased haze and increased clarity of, for example, transparent polypropylene products [1, 2].

In the following, the influence of different nucleating agents on the crystallization of polypropylene and their benefit for its processing were investigated by means of DSC (Differential Scanning Calorimetry). For this purpose, dynamic and isothermal crystallization measurements were carried out, followed by thermokinetic modeling of the isothermal results. The results were used to predict the crystallization behavior for user-specific temperature programs.

Experiments for the Crystallization Behavior

Besides pure isotactic polypropylene homopolymer (grade: Moplen HP500V, manufacturer: Basell Polyolefine GmbH, Wesseling, Germany), two additional samples – each containing a different nucleating agent – were investigated. One of these additives was a commercial trisamide-based clarifier (grade: Irgaclear XT 386, manufacturer: BASF SE, Ludwigshafen, Germany) with a concentration of 200 ppm, the other one a β -nucleator (grade: Njstar NU-100, manufacturer: New Japan Chemical Co. Ltd., Osaka, Japan) with a concentration of 400 ppm.

The crystallization behavior was examined by means of dynamic and isothermal DSC measurements using a »

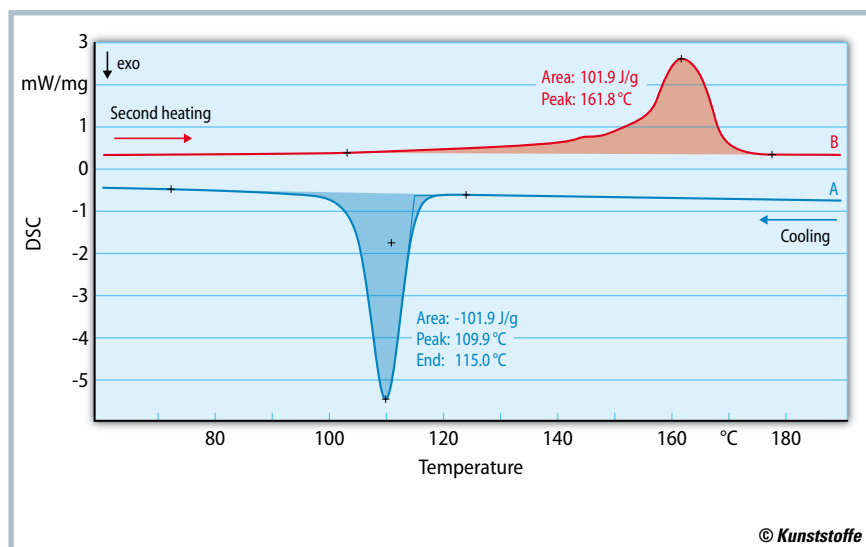


Fig. 1. Cooling (bottom) and second heating (top) of pure polypropylene: crystallization peak in the cooling segment at 110 °C (A) and melting peak in the second heating segment at 162 °C (B)

(source: Netzsch)

ejection of the finished part. The crystallinity of the final product, and thus its mechanical properties, is not only influenced by the structure of the polymer, but also by the mechanism of nucleation and processing parameters such as molding temperature and time [1].

During nucleation of thermoplastic polymers, domains of crystal growth form from foreign particles present in the

They are of interest in terms of both economic and scientific aspects.

Firstly, they increase the crystallization temperature of the polymer so that the cooling time of the molding cycle is reduced, leading to an increased productivity. Secondly, they provide numerous nucleating domains so that the formed spherulites remain smaller. This has an impact on the mechanical properties of the

