



Isothermal and non-isothermal crystallization of isotactic polypropylene nucleated with 1,3,5-benzenetricarboxylic acid tris(cyclohexylamide)



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ABSTRACT

Isothermal and non-isothermal crystallization kinetics of isotactic polypropylene (iPP) nucleated with 1,3,5-benzenetricarboxylic acid tris(cyclohexylamide) (BTCA-TCHA) were investigated by differential scanning calorimetry (DSC). The classical Avrami equation and the Mo method were used to analyze the experimental data. The results showed the Avrami equation and the Mo method described the isothermal and non-isothermal crystallization processes of iPP accurately, respectively. During isothermal crystallization, addition of BTCA-TCHA shortened half crystallization time ($t_{1/2}$) and increased crystallization rate of iPP greatly. In addition, addition of BTCA-TCHA decreased the crystallization activation energy ΔE from 370 kJ/mol of virgin iPP to 312 kJ/mol. During non-isothermal crystallization, half time of the crystallization ($t_{1/2}$) of virgin iPP was larger than that of nucleated iPP under the same cooling rate and the required cooling rate of virgin iPP to reach the same relative crystallinity was higher than that of nucleated iPP, indicating that addition of BTCA-TCHA increased the crystallization rate obviously.

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1. Introduction

Isotactic polypropylene (iPP) is one of the most common thermoplastics due to its advantages including relatively low production cost, feasible processing, and good mechanical properties in engineering applications [1–6]. Due to large spherulite size, however, iPP had low transparency and low impact strength under low temperature, limiting expansion of its application fields. From the commercial point of view, therefore, it is of important meanings to improve the mechanical and optical properties of iPP using proper methods.

Incorporation of nucleating agents into iPP during processing plays an important role for improving the mechanical and optical properties of iPP related to crystallization and morphology [7–10]. After addition of nucleating agents, nucleation and crystallization rate of iPP are increased and spherulite size is reduced. Size reduction of spherulites and increase of crystallinity can improve mechanical properties such as tensile strength and flexural modulus. Furthermore, small spherulites can improve optical properties of iPP, causing

lower haze value and better transparency. Moreover, the molding cycle time can be considerably reduced after incorporation of nucleating agents, especially in injection molding, which has decisive effects on the processing costs and production efficiency of iPP.

At present, nucleating agents with high nucleation efficiency which were commonly used in iPP mainly include organic carboxylates, aromatic heterocyclic phosphate salts and sorbitol derivatives. Many researches focused on effects of nucleating agents on properties and crystallization behaviors of iPP [11–19]. However, these conventional nucleating agents have certain disadvantages while they have excellent nucleation abilities. Dispersion of organic carboxylates and aromatic heterocyclic phosphate salts in iPP is nonuniform and conglomeration of nucleating agent particles might exist in the iPP blends, so nucleation efficiency of these nucleating agents in iPP is compromised and such defects as “Fish eye” (white spot) might appear in injection molding products. Sorbitol derivatives have drawbacks such as limited applicability and relatively poor thermal stability [8].

Amide derivatives of 1,3,5-benzenetricarboxylic acid are a type of novel nucleating agents for iPP which were developed in recent years. To overcome drawbacks of conventional nucleating agents, a

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series of derivatives of 1,3,5-benzenetricarboxylic acid were synthesized and their potential uses as nucleating agents for iPP were studied [20–24]. These researches showed that many 1,3,5-benzenetricarboxylic acid derivatives were highly efficient nucleating agents for iPP and they were capable of significantly reducing the haze value of iPP. Moreover, some of these derivatives had better nucleation effects at substantially lower concentrations than conventional sorbitol derivative nucleating agents and they can also be used as nucleating agents for other polymers [25,26]. In our previous work, the effects of nucleating agent 1,3,5-benzenetricarboxylic acid tris(cyclohexylamide) (BTCA-TCHA) on properties and crystallization behaviors of iPP were studied [27]. The results showed that BTCA-TCHA was a highly effective nucleating agent for iPP and the nucleation efficiency of BTCA-TCHA was comparable to that of a commercial sorbitol-based nucleating agent Millad 3988.

It is well known that the properties of semi-crystalline polymers, such as iPP, strongly depend on their crystal structure and morphology, which in turn is affected by crystallization behaviors of the polymer. Therefore, investigation of crystallization kinetics is of important meanings for understanding the properties and morphology of a polymer and it is also useful for explaining the nucleation mechanism of a nucleating agent in iPP. Isothermal crystallization is most applicable to theoretical analysis and comparison with experimental results. However, practical processing such as extrusion and injection molding are usually performed under non-isothermal crystallization conditions. In order to optimize processing conditions in industrial processes and achieve better properties as well as to understand the nucleation mechanism, it is necessary to study the isothermal and non-isothermal crystallization processes of a polymer quantitatively [18,28–30]. For isothermal crystallization kinetics, the classical Avrami method was commonly used for analysis of the experimental data [31–33]. For non-isothermal crystallization behaviors, many methods were adopted at present, including the Jeziorny method [34], the Ozawa method [35], the Mo method [36,37]. In this paper, the Avrami method and the Mo method were adopted to investigate the isothermal and non-isothermal crystallization kinetics of iPP nucleated with 1,3,5-benzenetricarboxylic acid tris(cyclohexylamide) (BTCA-TCHA), respectively.

