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Influence of a particulate nucleating agent on the quiescent and flow-induced crystallization of isotactic polypropylene

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ABSTRACT

Flow induced crystallization of commercial isotactic polypropylene (iPP) and its blends with sodium 2,2′-methylene bis-(4,6-di-tert-butylphenyl) phosphate (also known as NA11) is studied by means of in-situ time resolved small-angle X-ray scattering (SAXS). The isothermal crystallization at 145 °C (i.e. well below melting temperature of polymer) is performed after the application of steady shear to probe the anisotropic structure formation. In order to separate the influence of shear rate and shear time on polymer crystallization, four different shear conditions (60 s^{-1} for 1 s, 30 s^{-1} for 2 s, 15 s^{-1} for 4 s and 6 s^{-1} for 10 s) are applied while maintaining the same imposed strain in the polymer melt. Further the effect of different concentration of nucleating agent on the crystallization kinetics of iPP is examined both under quiescent and shear flow conditions. For instance, under quiescent condition, the crystallization half-time ($\tau_{1/2}$) decreases with the increasing concentration of nucleating agent in the polymer. Under shear flow conditions, our observations are as follows: In the case of neat iPP, $\tau_{1/2}$ decreases significantly at higher shear rates ($\geq 30\ s^{-1}$). Compared to the neat iPP, for the same concentration of NA11 in the NA11/iPP blends differences in $\tau_{1/2}$ with the increase in applied shear rates are significantly smaller. In other words, the crystallization kinetics is dominated by the amount of nucleating agent in the NA11/iPP blends as opposed to shear rates in the neat iPP. The present study shows that the critical value of shear rate required for chain orientation in the molten polymer is lower in the presence of the nucleating agent compared to neat iPP. The self-nucleation process investigated with the aid of differential scanning calorimetry (DSC), indicates that the nucleating efficiency of NA11 on iPP is around 60%.

1. Introduction

Nucleating agents offer exceptional mechanical and optical properties to semi-crystalline polymers [1–3]. It is often desired to reduce the processing time while maintaining the desired polymer morphology [4,5]. These objectives are achieved by enhancing the nucleation density with the addition of nucleating agents in the polymer [6], which can be roughly categorized into particulate and soluble systems [3]. Several studies based on transmission electron microscopy (TEM) and atomic force microscopy (AFM) showed that the good epitaxial matching between the crystals of nucleating agent and the polymer enhances heterogeneous nucleation rate [7–20]. Hikosaka et al. [21] reported the increase in the number density of crystals of polyethylene by 10^4 times after addition of the (particulate) organophosphate-type nucleating agent, NA11. Subsequently they monitored the nucleation process using small-angle X-ray scattering (SAXS). Kristiansen et al. [22] studied the phase behavior of the binary system consisting of 1,3: 2,4-bis (3,4-dimethylbenzylidene) sorbitol (DMDBS) and isotactic polypropylene (iPP). They reported increase in the crystallization temperature of iPP due to the nucleating action of DMDBS (soluble nucleating agent). The optical measurements of iPP/DMDBS provided insight on the DMDBS as “clarifying agent” where the increase in the clarity of injection molded samples was observed with the increase in the DMDBS concentration up to 1.0 wt%.

It is believed that application of flow promotes the transition from isotropic to anisotropic precursors and that the latter can grow into crystalline structures with cylindrical symmetry leading to shish-kebab morphology [23–25]. In the simplest case, a shish is

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made up of a fibrillar extended chain crystal bearing periodically spaced disk-like lamellae [26]. The final morphology of the polymer and the physical properties depend on the thermal and flow history to which the polymer undergoes crystallization from melt [27–30]. The influence of flow on the resultant morphology of iPP in the presence of nucleating agents has been widely reported [31–33]. Lipp et al. [34,35] studied the fibril formation of DMDBS in polypropylene (PP) melt. They reported the formation of nanofibrillar network of DMDBS during crystallization from melt. The detailed investigations on the fibrillar structure by TEM indicated the complex arrangement where length of fibril exceeds micrometer range and fibrils (less than 100 nm in cross-section) were composed of thinner nanofibrils (less than 10 nm in cross-section). Further investigations on the flow induced crystallization of polypropylene in the presence of DMDBS as nucleator revealed that the orientation of DMDBS nanofibrils during shear flow in the polymer melt is a prerequisite to obtain the oriented morphology. The oriented nanofibrils act as nucleation sites for oriented polypropylene crystallization, most likely in shish-kebab morphology. Moreover, modified shish-kebab morphology (double-orientation structure) was observed whereby daughter lamellar oriented with the normal along the radial direction is epitaxially grown on the kebab lamellae. Balzano et al. [36,37] studied the flow induced crystallization of DMDBS/iPP blends. They reported the possibility of breaking the nanofibrillar network and alignment of nanofibrils of DMDBS both above and below the crystallization temperature of DMDBS. The subsequent epitaxial (orthogonal) growth of iPP lamellae yielded a highly oriented lamellar morphology upon crystallization of polymer.