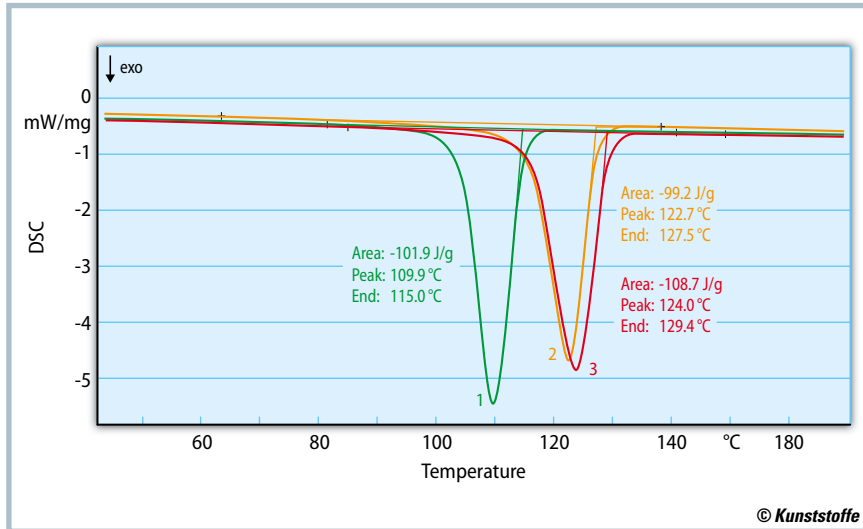


Fig. 2. DSC curves of pure PP and PP with different nucleating agents during cooling at 20 K/min: Pure polypropylene (green), polypropylene with NU-100 (yellow) and polypropylene with trisamide (red) (source: Netzsch)

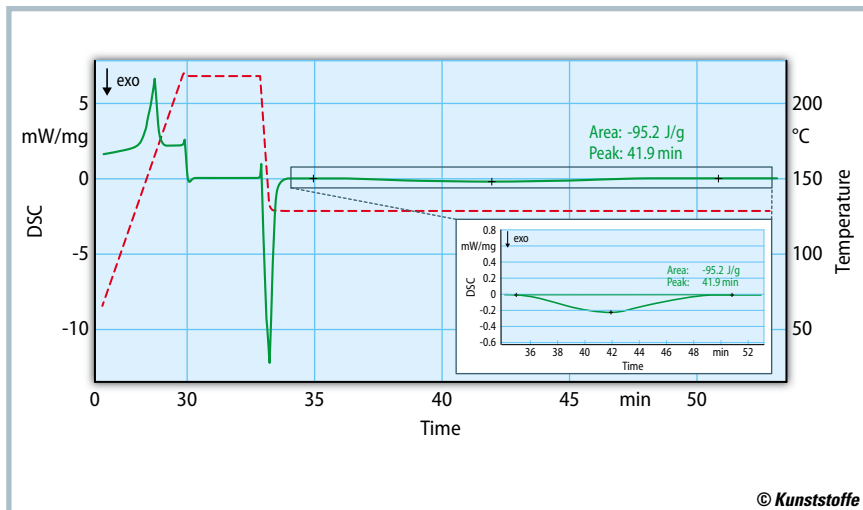


Fig. 3. Isothermal crystallization of pure polypropylene at 128°C (dashed curve: temperature; solid curve: DSC signal); The detail excerpt clearly illustrates the marked, broad exothermal crystallization peak thanks to modified scaling (source: Netzsch)

heat-flow differential scanning calorimeter (DSC 214 Polyma, manufacturer: Netzsch-Gerätebau GmbH, Selb, Germany). All measurements were carried out in closed aluminum crucibles with pierced lid and in a dynamic nitrogen atmosphere. Low sample masses (< 4 mg) were used to ensure that the samples could follow the fast temperature changes during isothermal crystallization tests.

The measurement curves were used to determine the kinetic parameters of the crystallization reaction. For that, the accelerating Avrami equation for modeling of the crystallization rate (method described in ASTM standard E2070-13 [3]) was used. The calculation was also car-

ried out with Kinetics Neo (manufacturer: Netzsch-Gerätebau GmbH). This comprehensive software allows for modeling the kinetics of the reactions of one or more steps, where each individual step can be assigned to different reaction types.

Dynamic Measurements

The prepared samples were heated up to 220°C in order to ensure their complete melting. After a one-minute isothermal step, they were cooled down to room temperature before they were heated to 220°C again. The heatings and cooling were carried out at a linear heating rate of

20 K/min. Presented in **Figure 1** are the DSC curves of the cooling and the second heating of pure polypropylene. The exothermal peak detected during cooling (lower curve) corresponds to the crystallization of the polymer. During the following heating segment, this crystalline phase melts again (endothermic peak in upper curve).

The difference between both peak temperatures (162°C during the second heating vs. 110°C during cooling) is due to the supercooling behavior of polypropylene. It clearly shows that during, for example, the molding process, the mold temperature must be far below the melting temperature in order to initiate crystallization.

Adding appropriate nucleating agents reduces the supercooling effect. **Figure 2** displays the cooling curves of pure polypropylene (green) in comparison to polypropylene with NU-100 (yellow) and polypropylene with trisamide (red). The deviation of the DSC curve from the baseline indicates the start of the crystallization represented by the extrapolated endset. Pure PP shows the endset at 115°C. This temperature is shifted by 17°C and 19°C, respectively, to higher temperatures concerning the two polymers containing nucleating agents. This clearly demonstrates the great advantage of nucleating agents: they increase the crystallization temperature, leading to a decrease in cooling time between molten and crystallized sample.

This property can be applied to injection molding applications: The crystallization time in the mold is reduced when nucleating agents have been incorporated into the polymer mixture, leading to a reduction in cycle times.

Isothermal Crystallization Measurements

During the second test series, the prepared samples were heated to 220°C to ensure complete melting of the PP spherulites. After a 3-minute isothermal step, the samples were cooled down at a nominal cooling rate of 300 K/min to the specified isothermal temperature. This temperature was then kept constant until the end of the crystallization peak.

The isothermal temperature was chosen in such a way that the complete exothermal crystallization peak could be re-

corded during the isothermal segment. This makes high demands on the temperature control of the DSC instrument because the isothermal segment has to be reached quickly but without temperature underflow. In fact, a cooling rate that is too low can lead to the beginning of crystallization already during cooling, as a temperature underflow would also do.

Figure 3 shows the temperature profile of the cooling segment from 220 °C to 128 °C and the isothermal step at 128 °C (dashed line) along with the corresponding DSC signal (continuous line) of pure polypropylene. The exothermic peak (magnified in the insertion) is due to crystallization of the polymer detected during the isothermal segment. This effect is well

separated from the DSC effect resulting from the change of the segment with fast cooling rate into the isothermal segment. This allows for correct evaluation of the total crystallization peak enthalpy (95 J/g).

This procedure was repeated at four further different isothermal temperatures: 124 °C, 125 °C, 126 °C and 127 °C. Figure 4 shows the DSC signals at these four isothermal segments together with the measurement at 128 °C. As expected, crystallization occurs faster with decreasing isothermal temperature. At 124 °C, the peak minimum of the exothermal crystallization peak is detected at 2.8 min after switching from the cooling to the isothermal segment. However, using a higher isothermal temperature at, for example, »

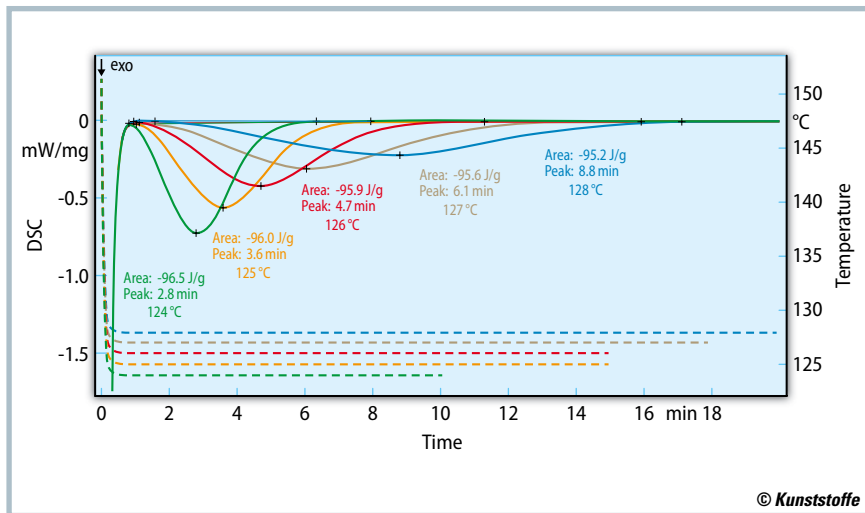


Fig. 4. Isothermal crystallization of pure polypropylene at five temperatures between 124 °C and 128 °C (dashed: temperature, continuous: DSC signal) (source: Netzsch)

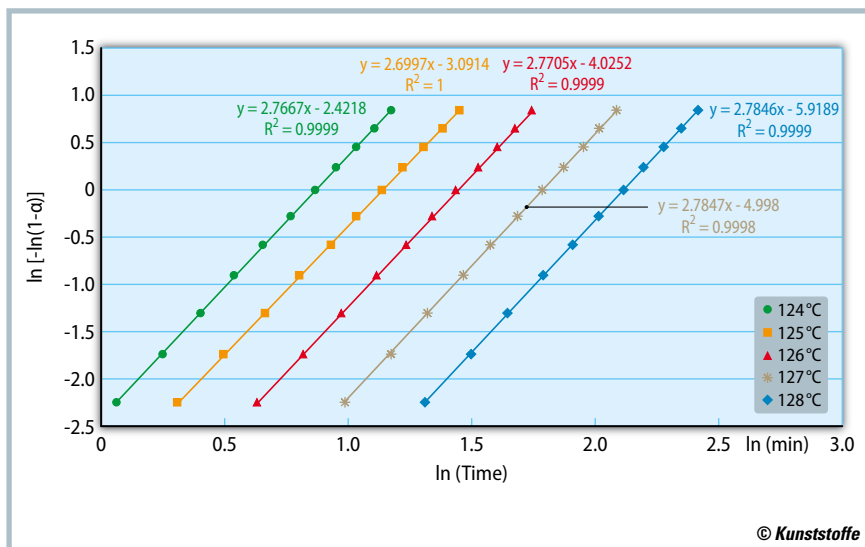


Fig. 5. Avrami plot for the isothermal crystallization of pure polypropylene at different temperatures. Points are calculated for the conversion rates from 10 to 90 % of the total peak area (source: Netzsch)

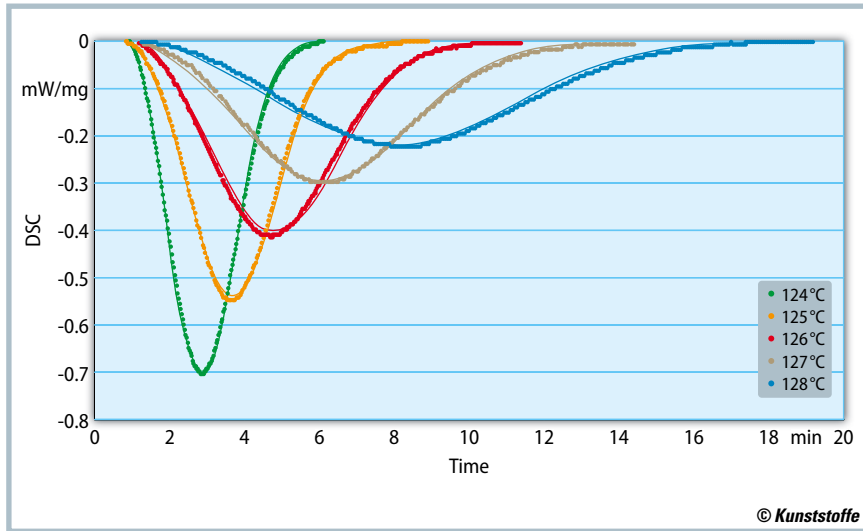


Fig. 6. Comparison of the measured and calculated crystallization behavior of pure PP: The simulation (lines) on the basis of a one-step reaction according to the Avrami equation is in good agreement with the DSC measuring points (correlation coefficient: 0.998) (source: Netzsch)

128°C, the minimum of the crystallization peak is monitored 6 min later. The crystallization enthalpy is between 95.2 J/g and 96.5 J/g, increasing with decreasing crystallization temperatures.

Similar tests were carried out on two nucleated polypropylenes (PP+NU-100 and PP+trisamide). Due to nucleation of these samples, higher crystallization temperatures were expected. For this reason, the isothermal test temperatures were increased to 137–142°C for PP+NU-100 and to 142–145°C for PP+trisamide (not displayed). An overview of all results can be found in **Table 1**.

Here again, the influence of the isothermal temperature on crystallization is

demonstrated. Lowering the isothermal temperature leads to an earlier and faster reaction (lower peak maximum time), as well as to a higher crystalline proportion (higher enthalpy value).

The crystallization enthalpies of two different samples can only be compared for identical temperatures. Examining both PP with trisamide and PP with NU-100 at the isothermal temperature of 142°C reveals that the crystallization enthalpy is higher for the sample with NU-100 (116 J/g vs. 93 J/g). The used temperature range of pure PP is lower (124°C to 128°C) than for PP+NU-100 (137°C to 142°C). However, the crystallization enthalpy is significant higher for PP+NU-100.

Table 1. Results of the isothermal crystallization or pure polypropylen and PP with trisamide or NU-100

(source: Netzsch)

	Isothermal temperature [°C]	Crystallization peak minimum [min]	Crystallization enthalpy [J/g]
Pure PP	124	2.8	96.5
	125	3.6	96.0
	126	4.7	95.9
	127	6.1	95.6
	128	8.8	95.2
PP with trisamide	142	5.3	93.0
	142.5	5.9	92.9
	143	6.7	92.0
	143.5	7.8	91.6
	144.5	10.9	90.3
PP with NU-100	145	12.3	88.3
	137	3.6	122.6
	138	4.7	118.4
	139	6.1	118.0
	140	8.0	117.5
	141	10.1	116.9
	142	13.2	116.0

From DSC Curves to Predictions for Process Optimization

The kinetic parameters of the crystallization were determined using the accelerating Avrami equation for modeling of the crystallization rate [3]. The crystallization rate can be modeled with:

$$d\alpha / dt = k(T)f(\alpha) \quad (1)$$

da/dt : reaction rate [s⁻¹]
 $k(T)$: specific rate constant at temperature T
 $f(\alpha)$: conversion function

The accelerating Avrami equation described the nucleation and the crystal growth of the polymer crystals well. It is used as a conversion function:

$$f(\alpha) = p(1-\alpha)^{-1}[-\ln(1-\alpha)]^{(p-1)/p} \quad (2)$$

p : reaction order
 α : fraction reacted

For a reaction at the specific temperature T, the following equation is obtained from (1) and (2):

$$\ln[-\ln(1-\alpha)] = p \cdot \ln[t] + \ln[k(T)] \quad (3)$$

$$k(T) = Z \cdot e^{-E/RT} \quad (4)$$

According to the **Equation 3**, Avrami exponent p and $\ln[k(T)]$ are calculated. For that, the Avrami plots for each isothermal temperature and for conversion rates between 10% and 90% are displayed in **Figure 5** for pure PP. For the calculation of the time, the starting time of the crystallization peak is important not the time of the segment start, because the peak does not start at the same time for all isothermal temperatures. Therefore, the time is set at 0 at the beginning of the peak. The Avrami plots are used for the determination of the reaction order p (slope of the linear fitting) and the rate constant $\ln(k)$ (intercept of the linear fitting) [4].

The corresponding results are given in **Table 2**. The half-time $\tau_{1/2}$, defined as the time elapsed from the beginning of the crystallization peak to a relative crystallinity of 50%, is also calculated. From the half-time $\tau_{1/2}$ and the rate constants $\ln(k)$, conclusions regarding the reaction speed can be drawn. $\tau_{1/2}$ increases whereas $\ln(k)$ decreases with increasing temperature because of the influence of the temperature on the speed of reaction: the lower the isothermal temperature, the faster the