2. Experimental

2.1. Materials

iPP powders (MFR=2.5 g/10 min) used in this work were supplied by SINOPEC Jiujiang Company (China). Nucleating agent 1,3,5-benzenetricarboxylic acid tris(cyclohexylamide) (BTCA-TCHA), whose structure is shown in Fig. 1, was synthesized according to literature [20]. Antioxidants 1010 and 168 were obtained from Ciba Specialty Chemicals (Switzerland).

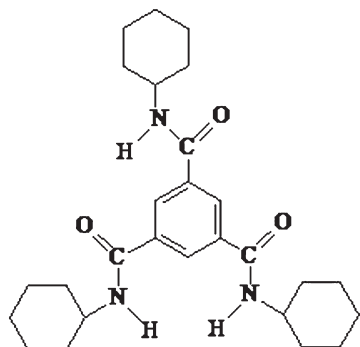


Fig. 1. Molecular structure of 1,3,5-benzenetricarboxylic acid tris(cyclohexylamide).

2.2. Sample preparation

The iPP powders and nucleating agent BTCA-TCHA (0.2 wt% in iPP) in combination with antioxidants 1010 and 168 (concentration of both 1010 and 168 in iPP is 0.1 wt%) were mixed at ambient temperature in a SHR 100 high-speed mixer (Zhangjiagang HaiChuan Machinery Co., Ltd., China) for 5 min. Then the mixture was extruded by a SHJ-20B twin-screw extruder (Nanjing GIANT Machinery Co., Ltd., China) and pelletized. The extruder has seven temperature zones and the temperature in the seven zones is 190 °C, 210 °C, 210 °C, 220 °C, 220 °C, 205 °C, and 195 °C, respectively. The pellets were used for subsequent DSC analysis.

2.3. DSC (differential scanning calorimetry) analysis

Isothermal and non-isothermal crystallization behaviors of virgin iPP and iPP nucleated with BTCA-TCHA were investigated by using a TA Q2000 DSC (TA Company, USA). All DSC operations were carried out under a nitrogen atmosphere. Weight of every sample was 2–3 mg and both samples were heated to 200 °C and maintained at the temperature for 5 min to erase the thermal history. During isothermal crystallization, the molten sample was rapidly cooled to the predetermined crystallization temperature at the cooling rate of 100 °C/min and maintained until the crystallization was completed. The exothermal curves of heat flow as a function of time were recorded at given crystallization temperatures. During non-isothermal crystallization, the molten sample was cooled from 200 °C to 50 °C at a constant cooling rate Φ (selected from 2.5 °C/min to 40 °C/min) and the exothermal curves of heat flow as a function of temperature were recorded.

3. Results and discussion

3.1. Isothermal crystallization kinetics

Fig. 2 shows the DSC cooling curves of virgin and nucleated iPP during isothermal crystallization at different temperatures. With increasing the crystallization temperature, the exothermal peak of DSC curves shifts right obviously, indicating shorter crystallization time and lower crystallization rate. In addition, it can be seen from Fig. 2 that iPP nucleated with BTCA-TCHA has shorter time for finishing crystallization under higher crystallization temperature than virgin iPP, indicating that BTCA-TCHA accelerates crystallization of iPP greatly.

According to the classical Avrami theory, the relative crystallinity of a polymer as function of time t at a given crystallization temperature T can be expressed by the following equation: [31–33]:

$$1 - X_t = \exp(-Z_t t^n) \quad (1)$$

where Z_t is the crystallization rate constant, n is the Avrami exponent, and X_t is the relative crystallinity at time t , defined as:

$$X_t = \frac{\int_0^t (dH(t)/dt) dt}{\int_0^\infty (dH(t)/dt) dt} \quad (2)$$

where $(dH(t)/dt)$ is the heat evolution rate during the crystallization process. The kinetic parameters n and Z_t are commonly used to qualitatively explain the nucleation mechanism and overall crystallization rate of the polymer.

The Avrami equation can also be expressed by the following form:

$$\ln[-\ln(1 - X_t)] = n \ln t + \ln Z_t \quad (3)$$

From the slope and intercept of straight lines regressed from the plots of $\ln[-\ln(1 - X_t)]$ versus $\ln t$, the kinetic parameters n and Z_t

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