



Crystallization kinetics of polyamide 66 at processing-relevant cooling conditions and high supercooling



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ABSTRACT

Processing of polyamide 66 (PA 66) by injection molding includes cooling of the melt at rates between 10^0 and 10^3 K/s and its solidification at high supercooling. The kinetics of crystallization at such conditions is unknown and has been evaluated in this work using fast scanning chip calorimetry. Slow cooling of the melt of PA 66 leads to formation of crystals, with the maximum crystallinity being about 30%. It has been found by analysis of the crystallinity as a function of the cooling rate that crystallization is suppressed on cooling faster than about 300 K/s. Isothermal analysis of the crystallization rate revealed a bimodal temperature dependence, with maxima obtained at about 165 and 110 °C. It is suggested that the observation of two distinct crystallization-rate maxima is related to a change of the nucleation mechanism on temperature variation or the formation of different crystal polymorphs exhibiting different growth rate. The findings provide a fundamental step towards accurately predicting the solidification behavior, the skin–core morphology, and properties of injection moldings of PA 66.

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1. Introduction

Polyamide 66 (PA 66) is a versatile and highly utilized engineering thermoplastic homopolymer. The polymer exhibits high strength over a broad temperature range, has excellent impact and chemical resistance, and can withstand high wear. Besides its use for production of fibers, applications include automotive, aerospace, and industrial replacements for metal gears, bearings and engine components [1–4]. The material is typically injection molded and is particularly prone to shrink and warpage problems. The material is known to be very sensitive to changes in melt processing, presenting a challenge for engineers that design manufacturing processes for high-end part production [5].

Both the excellent physical properties and the challenging design drawbacks of PA 66 are due to the inherent semi-crystalline microstructure. During injection molding, this semi-crystalline microstructure forms under shear and thermal gradients, typically leading to the development of skin–core morphologies with implications on the property profile [6]. In addition, the molten polymer volume densifies to a greater extent in crystallizing regions than in areas which remain macroscopically amorphous, resulting in problematic variations in shrinkage across a part [7]. To

control and maximize the benefits resulting from a uniform microstructure it is critical to develop an understanding of the crystallization process, at conditions relevant in processing.

The process of injection molding can subject PA 66 to a wide range of cooling rates. Conventional injection molding employs a steel mold held at a constant temperature, and a mold temperature in the range between 0 and 90 °C is often used [8]. Oftentimes, lower mold temperatures will be used to “quench” the melt and to allow for more rapid production rates. Melt temperatures range from 280 to 305 °C, and the material is also subject to injection pressures between 35 and 140 MPa [8]. After the mold cavity is filled, time to solidification is dictated by the heat transfer out of the mold and can vary greatly with mold and melt temperature, and the wall thickness. Cooling rates in injection-molding of PA 66 range from about 3 K/s in the center of a molded tensile test bar to more than 1200 K/s at the interface of the polymer/mold surfaces [9].

Despite the potential usefulness of such information, there are no published resources available that describe the crystallization kinetics of PA66 at processing-relevant high cooling rates, nor is there published information regarding the crystallization rate of PA 66 at temperatures experienced during the cooling processes of injection molding, extrusion, or thermoforming. Prior studies of the crystallization behavior of PA 66 were mainly performed by differential scanning calorimetry (DSC) which, however, only allows analysis of crystallization processes at cooling rates lower

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than about few 100 K/min, or at temperatures at which the melt-crystal phase transition is longer than several ten seconds, [10,11] both being insufficient to derive conclusions regarding the materials behavior at conditions present in polymer processing. Therefore, we have utilized a fast scanning calorimetry technique [12,13] to study the crystallization process of PA 66 at rapid cooling and at low temperature.

The primary chemical structure of the PA 66 macromolecule consists of amide groups separated by methylene sequences. PA 66 is a polymorphic polymer and forms different supermolecular structures depending on the condition of crystallization. Slow cooling of the quiescent melt or crystallization at rather high temperature leads to formation of triclinic α -crystals with sheet-like arrangement of hydrogen bonds at room temperature, connecting amide groups of neighbored chain segments [14]. The equilibrium melting temperature and bulk heat of fusion of the α -phase, as listed in the ATHAS data base, are 301 °C (574 K) and 255.4 J/g, respectively [15–17]. The triclinic α -form converts on heating at the Brill transition temperature into the high-temperature α' -form with a pseudo-hexagonal unit cell and a three-dimensional network of hydrogen bonds [18,19]. The Brill transition is reversible, that is, the α' -phase reverts on cooling into the α -phase. The formation of α/α' -crystals on slow cooling/low supercooling typically is connected with formation of lamellae and spherulites [20–22]. Regarding the kinetics of formation of α' -crystals it is known that on cooling at rates lower than 20 K/min, as is typically applied in DSC analyses, crystallization occurs at 220–240 °C [23–29]. Isothermal DSC experiments revealed that at a temperature of 230 °C crystallization is finished after about 1–2 min, with the crystallization time rapidly increasing with crystallization temperature [29–31]. Besides formation of the α -polymorph as a result of slow cooling or crystallization at high temperature, there has been reported the development of a pseudo-hexagonal mesophase with non-planar arrangement of hydrogen bonds upon quenching of the melt [32]. The mesophase is metastable at room temperature and converts irreversibly into α/α' -crystals on heating [33]. Details of the morphology and superstructure of the mesophase of PA 66, and their exact conditions of formation are not known yet. In case of PA 6, which exhibits a similar cooling-rate/supercooling controlled crystal/mesophase polymorphism as PA 66 [32–35], it has been proven that the mesophase domains are of non-lamellar habit and not spatially organized in a higher-order superstructure [36,37].