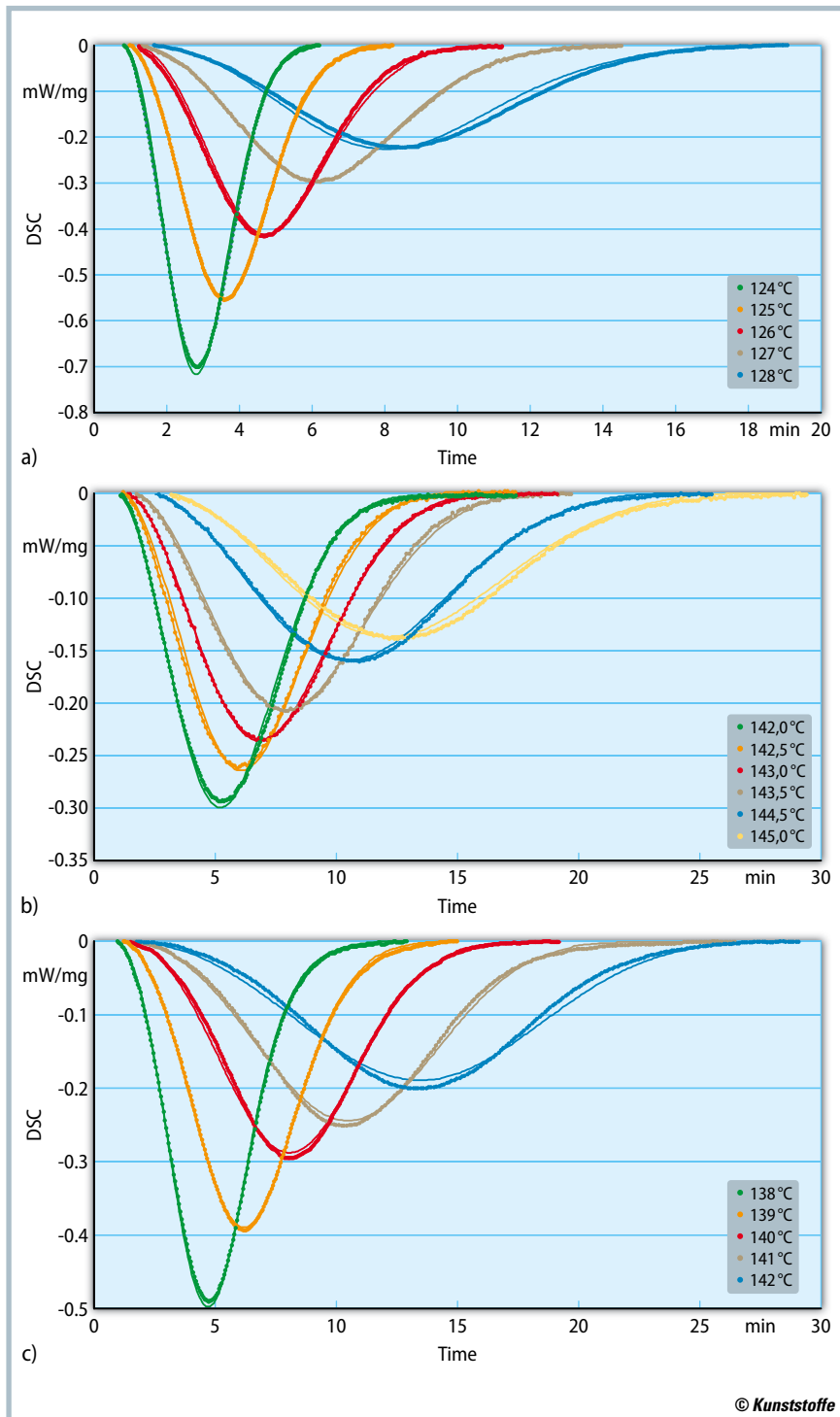


Fig. 7. The two-step reaction model according to the Avrami equation and an n^{th} order reaction leads to even better concordance (correlation coefficient: 0.999) between simulation (lines) and DSC measurement points (crystallization peaks): a) pure PP, b) PP with trisamide and c) PP with NU-100 (source: Netzsch)

reaction. At the same temperature (142 °C), $\tau_{1/2}$ is higher for PP+NU-100 than for PP+trisamide, indicating a faster crystallization speed for the sample with trisamide.

