

Nucleation activity at high supercooling: Sorbitol-type nucleating agents in polypropylene



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HIGHLIGHTS

- Crystallization kinetics of polypropylene with sorbitol-based nucleating agents.
- Results of Fast DSC measurements correlate with optical properties.
- Introduction of an approach to describe the nucleating efficiency by Fast DSC.
- Measurement of a structural transformation driven by nucleating agent content.
- Nucleating efficiency and haze correlate for parts produced by injection molding.

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ABSTRACT

Crystallization kinetics of polypropylene (PP) nucleated with sorbitol-type nucleating agents was studied with fast differential scanning calorimetry (FDSC) at high supercooling and correlated to the optical characteristics of mold injected parts. FDSC was used for determination of the critical cooling rate for occurrence of non-isothermal crystallization and the time to maximum crystallization rate during isothermal crystallization after rapid cooling. The nucleating agents studied were 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) and 1,2,3-tridesoxy-4,6:5,7-bis-O-[(4-propylphenyl) methylene]-nonitol (TBPMN). In contrast to particulate nucleating agents, where the number of particles determines the number of heterogeneous nuclei, sorbitol-type nucleating agents self-assemble a nano-fibrillar super-structure by phase separation of sorbitol-type molecules that were previously dissolved in the polymer melt. An approach is proposed to describe the efficiency of nucleating agents self-assembly. In combination with haze data two different crystallization mechanisms are identified, which are interpreted as three-dimensional spherulitic crystallization at high haze and one-dimensional (rod or shish-kebab-like) crystallization at low haze.

1. Introduction

Nucleating agents are used to modify the crystallization behavior and morphology of semi-crystalline polymers to improve the material properties [1,2] such as optical transparency or mechanical performance. The activity of nucleating agents is related to their capability to form nuclei during polymer processing. It is shown for different systems that the activity of nucleating agents depends on the temperature of crystallization [3–5] and/or the cooling rate. Typical cooling rates in polymer processing such as injection molding or film blowing are in the order between 1000 and 10 K/s [6,7]. The fast differential scanning calorimetry (FDSC) has been developed for the measurement of such high cooling rates [8–10].

In a previous work [11] we studied the heterogeneous crystallization of polypropylene (PP) containing carbon nanotubes (CNT) at high supercooling. As a result we have derived an approach for the description of the nucleating activity of the nanotubes for isothermal and non-isothermal crystallization in a wide range of the crystallization temperature. It was found that the acceleration of the crystallization process of PP due to CNT is driven by the mass content of the nanotubes, α_{NA} . The corresponding structural model assumed that the crystallization seeds are arranged along the length of the nanotube with a characteristic average distance. This model is supported by structural investigation which indicate the formation of shish-kebab like structures based on CNT [12–14] with a tendency to increase the dimensions of the crystalline structures [15]. Assuming a constant

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length of the CNT and a characteristic average distance of the crystallization seeds, the number of particles (CNT) determines the number of heterogeneous nuclei.

Without nucleation agent in the core region of micro injection molded polypropylene parts, spherulites with a typical dimension of 1 μm or larger are formed [16], which results in an opaque appearance of the parts. In order to get transparent materials, the crystallization rate and the nucleation density is increased by addition of nucleating agents with a high efficiency (so-called clarifiers). Sorbitol-type clarifiers are frequently used for PP [1,2]. The mechanisms of such nucleation agents are widely investigated [17–21]. Above a critical concentration of those nucleating agents, a three dimensional fibrillary network structure with a diameter of the fibrils in the order of 10 nm is formed [18,22]. This structure seems to induce the formation of shish-kebab like crystalline structures in PP [23,24]. The fibrillary structure in the PP melt is the consequence of a phase separation of a previously homogeneous melt during cooling [17]. The nucleating effect of sorbitol-type nucleating agents depends on phase separation occurring prior crystallization. In contrast to particulate nucleating agents such as CNT this leads us to the hypothesis that the number of the induced nuclei is not a linear relation to the content of the nucleating agent, α_{NA} . One aim of this paper is the test of this hypothesis and the adaption of the approach of the activity of the nucleating agent to the case of fibrillary structures formed by phase separation.

Most of the calorimetric studies of the crystallization of PP nucleated with sorbitol-type clarifiers are performed at relatively low supercooling by conventional differential scanning calorimetry (DSC) [5,20,25–27]. At such conditions sorbitol-type clarifiers act as nucleating agents for α -phase formation [28] and the large number of nuclei at low undercooling results in the formation of significantly smaller spherulites during fast cooling [17,27,29]. According to Bernland et al. [21] the decrease of the spherulite size cannot alone explain the measured increase in transparency due to sorbitol-type clarifiers. In polymer melt processing such as injection molding or film blowing, crystallization occurs at high supercooling due to cooling rates of up to several hundreds of Kelvin per second [6]. For such conditions it has been found, that sorbitol-type nucleation agents initiate α -phase and additionally γ -phase crystallization, corresponding to the formation of shish-kebab-like structures [23,24]. Bernland et al. discussed the formation of a randomly ordered, rod- or shish-kebab-like crystalline structure [21] as a consequence of a nanofibrillar network with a high density of nucleation sites.