Summarizing the scope of the present study, we attempt to gain information about the crystallization kinetics of PA 66 at conditions being typical in injection molding, for example on cooling at rates between 1 and 1000 K/s, and at temperatures lower than 200 °C, not yet reported. The observed data may then be used to predict the solidification behavior of injection moldings, their skin–core morphology and, with that, their properties. In a wider view, the study is also considered as a continuation of our research efforts to obtain information about a possible change of the mechanism of crystal nucleation on variation of the supercooling, as has been suggested for the cases of isotactic polypropylene (iPP) [38,39], polyamide 11 [40], or poly(ϵ -caprolactone) [41].

2. Experimental

2.1. Materials

For the analysis of the crystallization kinetics of PA 66 we used a commercial general purpose injection-molding grade Zytel 101 L from DuPont (USA) with a number-average molar mass of 17 kg/mol [42,43]. This grade of PA 66 contains a small amount of additive that functions as a lubricant during injection molding.

2.2. Sample preparation

The as-received, dry pellets were injection-molded to standard tensile test bars using a 100 t Sodick Plustech injection molding machine. The molded bars were then microtomed parallel to their thickness direction, to obtain sections with a thickness of 13 μ m. These thin sections were then further prepared for subsequent analysis of the crystallization behavior using FSC by reduction of their lateral size to 50–100 μ m, using a scalpel and a stereomicroscope.

2.3. Fast scanning calorimetry

FSC analysis was performed using a power-compensation Mettler-Toledo Flash DSC 1, attached to a Huber intracooler TC100. Prior positioning of the specimen on the heatable area of the sample calorimeter, the UFS 1 FSC sensor was conditioned and temperature-corrected according to the specification of the instrument provider. The calorimeters were purged with dry nitrogen gas at a flow rate of 35 mL/min. As will be outlined below, experiments were partly performed using different, but identically configured instruments, with the sample preparation and instrument handling done by different operators, for the sake of estimation of errors. The sample mass was between 120 and 300 ng, and was estimated by comparing the measured heat-capacity increment on heating a fully amorphous sample at the glass transition temperature T_g in units of J/K with the expected mass-specific heat-capacity increment of 0.51 J/(gK) [15]. Further details about the instrument/sensor are reported in [13,44,45].

2.4. Differential scanning calorimetry

DSC was used to obtain information about the non-isothermal crystallization behavior on cooling at rates of 2, 5 and 10 K/min. DSC data were collected with a calibrated heat-flux calorimeter DSC-1 from Mettler-Toledo. The sample mass was about 5 mg, and the furnace was purged with nitrogen gas at a flow rate of 30 mL/min. Calibration and operation of the instrument was performed as described in textbooks [46].

3. Results and discussion

3.1. Non-isothermal crystallization

Fig. 1 shows the temperature–time profile of FSC experiments for analysis of non-isothermal crystallization of PA 66. The sample was melted by heating to 300 °C, and kept at this temperature for 0.5 s to achieve equilibration of the melt, and then cooled at the

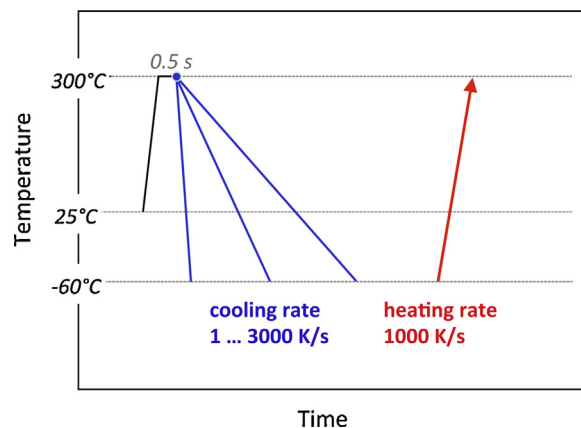


Fig. 1. Temperature–time profile for analysis of non-isothermal crystallization of PA 66.

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