Effects of high cooling rates on solidification for nucleated and non-nucleated semi-crystalline thermoplastics

During polymer processing the polymer melt usually undergoes a rapid cooling. This affects the solidification of the material, especially the crystallization behaviour. This paper investigates the solidification of semi-crystalline thermoplastic polymers at varied cooling conditions with respect to the presence of nucleating agents to analytically evaluate the application potential for micro injection moulding. For this a high speed DSC is used with cooling rates up to 2000 K s⁻¹. The investigations reveal that increased cooling rates shift the crystallization temperatures to lower temperatures. Especially for slow crystallizing PA 66 sufficient high cooling rates suppress the crystallization of the melt. A nucleation of the material favours the crystallization as it takes place at already higher temperatures as well as at high cooling rates which are evident for micro injection moulding processes.
Effects of high cooling rates on solidification for nucleated and non-nucleated semi-crystalline thermoplastics

S. Meister, C. Fischer, D. Drummer

1 INTRODUCTION

In thermoplastic polymer processing, a fast cooling of the polymer melt takes place. This is especially considerable in thin-wall and micro injection moulding processes [1, 2]. Recent investigations try to determine the cooling rate near the surface. This was carried out only by approximation because a reliable measurement is restricted due to the local and rapid effects. However, in literature several valuations were carried out, figure 1: Wuebken [3] calculated the cooling behaviour for polycarbonate and polystyrene in plates with 3 mm and 2 mm respectively. Here, a cooling rate in the surface area (0.2 mm distance to the mould) between 70 K s\(^{-1}\) and 35 K s\(^{-1}\) can be determined. Hoffmann [4] reveals the same dimensions for a polypropylene with a cooling rate of 35 K s\(^{-1}\) in a distance of 0.1 mm to the surface. Jungmeier [5] has simulated the cooling of a 0.5 mm PA66 part and revealed a cooling rate of 662 K s\(^{-1}\) at the mould surface.

Figure 1: Calculated cooling conditions for exemplarily three materials at typical process conditions (according to [3, 4])

These calculated or simulated cooling rates are iterations on a particular cooling phase. Thus, the real maximum cooling rate can be expected at 1000 K s\(^{-1}\) or higher, especially in thin wall injection moulding processes. A distinct and
accurate assessment of the occurring cooling rate and the temperature development in the surface area is currently not possible.

The effect of a fast melt cooling during the filling stage of the cavity is a reduced flow length and hence an insufficient filling efficiency of the mould [6-8] or replication of micro-structured surfaces [9-11] due to a fast melt solidification. Furthermore, modified cooling conditions affect the development of internal structures of the part. Thus, an increased cooling rate favours the formation of orientations and residual stresses [12, 13] as well as an inhomogeneous morphology [14] associated with a modified crystalline structure [15-20].

The measurement of the crystallization behaviour of polymer materials can be investigated analytically using differential scanning calorimetry (DSC). In DSC measurements the phase transition, e.g. the crystallization of polymers, correlates with the determined heat flow changes during cooling and heating a sample [21]. Thus, the heat flow $\Delta Q$ can be calculated with the following equations:

$$\Delta Q = C \cdot \Delta T = c \cdot m \cdot \Delta T$$

(1)

$$\frac{d\Theta}{dt} = C \cdot \frac{dv}{dt} = c \cdot m \cdot v$$

(2)

where C is the heat capacity, c the specific heat capacity ($c = C/m$), $\Delta T$ the temperature change due to exchanged heat, m the mass of the sample, $\Theta$ the heat flow rate and v the (heating or cooling) rate. With standard DSC measurement equipment, a typical cooling rate up to 0.7 K s$^{-1}$ (40 K min$^{-1}$) can be feasibly carried out [21]. A reduced sample mass allows a cooling rate up to 3.3 K s$^{-1}$ (200 K min$^{-1}$) [22] which is limited by the cooling power of the DSC equipment. In addition, a thermal lag of the measurement caused by the sample mass has to be taken into account. For material characterization at high cooling rates, which are comparable to process conditions, new DSC instruments are reported with cooling rates up to 10,000 K s$^{-1}$ [22-27]. These systems use chip sensors with which the temperature lag can be reduced. Generally, with these chips a sample weight of less than 10 µg is used. The first commercial available fast scanning calorimeter is the Mettler-Toledo Flash DSC 1 [25].

Different investigations are carried out in the last years to investigate the material behaviour at high cooling rates. For example, Kolesov et al. [28] showed for PA6 a decreasing crystallization with cooling rates above 10 K s$^{-1}$. A cooling rate higher than approx. 120 K s$^{-1}$ causes a complete vitrification of the melt and an amorphous morphology develops [25, 29]. Furthermore, the crystalline modification is also affected by the cooling rates [30]. Schawe [27] revealed that a cooling rate of 1,000 K s$^{-1}$ inhibits the crystallization of PP. Uthaipan et al. [31] showed for EPDM/PP and EOC/PP that particles acting as nucleating agents can counteract the suppressed crystallization at undercooling. For amorphous polymers like PS [32] or PC [33] a shift of the
glass transition temperature to a higher value with increasing cooling rate was reported.

2 SCOPE OF THE PAPER

Knowledge about the material behaviour at high cooling rates is important for process and part design to influence the melt solidification or the morphology development. The material’s behaviour can be considered more in detail in the designing process to optimize the processing and the resulting part properties, e.g. for a sufficient replication of micro structures or to improve the durability of mechanical properties due to an adapted morphological structure.

Figure 2: Morphology of injection moulded micro parts in dependence on nucleation of the material

Figure 2 shows exemplarily the influence of nucleating agents on the morphology development in micro injection moulded parts. The nucleation of polyamide for example increases the degree of crystallinity and can favour slightly the mechanical properties as shown by Jungmeier [5]. It has to be taken into account that influences on the visual morphological structure (i.e. the spherulitic structure) must not correlate with the effects on degree of crystallinity.

Thus, the scope of this paper is to qualitatively investigate the effect of nucleating agents by fast scanning calorimetry (FSC) for materials with different crystallization kinetics (PA 66 and POM) with respect to micro injection moulding processing conditions. Therefore, the resulting crystallization
properties are correlated with typical cooling conditions (which result from the reduced part thickness and the high fraction of the surface) with regard to the injection moulding process. Gained results can allow a designer to choose a material with specific properties suitable for processing and part demands. Also, the analytical results may help to evaluate, if the use of a more expensive nucleated material is useful regarding the effects of crystallization at process based cooling conditions.

3 EXPERIMENTAL SECTION

3.1 Materials

In the work different standard types of semi-crystalline thermoplastic polymers were used to investigate the crystallization behaviour: A polyoxymethylene (POM, Hostaform C9021, Ticona GmbH), as a material with fast crystallization kinetics [34, 35], and a polyamide 66 (PA66, Ultramid A3K and A3SK respectively, BASF SE), as a material with medium crystallization kinetics [36]. These polymers have distinct crystallization properties, e.g. different crystallization temperatures. In addition, for each type a non-nucleated and a nucleated type where chosen to realize different crystallization behaviour. Characteristic values of these materials are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>POM1</th>
<th>POM2</th>
<th>PA1</th>
<th>PA2</th>
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<td>Hostaform C9021</td>
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<td>Ultramid A3SK</td>
</tr>
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<td>1.41</td>
<td>1.13</td>
<td>1.14</td>
</tr>
<tr>
<td>melting temperature (°C), ISO 11357 (10 K min⁻¹)</td>
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<td>166</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>crystallization temperature (°C), ISO 11357 (10 K min⁻¹)</td>
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<td>148</td>
<td>236</td>
<td>241</td>
</tr>
<tr>
<td>glass transition temperature (°C), ISO 11357 (10 K min⁻¹)</td>
<td>-70</td>
<td>-70</td>
<td>72</td>
<td>72</td>
</tr>
</tbody>
</table>

Table 1: Characteristics of the investigated materials
3.2 Fast scanning calorimetric measurements

Fast scanning calorimetric (FSC) measurements were carried out using a Flash-DSC 1 (Mettler-Toledo GmbH). It allows an investigation of the material behaviour at high cooling rates. The test sample was prepared out of a 10 μm thin-cut using a scalpel and a microscope and placed on the sensor area of the FSC instrument. The sample was cooled at varied cooling rates between 10 K min⁻¹ (0.17 K s⁻¹, cooling rate for most standard DSC measurements) and 120,000 K min⁻¹ (2000 K s⁻¹). These high cooling rates correlate to typical process conditions (also see Figure 1). The heat flow is investigated to compare the influence of varied cooling rates on the solidification of the material crystallization behaviour. Based on the heat flow curves typical transition temperatures are investigated at varied cooling conditions. To investigate the effect of varied cooling rates, the heat flow during melting after varied cooling conditions (second heating) is investigated. For this, a heating rate of 500 K s⁻¹ for the samples is applied. Furthermore, by integrating the measured cooling peaks and correlating DSC and FSC measurements at a same cooling rate of 1 K s⁻¹ for a quantitative assessment of the respective sample masses, the specific enthalpy was calculated.

4 RESULTS

4.1 Heat flow at varied cooling conditions

The following figures show the heat flow of the samples at varied cooling rates for the investigated materials.

4.1.1 POM

Figure 3 shows the measured heat flows of the non-nucleated POM (POM1) in dependence of the examined cooling rates. The exothermic peak for the cooling rates indicates that crystallization of the material occurs. With increasing cooling rate, the onset temperature (the temperature where the crystallization and the exothermic peak respectively is initiated) as well as the peak temperature is shifted to slight lower temperatures. This indicates that the crystallization process is retarded by fast cooling of the material and shifts the crystallization to lower temperatures. Furthermore, at elevated cooling rates the end of the crystallization peak (i.e. the offset temperature, where the crystallization of the material is completed) runs out at significantly lower temperatures. As a consequence, the crystallization and the recognizable heat flow peak respectively occur over a larger temperature range due to a flatter peak slope. Nevertheless, it can be summarized that for all investigated cooling rates a measurable crystallization occurs.
Analogous to the non-nucleated POM1 the heat flow curves of the nucleated POM2 are shown in Figure 4. These curves again show similar behaviour compared to the non-nucleated material. An increasing cooling rate leads to a shift of the crystallization temperature (i.e. crystallization onset, peak and offset temperature) towards lower temperatures. Nucleation of POM exhibits no significant effect on the heat flow curves and crystallization occurs at all investigated cooling rates. Here, it is assumed that the crystallization of POM is less affected by nucleating agents because of its rapid crystallization kinetics.

4.1.2 PA66

The measured heat flow curves of the non-nucleated polyamide material (PA1) in dependence of the varied cooling rates are shown in figure 5. Analogous to
POM the crystallization peak shifts towards lower temperatures with increasing cooling rate. In contrary, for high cooling rates above 200 K s⁻¹ (i.e. 500 K s⁻¹, 1000 K s⁻¹ and 2000 K s⁻¹) no exothermic peak can be detected for the non-nucleated PA. Here, the material solidifies without any measurable crystallization effects.

**Figure 5**: Cooling curves of the non-nucleated PA1 at varied cooling rates

The heat flow curves for the nucleated PA2, figure 6, show a significant crystallization peak at higher cooling rates. Only at cooling rates of 2000 K s⁻¹ the crystallization peak disappears. Thus, for PA66 the presence of nucleating agents affects the crystallization process at elevated cooling rates significantly and can induce crystallization during processing relevant cooling conditions.

**Figure 6**: Cooling curves of the nucleated PA2 at varied cooling rates
4.2 Heat flow at heating the material after varied cooling conditions

Due to varied cooling conditions the solidification or the crystallization of the materials are affected. To reveal this effect, the samples are heated after varied cooling rates at constant heat rates.