The Avrami exponent p is associated with the nucleation manner and the dimension of crystal growth. Here, a value

between 2 and 3 can be attributed to a heterogeneous nucleation due to the presence of impurities, followed by spherulitic growth [5]. As the orders of reaction of pure PP, PP with trisamide and PP with NU-100 are close to one another, the nucleation agent has no »

significant effect on the mechanism of the nucleation.

In addition, the calculation was done with the Kinetics Neo software. A one-step reaction according to the Avrami nucleation equation was employed which has been proven for isothermal crystallization processes [6]. **Figure 6** clearly demonstrates the good correlation between the measured (DSC) and calculated crystallization behavior based on the Avrami model for the pure PP sample. The software automatically calculates the reaction order ($p=2.72$) as well as the activation energy ($E=-417\text{ kJ/mol}$) and the decimal logarithm pre-exponential factor ($\text{Log}(Z)=-57$, $\text{ln}(Z)=131.9$).

These results determined by means of the commercially available software program are in good agreement with the values of the reaction order calculated according to the Avrami equation ($p=2.76 \pm 0.03$). However, trying to find a

reaction model leading to an improved adaptation of the calculated curves, a second model is selected containing two consecutive steps $A \rightarrow B \rightarrow C$. The first step, $A \rightarrow B$, describes the nucleation following the Avrami equation and the second step, $B \rightarrow C$, describes the crystal growth for which a reaction of n^{th} order is assumed. **Figure 7a** shows both measured and calculated curves. Compared to the single stage reaction, the two-stage model achieves a higher correlation coefficient (0.999).

In the following, Netzsch Kinetics Neo is used to determine the kinetics of crystallization of the samples with nucleation agents. Again, a two-step reaction is assumed for the reaction. The measured DSC curves and the calculated curves based on the Avrami equation followed by an n^{th} order reaction step are depicted in **Figures 7b and 7c**. The good correlation between the measured and calculated

curves confirms the hypothesis that the reaction follows a two-step model. **Table 3** summarizes the results of the kinetic evaluation for the three samples.

The values of p are determined between 2.5 and 3.1 for both the manual evaluation method and evaluation by means of Kinetics Neo. The activation energy of the second reaction step is significantly lower for the samples with nucleating agents than for pure PP. This indicates that the crystal growth takes place faster if a nucleating agent is added to the polymer. The values of the reaction order are close for all three samples. This means that the geometry of the formed crystals is similar in all samples irrespective of the presence of a nucleating agent.

The kinetic parameters can be used to predict the crystallization behavior for different temperatures. **Figure 8** shows the progress of crystallization for all three samples at a constant temperature of 130°C . Based on the selected kinetic model, the pure polypropylene requires nearly 30 minutes to finish the crystallization reaction. Adding nucleation agents considerably influences the crystallization process; for example, by reducing the time. The two nucleation agents can also be compared: trisamide influences the speed of crystallization slightly more than NU-100.

The results of isothermal crystallization are crucial for a fast and straightforward investigation and prediction on the influence of an additive on the crystallization behavior of a mixture. In particular, such data can be transferred to the molding process of thin-walled products to optimize the type or the amount of the nucleating agent for a polypropylene mixture.

Sample	Crystallization temperature [$^\circ\text{C}$]	p	$\text{ln}(k)$	$\tau_{1/2}$ [s]	Mean value p
Pure PP	124	2.77	-2.42	126	2.76 ± 0.03 (1)
	125	2.70	-3.09	164	
	126	2.77	-4.03	224	
	127	2.78	-5.00	315	
	128	2.78	-5.92	439	
PP with trisamide	142	2.50	-1.53	270	2.70 ± 0.16 (1)
	142.5	2.56	-1.70	311	
	143	2.65	-1.89	358	
	143.5	2.79	-2.16	423	
	144.5	2.81	-2.48	561	
	145	2.91	-2.72	654	
PP with NU-100	138	2.77	-4.18	235	2.83 ± 0.06 (1)
	139	2.82	-5.04	312	
	140	2.93	-6.05	408	
	141	2.80	-6.16	545	
	142	2.83	-7.12	655	

(1) The error is calculated as standard deviation.