In this paper we study the role of metal salts of substituted aromatic heterocyclic phosphate such as sodium 2,2′-methylene bis-(4,6-di-tert-butylphenyl) phosphate (also known as NA11) on the crystallization kinetics of iPP, for which crystal lattice matching has been proven before [16]. Self-nucleation process is investigated with the aid of DSC to obtain the nucleation efficiency of nucleating agent for NA11/iPP blends. The isothermal crystallization at 145 °C (well below the melting point of iPP) is investigated for neat iPP and NA11/iPP blends during quiescent and flow conditions. To provide an insight on the anisotropic structure formation in the neat iPP and NA11/iPP blends, the flow induced isothermal crystallization at 145 °C is monitored using time resolved small-angle X-ray scattering (SAXS). Further, to understand the role of shear rate on the polymer crystallization, the evolution of relative crystallinity after the application of different shear flow conditions during the isothermal crystallization is analyzed for both neat iPP and NA11/iPP blends. Finally, the stiffness increase caused by nucleation is verified by determining the flexural modulus on injection molded specimens according to industrial standard procedure.

2. Experimental section

2.1. Materials

The iPP ($M_w = 365{,}000$ g/mol and $M_w/M_n = 5.4$; isotacticity ~ 97%) used in the present study is a PP homopolymer (commercially known as HD120MO) kindly provided by Borealis GmbH, Linz, Austria. Sodium 2,2′-methylene bis-(4,6-di-tert-butylphenyl) phosphate (commercially known as Irgastab® NA11) is obtained from Ciba Speciality Chemicals Inc. (now part of BASF SE), Basel, Switzerland. Irgastab® NA11 is a metal salt of substituted aromatic heterocyclic phosphate (chemical structure shown in Fig. 1). The nucleating agent has been blended at three different concentrations (0.1, 0.2 and 0.5 wt %) with the iPP in a co-rotating twin-screw extruder at 220 °C at Borealis GmbH, Linz, Austria, where also the mechanical tests are performed. Test bars of 80 × 10 × 4 mm^3 dimension comply with ISO 294-1 are prepared by injection molding process and later subjected to a 3-point flexural test according to ISO 178 to determine the modulus from the initial linear part of the stress–strain curve.

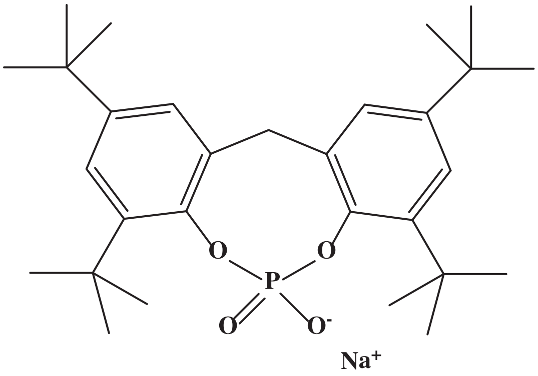

Fig. 1. Chemical structure of Irgastab® NA11.

2.2. Differential scanning calorimetry (DSC)

Thermal measurements are performed on TA instruments Q2000 calibrated to maximum precision with nearly 100% pure indium reference under ultra-high purity nitrogen atmosphere having a purge rate of 50 ml/min. Samples of 2–3 mg are weighed on a Mettler-Toledo XS3DU microbalance and subsequently placed in the Tzero aluminum pan. To erase thermal history of iPP, the samples are held at 200 °C for 5 min prior to the measurements. The controlled rate of 10 °C/min in the nitrogen atmosphere is adopted during heating and cooling process from/to the room temperature to determine the peak melting temperature (T_m), peak crystallization temperature (T_c), degree of crystallinity (X_c) and enthalpies of crystallization (ΔH_c) and melting (ΔH_m). To obtain the degree of crystallinity, the observed enthalpy of crystallization is normalized with the ideal 100% crystalline iPP sample [38] ($\Delta H_o = 207.1$ J/g) using the relation,

$$X_c = \left(\frac{\Delta H_c}{\Delta H_o}\right) \times 100$$

where, observed enthalpy of crystallization can be obtained by

$$\Delta H_c = \int_{T_s}^{T_e} (\mathrm{d}H/\mathrm{d}T)\mathrm{d}T$$

Self-nucleation process [39] is adopted to estimate the nucleation efficiency (NE) of nucleating agent for NA11/iPP blends using the equation below. For the purpose of evaluation, the two limits, viz. non-nucleated system (lower limit) and fully self-nucleated system (higher limit) on the nucleation efficiency scale are considered [40].

$$\mathrm{NE} = \left[\frac{(T_{c-NA} - T_{co})}{(T_{c-max} - T_{co})}\right] \times 100$$

where, $T_{c\text{-max}}$ represents the maximum crystallization temperature (higher limit) achievable after following the self-nucleation. T_{co} represents crystallization temperature of neat iPP (lower limit) determined via cooling with controlled rate. $T_{c\text{-NA}}$ is the crystallization temperature of iPP in presence of the nucleating agent. $T_{c\text{-max}} = 139.8$ °C is determined after self-nucleation process using the procedure (schematic representation shown in Fig. 2) as follows: