



Influence of different beta-nucleating agents on the morphology of isotactic polypropylene and their toughening effectiveness



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ABSTRACT

The influence of two 1,3,5-benzenetrisamide beta-nucleating agents in comparison to a commercial bisamide beta-nucleating agent on the morphological and mechanical properties of isotactic polypropylene (iPP) is presented. To complete the study, the neat iPP and iPP containing a 1,3,5-benzenetrisamide alpha-nucleating agent was investigated. To evaluate the effectiveness of the different supramolecular polymer additives with regard to their influence on the toughness of iPP, a difficult-to-toughen high melt flow rate (MFR) iPP grade was selected. Investigations by wide-angle X-ray scattering (WAXS) confirm that the two 1,3,5-benzenetrisamides and commercial beta-nucleating agent induce the beta crystal modification of the polymer, whereas only the alpha modification is observed for the neat polymer and the 1,3,5-benzenetrisamide alpha-nucleating agent. Scanning electron microscopy (SEM) pictures on etched samples clearly reveal a shish-kebab structure in beta-nucleated iPP with 1,3,5-benzenetrisamides. For these two samples, Charpy impact investigations show a pronounced increase in toughness, also compared to the commercial bisamide beta-nucleating agent.

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1. Introduction

Isotactic polypropylene (iPP) exhibits a good combination of properties and low price and is therefore a widely used commodity plastic. It is a polymorphic material, which means it can crystallize in different modifications: a monoclinic alpha modification, a trigonal beta modification, and an orthorhombic gamma modification [1]. Under standard processing conditions, mainly the alpha modification is obtained [2–4], which is the thermodynamically stable modification consisting of a so called “cross-hatched” lamellar morphology with daughter lamellae growing in a 100° branching angle from the mother lamellae [4,5]. The thermodynamically metastable beta modification is usually not found under normal processing conditions, but can be induced by shear [6–10], temperature gradients [11,12] or by adding special beta-nucleating agents [10,13–16]. Beta spherulites consist of lamellae growing only radially from the center of the spherulites without any branching [5]. The gamma modification can be obtained under high pressures

and is industrially not relevant for iPP homopolymers [5]. The influence of the crystal modification on the mechanical properties of iPP has been widely discussed in the literature and different models have been proposed to explain the higher toughness of beta-iPP compared to alpha-iPP. The toughening effect of the beta modification has been explained by the different morphology of the spherulites and a phase transformation. Riekkel et al. [17] showed that beta-iPP undergoes a transformation from beta-iPP to alpha-iPP under tensile loading, which is accompanied by the formation of microvoids and causes higher toughness of the material. Aboulfaraj et al. [18] explained the brittle failure of alpha-iPP in comparison to beta-iPP by the different ability of crystallites to glide and reorient under mechanical loading due to the different structure of the spherulites. Crystal glide is much easier if the crystals consist of beta modification, since the crystalline lamellae are only linked by rubber-like chains. In the alpha modification, the daughter lamellae hinder crystal glide. Crazes appear mainly in the center of the alpha spherulites between the crystalline lamellae perpendicular to the tensile axis finally leading to a brittle failure of the material. Kotek et al. [19] suggested a model based on a higher continuity of the amorphous phase in the presence of crystal lamellae with beta-modification compared to the alpha-modification resulting in a higher drawability and toughness of

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beta-iPP. However, most of these studies were performed with low MFR-iPP. Only little data are available for iPP with high flowability [20].

The easiest and most industrially relevant method to obtain the beta modification is the use of nucleating agents, as they can be easily added to the polymer in the production process. Different nucleating agents are known to induce the beta modification in the polymer. The first reported beta-nucleating agent was γ -quinacridone which showed high nucleating efficiency at low concentrations [21]. Its red color, however, limits the use for a broad range of applications. More recent literature reports calcium pimelate and *N,N*-dicyclohexyl-2,6-naphthalene dicarboxamide as highly selective beta-nucleating agents [13,22]. A few studies [14,23] show the influence of the melt temperature and cooling rate on the morphology of iPP containing *N,N*-dicyclohexyl-2,6-naphthalene dicarboxamide. Higher melt temperatures lead to a higher solubility and subsequent self-assembly of the additive in the polymer melt, which lead to a higher amount of beta modification and a shish-kebab structure of the polymer instead of a spherulitic one.

A relatively new class of additives is the group of highly efficient, soluble nucleating agents based on 1,3,5-benzene-trisamides. It could be shown that, depending on their chemical nature, they can act as alpha- or beta-nucleating agents [24]. These additives are known to self-assemble in the polymer melt into long fiber-like structures that act as nucleating sites for the polymer [24,25]. Varga et al. found for the beta-nucleating agent (*N,N',N''*-tris(2,3-dimethylcyclohexyl))-1,3,5-benzenetricarboxamide a concentration-dependent behavior in iPP with a MFR of 0.35 and a maximum amount of beta modification at very low concentrations (around 100 ppm). However, no data regarding the mechanical properties of the beta-nucleated iPP were given [26]. In a previous study, we were able to show that this nucleating agent could be used to effectively increase the toughness of a high-MFR iPP [27]. A comparative study of different beta-nucleating agents [20] shows no clear correlation between the ability to increase the toughness of iPP and the amount of beta crystallinity in the material. The differences in the influence on the toughness are even more pronounced with increasing MFR of the polymer. For MFRs of ca. 0.3 g/10 min a quintuplication of the notched impact strength compared to the neat material could be achieved, whereas for MFRs of ca. 40 g/10 min only a doubling was observed with calcium pimelate. *N,N*-dicyclohexyl-2,6-naphthalene dicarboxamide, however did not influence the toughness of the material above a MFR of 15 g/10 min. So far, no clear explanation has been found for the different behavior. In this study, three different 1,3,5-benzenetricarboxamide nucleating agents and *N,N*-dicyclohexyl-2,6-naphthalene dicarboxamide are compared with regard to their ability to increase the toughness of iPP. The morphology of the different nucleated iPP is correlated with the mechanical properties and structure-property relationships are established providing an explanation of the different efficiency of beta-nucleating agents regarding the toughening of iPP.

2. Experimental

2.1. Materials

iPP (Moplen HP500V, MFR: 120 g/10 min according to ISO 1133) without any nucleating agents was kindly supplied as pellets by LyondellBasell. The 1,3,5-benzenetricarboxamide beta-nucleating agents, *N,N',N''*-tris(2,3-dimethylcyclohexyl))-1,3,5-benzenetricarboxamide (*beta NA1*) and *N,N',N''*-tris(1,1,3,3-tetramethylbutyl)-1,3,5-benzene-tricarboxamide (*beta NA2*) were obtained by the reaction of trimesic acid chloride and the corresponding amine (2,3-dimethylcyclohexylamine or *tert*-octylamine)

in anhydrous *N*-methylpyrrolidone as solvent, pyridine as base and LiCl. The synthesis and characterization were described in detail elsewhere [28–31]. They have been used as nucleation agents for iPP [24] and PVDF [32] and as supramolecular nanofibers [33,34]. As a reference alpha-nucleating agent, the commercially available nucleation agent, Irgaclear XT386 (*alpha NA*; supplier: BASF SE) and as a reference beta-nucleating agent (*beta Ref*), the commercially available nucleating agent, NJStar NU-100 (*N,N*-dicyclohexyl-2,6-naphthalene dicarboxamide, supplier: New Japan Chemical Co) were used as received.

2.2. Sample preparation

The optimum concentration for the benzenetricarboxamide additives was determined according to the method described in our previous study [27] taking into account the maximum nucleation efficiency and the lowest concentration leading to the highest possible amount of beta modification and was found to be 0.02 wt.% for *alpha NA*, 0.04% for *beta NA1* and 0.3% for *beta NA2*. For *beta Ref*, the optimum concentration for improving the toughness of iPP was taken from the literature as 0.03% [19,35–37]. Our own preliminary studies confirmed this concentration as the optimum regarding mechanical properties despite the fact that higher amounts of the beta modification could be achieved at higher additive concentrations.

The selected concentrations were then compounded in a co-rotating twin screw extruder (Brabender DSE 20/40). Along the length of the barrel, the temperature was gradually increased from 140 °C to 240 °C, resulting in a final melt temperature of 240 °C at the die. The screw speed was set to 90 rpm. Charpy test specimens were cut from the parallel section of tensile test specimens that were prepared by injection molding with an ENGEL e-max 200/50 injection molding machine with a mold temperature of 30 °C.

2.3. Thermal analysis

The crystallization temperatures and the degree of crystallinity of the samples were determined using a Mettler Toledo DSC/SDTA 821e DSC. The measurements were performed over a temperature range of 0 °C–250 °C at a heating/cooling rate of 10 °C/min under nitrogen atmosphere. The degree of crystallinity was determined from the first heating curve according to the following equation [1]:

$$X_c = \frac{\Delta H_m}{\Delta H_{m,0}} \quad (1)$$

with ΔH_m as the measured melting enthalpy and $\Delta H_{m,0}$ as the melting enthalpy of a 100% crystalline iPP (207 J/g) [38]. In order to confirm the nucleating effect of the additives, the crystallization temperature was determined from the cooling curve.

2.4. X-ray diffraction analysis (WAXS)

The crystal modification of the samples (tensile test specimen) was studied using a Seifert ID 3000 X-ray diffractometer operating at a voltage of 40 kV and a current of 30 mA. Using nickel-filtered Cu $K\alpha$ radiation (1.54 Å), the diffraction pattern was recorded with a step size of 0.05° between $2\theta = 8^\circ$ – 30° . The amount of beta modification was determined using the Turner-Jones method (Eq. (2)) [39].

$$k = \frac{H\beta}{H\beta + (H\alpha_1 + H\alpha_2 + H\alpha_3)} \quad (2)$$

with $H\beta$ as the height of the beta peak at $2\theta = 16.1^\circ$ and $H\alpha_1$, $H\alpha_2$

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