Table 2. Isothermal crystallization results (source: Netzsch)

First reaction step (Avrami) to describe the nucleation				
	E (kJ/mol)	p	$\text{Log}(Z)$	Contribution
Pure PP	-405	2.90	-55	0.513
PP+trisamide	-373	2.52	-49	0.538
PP+NU-100	-399	3.1	-53	0.509
Second reaction stage (n^{th} order) to describe the crystal growth				
	E (kJ/mol)	n	$\text{Log}(Z)$	Contribution
Pure PP	-408	0.70	-55	0.487
PP+trisamide	-272	0.77	-36	0.463
PP+NU-100	-233	0.75	-32	0.491

Table 3. Kinetic parameter of the isothermal crystallization of pure PP, PP+trisamide and PP+NU-100, according to a two-step reaction model (source: Netzsch)

Conclusion

The thermokinetics of the crystallization behavior of PP and two nucleated PP samples were determined on the basis of isothermal crystallization measurements at different temperatures by means of DSC. A heat-flux DSC with a furnace of low thermal mass was used, allowing fast cooling rates and fast stabilization at a specified temperature, both of which are required for isothermal crystallization tests.

The kinetics of the reaction are usually carried out using the Avrami equation for one-step reactions. However, better re-

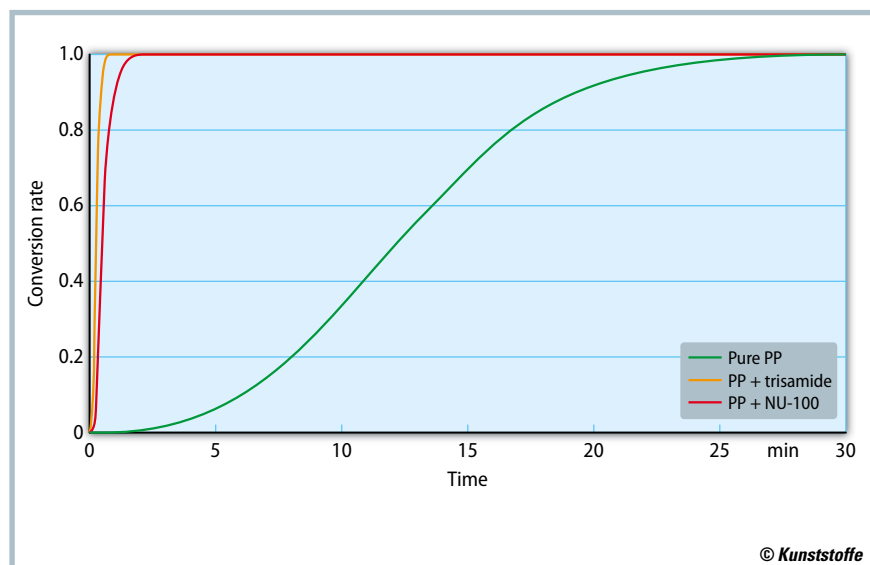


Fig. 8. Prediction of the crystallization behavior of the three samples at an isothermal temperature of 130°C (source: Netzsch)

sults can be achieved by using a two-step reaction model in which the first step (nucleation) is described by Avrami equation and the second step (crystal growth) by an n^{th} order reaction. The values of activation energy and reaction order indicate that the nucleating agents accelerate the crystal growth but have insignificant influence on the geometry of the formed crystals.

Kinetic evaluation by means of Kinetics Neo software allows for predictions of

sample behavior at specified temperature programs. For the production process, such investigations can be useful for determining the effectiveness of nucleating agents on the crystallization behavior of semi-crystalline thermoplastics. Moreover, this information can also be used to optimize compound formulations (additive content), estimate suitable molding temperatures or predict possible reduction of cooling times to increase molding productivity. ■

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