The differences in the crystallization mechanism at low and high supercooling and the temperature dependence of the activity of the nucleating agent [3] make it questionable to extrapolate experimental results measured at low supercooling to processing relevant conditions. This was discussed extensively in our recently published report [5]. The analysis of the crystallization delivers information for the understanding of the cooling rate dependence of the optical behavior as it is reported in Ref. [17].

The FDSC technique can be used to study crystallization at processing relevant cooling rates [10]. FDSC measurements of the crystallization of sorbitol-type nucleated PP are reported before in references [5,30].

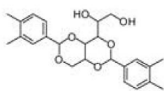
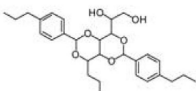
In this paper we study the isothermal and non-isothermal crystallization behavior in a wide range of supercooling of PP nucleated with two commercial available sorbitol type clarifiers by FDSC. These investigations are combined with haze measurements of mold injected parts.

In this study we follow three major goals:

- Testing of the approach to describe the nucleating efficiency of particulate nucleation agents (introduced in Ref. [11]) for sorbitol type nucleating agents.
- Development of an approach to describe the nucleating efficiency for nucleating agent self-assembly by phase separation.

Table 1

Characteristics of the sorbitol-type nucleation agents/clarifiers [2,26].

	DMDBS	TBPMN
Chemical name	1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol	1,2,3-tridesoxy-4,6:5,7-bis-O-[(4-propylphenyl) methylene] nonitol
Chemical structure		
Molecular weight	414 g mol ⁻¹	484 g mol ⁻¹
Melting temperature	273.7 °C	245.7 °C
Trade name	Millad® 3988, Milliken Chemical	Millad® NX 8000, Milliken Chemical

- Linking between the crystallization kinetics at fast cooling with the optical behavior of polymer parts processed by injection molding.

2. Experimental

2.1. Samples

A commercial isotactic polypropylene homo polymer (iPP) Moplen® HP 500 N from LyondellBasell with a weight and number average molecular weight of $\overline{M}_w = 393 \text{ kg mol}^{-1}$ and $\overline{M}_n = 47 \text{ kg mol}^{-1}$ is used. The mold flow index (MFI) at 230 °C is 12 g/10 min (with 2.16 kg).

The sorbitol-type nucleating agents/clarifiers 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) and 1,2,3-tridesoxy-4,6:5,7-bis-O-[(4-propylphenyl) methylene] nonitol (TBPMN) from Milliken Chemical are chosen. The characteristics of these clarifiers are listed in Table 1. The clarifier content in iPP is 0.03, 0.15, 0.3, 0.45 and 0.6 wt%.

To increase the stability of the PP Moplen® HP 500 N the material was stabilized by adding 0.1 wt% Irgafos® 168, 0.1 wt% Irganox® 1010 and 0.1 wt% calcium stearate. The powdery PP stabilizers and clarifiers were dry blended in a plastic bag by shaking until good distribution.

This mixture was compounded at 100 rpm in three cycles in a single screw extruder (Weber ET20, 20 mm, 25D) at 220 °C (5 Zones).

Injection molding was performed with an Arburg Allrounder 2200 S 250-60 (22 mm, 20D). The previously pelletized, compounded granulate was melted at 220 °C and injection molded in a polished mold with a pressure of about 600 bar. The mold temperature was about 50 °C. The “drop shaped” test specimen had a thickness of 1.0 mm with a length of 6.0 mm and width of 4.0 mm in perpendicular and parallel to the sprue, respectively.

The samples are characterized by optical microscope [5]. At clarifier content up to 0.15% structures smaller than 10 μm are observed. About 0.3 wt% is identified as the threshold from a large spherulitic morphology to considerably smaller structures.

2.2. FDSC measurements

The fast differential scanning calorimetry (FDSC) experiments were performed using a METTLER TOLEDO Flash DSC 1 fitted with the sensor UFS 1. The sample support temperature was set to -80 °C . To reach cooling rates up to 10000 K/s in the temperature range between 190 °C and 20 °C, a gas mixture of approximately 90% helium and 10% nitrogen was used [11]. The mixing procedure is described in Ref. [5]. The typical sample size was between 50 and 150 ng. More details about the use of the instrument and sample preparation are given in Refs. [5,31].

In preliminary crystallization experiments by FDSC it was found that the crystallization kinetics depends on the thermal history, since the samples are not stable for a large number of heating-cooling cycles

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