4.2.1 POM

The second heating of the non-nucleated POM1 after varied cooling conditions is shown in figure 7. It can be seen that the onset temperature and the peak temperature as well are not dependent on previous cooling conditions of the material. However, the endothermic peak decreases with a higher previous cooling of the material. This goes along with a slightly shift of the offset temperature towards higher temperatures.

Figure 7: Heating curves of the non-nucleated POM1 after varied cooling rates

The nucleated POM2 reveals comparable melting curves, figure 8, as seen for the non-nucleated POM1. Thus, a previous faster cooling of the melt leads to a reduced peak height as well as to a shift of the offset temperature to a higher value. For the sample cooled with 2000 K s\(^{-1}\) a slight shift of the peak temperature can be detected which can be a result of a measurement fault. In summary, for POM, no significant effects on crystallization of nucleating the material can be measured analytically, what can be reduced to the fast crystallization kinetics of POM.
4.2.2 PA66

Figure 9 shows the heating curves of the non-nucleated PA1 after varied cooling rates. In all cases an endothermic melting peak at approx. 235 °C can be found. However, the specimens which have previously crystallized at cooling rates of 200 K s\(^{-1}\) or higher reveal a crystallization peak during heating at approx. 140 °C. This correlates with the measured heat flow during cooling at cooling rates above 200 K s\(^{-1}\) as a crystallization peak cannot be found and indicates a cold crystallization of the material due to a thermal treatment. The amount of cold crystallization increases significantly up to a previous cooling rate of 500 K s\(^{-1}\) and 1000 K s\(^{-1}\) respectively. Above a previous cooling rate of 1000 K s\(^{-1}\) the cold crystallization remains constant. This can indicate that at these high cooling rates the crystallization process is suppressed what leads to a vitrification of the material. By the thermal treatment (e.g. during the heating of the sample) the inhibited crystallization process starts. Thus, during the heating of the sample a typical melting peak can be identified. However, the cold crystallized materials (especially the samples previously cooled at 500 K s\(^{-1}\) or higher) show a flatter melting peak which can be attributed to a modified crystalline structure.
The heating of the nucleated PA2 after varied cooling shows similar effects compared to the non-nucleated PA1, figure 10. However, the observed cold crystallization only takes place at a previous cooling at 1000 K s$^{-1}$ or higher. Due to the nucleating agents the crystallization of the material can be measured also at increased cooling rates compared to the non-nucleated material. In summary, for PA 66 the use of nucleating agents allows crystallization at processing relevant (i.e. injection moulding) cooling conditions.
5 DISCUSSION

As the varied cooling rates affect the solidification of the polymer melt subsequently, the crystallization temperature as characteristic value is discussed.

As seen before, the crystallization temperature is more affected by increased cooling rates. For the two POM materials the crystallization peak temperature in dependence of the cooling rate is shown in figure 11.

![Figure 11: Crystallization peak temperatures of POM materials at varied cooling rates](image)

It can be seen that a fast cooling of the melt shifts the crystallization temperature from approx. 147 °C (for a cooling rate of 0.33 K s\(^{-1}\)) towards less than 120 °C. The crystallization temperature nearly remains constant for cooling rates higher than 500 K s\(^{-1}\). In addition, the nucleation of POM (POM2) increases the crystallization peak temperature by about 5 K to higher temperatures. Thus, the nucleation promotes the crystallization process at higher cooling rates. However, the amount of crystallization seems to be less affected by temperature, as can be seen in the calculated specific crystallization enthalpy of the samples in figure 13 (left). With increasing cooling rate, the crystallization enthalpy remains nearly constant with only a slight decrease at elevated cooling rates. This indicates that the material's crystallization takes place even at high cooling rates even without nucleation agents. Comparing the enthalpies at same cooling rate, higher values can be measured for the nucleated materials, what could be explained with the higher crystallization kinetics due to nucleating agents.
With regard to the small differences in crystallization, from an analytical point of view, there is no need of nucleating agents for POM in micro injection moulding since the crystallization behaviour is not significantly being influenced what is related to the fast crystallization kinetics of the material. Therefore, albeit there are clear differences comparing morphological structures, figure 2, an influence on mechanical properties due to clear crystal differences can't be estimated what also could have been shown by Jungmeier [5].

The influence of varied cooling rates on the crystallization peak temperature of the PA66 materials is shown in Figure 12.

![Figure 12: Crystallization peak temperatures of PA 66 at varied cooling rates](image)

As already shown in the heat flow curves, a faster cooling rate leads to a shift of the crystallization to lower temperatures. For the non-nucleated PA1 a cooling rate of approx. 500 K s\(^{-1}\) or higher suppresses the crystallization of the material. Thus, a crystallization peak of the material cannot be measured at these high cooling rates. This goes along with a significant reduction of the calculated specific crystallization enthalpy of the non-nucleated PA1, figure 13, right, which indicates that the crystallization is inhibited. In contrast, the nucleated PA2 reveals a crystallization peak even at a high cooling rate of 2000 K s\(^{-1}\). The enthalpy also decreases with increasing cooling rate. Again, comparing the enthalpies at same cooling rate, higher values can be measured for the nucleated materials, what could be explained with the higher crystallization kinetics due to nucleating agents.
Nevertheless, compared with the non-nucleated PA 66, a significant decrease only occurs at cooling rates that are higher than the estimated process based cooling conditions. Accompanying, the nucleation of PA 66 allows for crystallization at already elevated cooling rates. With respect to the injection moulding process and due to the significant differences, the use of nucleating agents for slow crystallizing PA 66 could be useful from an analytical point of view since it is known that a more distinct crystallization can increase mechanical properties. Here, especially in micro component’s edge area, where the highest cooling rates are estimated due to the contact of the hot melt with the relatively cold mould, it can be assumed that the crystallization doesn’t get suppressed. This may lead to more distinct inner component structures and, therefore, to better mechanical and tribological properties.

6 CONCLUSION

This work investigated the solidification of different thermoplastic polymers at increased cooling rates using a high speed DSC. The results allow for the following statements:

- For semi-crystalline polymers like polyoxymethylene or polyamide 66 a fast cooling of the melt can inhibit the crystallization process and shift the crystallization temperature range to lower temperatures. This can be seen in a reduced crystallization peak temperature as well as in a flatter crystallization peak. Furthermore, for non-nucleated PA 66 a cooling rate of 500 K s\(^{-1}\) or higher suppresses the crystallization. Thus, no exothermic crystallization peak can be measured.
A nucleation used to support the crystallization of the semi-crystalline polymers reduces the shift of the crystallization peak temperature at increased cooling rates. For the used POM material a nucleation leads to a 5 K higher crystallization peak temperature compared to the non-nucleated at cooling rates above 200 K s\(^{-1}\) what is reduced to athermal nucleation. Nevertheless, for the non-nucleated and the nucleated POM no significant differences in crystallization can be measured regarding different cooling rates what can be explained with the fast crystallization kinetics of POM. For PA66 the nucleating agent shifts the crystallization peak temperature at a cooling rate at 200 K s\(^{-1}\) to more than 30 K higher temperatures. Here, regarding the effect of nucleating agent, it could be shown that a nucleation can enable crystallization at cooling rates that are relevant for micro injection moulding.

In a process with fast cooling rates, e.g. micro or thin-wall injection moulding, the use of nucleating agents can favour the solidification (i.e. the crystallization) of the melt especially for slower crystallizing materials. This can be helpful for part and process design with respect to achieve defined process induced part properties. Thus, a post-crystallization and resulting part shrinkage at elevated temperatures during use can be inhibited and defined part properties can be induced.

In future work, the FSC measurements should be taken by varying the sample mass to verify the results. Furthermore, regarding the FSC measurements, tests with several independent samples prepared from different portions of the bulk sample need to be done in order to estimate the influence of concentration fluctuation. Further work should investigate the measured analytical effects experimentally. Here, especially materials with low to medium crystallization kinetics should be used. Produced parts should be investigated for their mechanical and tribological behaviour. Also further work should investigate these effects on other polymer materials or the influence of fillers and reinforcements on the crystallization at elevated cooling rates.

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