Effect of Particle Size of *β*-nucleating Agent on the Crystallization and Mechanical Properties of Isotactic Polypropylene

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Abstract. In this paper, *β*-isotactic polypropylene (*β*-iPP) samples were prepared by adding two *β* nucleating agents with different particle sizes (NT-C and ST-C). The melting, crystallization and mechanical properties of *β*-iPP samples were investigated by means of differential scanning calorimetry (DSC) and mechanical tests. It is revealed that the *β* nucleation efficiency and crystallizaton ability of iPP/ST-C (fine size and narrow distribution) is better than those of iPP/NT-C (coarse size and wide distribution). It is also found that tensile strain at break and notched impact strength increase for the *β*-nucleated iPP specimens. The superior toughness is obtained for iPP/ST-C specimens.

Introduction

As a semicrystalline polymer, isotactic polypropylene (iPP) is widely used in different fields owing to its low manufacturing cost and rather versatile properties. According to the difference of formation conditions, iPP can crystallize in five modifications, i.e., monoclinic *α* form, trigonal *β* form, orthorhombic *γ* form, δ and smectic phases. The toughness and heat resistance of *β*-iPP are superior to *α*-iPP. However, the formation of *β*-modification occurs merely under some special conditions, such as isothermal crystallization at a certain temperature, crystallization in a temperature gradient field, shear-induced crystallization, or addition of *β* nucleating agents[1-5]. Among them, the addition of *β* nucleating agents is the most effective way to obtain *β*-iPP.

Shi and Dou[6] prepared *β*-iPP samples by adding a *β* nucleating agent NT-C, Izod notched impact strength reached the maximum (4.3 times greater than that of pure iPP) when 0.3 wt% NT-C was added. Guo and coworkers[7] studied the ultrafine dispersion of a phosphate nucleating agent in a polypropylene matrix, and found that finer dispersion of the phosphate nucleator improve the mechanical properties of PP.

In this article, *β*-iPP samples were prepared with two *β* nucleating agents with different particle sizes. The melting, crystallization behaviors and mechanical properties of the samples were investigated.

Experimental

Materials

iPP powder, Grade 001, was produced by Nanjing Jinling Plastic & Petrochemical Co. Ltd. (Nanjing, China). *β* nucleating agents (NT-C and ST-C) were supplied by Nanjing Chengkuan Trade Co., Ltd. (Nanjing, China). Industrial antioxidant (B215) was provided by Nanjing Hua Lim Chemical Co., Ltd. (Nanjing, China).

Particle Size Measurements

ST-C is prepared from NT-C by an ultrafine jet mill (STJ-100, Yixin Better Seishin Machinery Co., Ltd, Yixin, China). The particle sizes of NT-C and ST-C were measured by laser light scattering technique (Mastersizer 2000, Malvern Instruments Ltd., England). The particle sizes of

the original β nucleating agent NT-C and the ultrafine product ST-C are listed in Table 1.

Tab.1 The Particle Sizes of NT-C and ST-C

Nucleator	D10	D50	D90
NT-C	1.133μm	3.951μm	35.713μm
ST-C	0.680μm	1.645μm	3.564μm

Note: DX represents the value of the particle diameter at X% in the cumulative distribution curve.

Preparation of Samples

iPP powder was mixed with 0.1 wt% B215 and variable amounts of β nucleating agents, respectively. The mixtures were compounded in a single-screw extruder (SJ30-28, Zhongsu Haichuang Plastic Technology Co., Ltd., Wuhan, China). The melt was cooled and pelletized. Standard test specimens for mechanical measurements were injection-molded with a reciprocating-screw injection molding machine (CJ80M3V, Chen De Plastics Machinery Co., Ltd., Foshan, China).

A pellet was placed between two glass slides in a hot stage kept at 210 ℃ for 5 min to allow the sample to melt completely and remove thermal memory, squeezed on the top slide, and then placed in a hot stage kept at 120 ℃ for 30 min. After that, it was quenched at room temperature. The isothermally crystallized samples were used for DSC analysis.

DSC Measurements

The melting and crystallization behaviors of the isothermally crystallized samples were measured using a DSC apparatus (ZF-DSC-D2, Shanghai Zufa Industry Co., Ltd., Shanghai, China) under a dry nitrogen atmosphere. The instrument was calibrated with pure indium, tin and zinc for temperature and heat flow, respectively. For each measurement, ~ 5 mg of the sample was sealed in an aluminum pan. The sample was heated from room temperature to 210 ℃ at 10 ℃/min, and held at 210 ℃ for 5 min to remove the thermal history. Then, the melted sample was cooled to 100 ℃ at 10 ℃/min, and held at 100 ℃ for 5 min. At last, the sample was reheated to 210 ℃ at 10 ℃/min. The melting and cooling curves were recorded. The melting temperatures of α-phase ($T_{m,\alpha}$) and β-phase ($T_{m,\beta}$) were obtained from the melting curves. The onset (T_c^{on}) and peak (T_c^p) crystallization temperatures were obtained from the cooling curves. The enthalpies of the α form ($\Delta H_{m,\alpha}$) and β form ($\Delta H_{m,\beta}$) were obtained by separating the areas of the α and β melting peaks by a "vertical line" method[8]. The crystallinity values of the α forms (X_α) and β forms (X_β) as well as the β crystalline form content (K_{DSC}) were calculated as follows:

$$X_\alpha = \Delta H_{m,\alpha}/\Delta H^0_{m,\alpha} \tag{1}$$

$$X_\beta = \Delta H_{m,\beta}/\Delta H^0_{m,\beta} \tag{2}$$

$$K_{DSC}(\%) = 100 \times X_\beta/(X_\alpha + X_\beta) \tag{3}$$

Where $\Delta H^0_{m,\alpha}$ is the enthalpy of fusion of α-iPP with 100% crystallinity (177 J/g), $\Delta H^0_{m,\beta}$ is the enthalpy of fusion of β-iPP with 100% crystallinity (168.5 J/g) [2].

(a) The First Melting Curves (b) The Second Melting Curves (c) The Cooling Curves
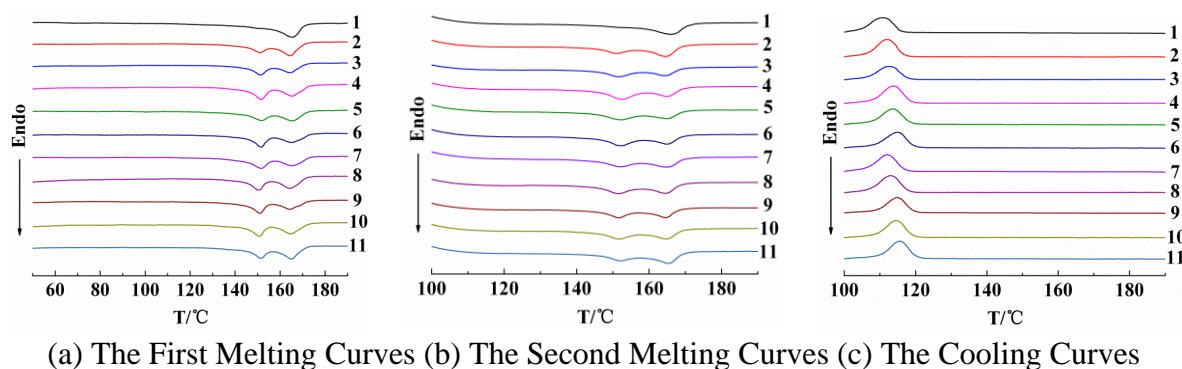
Fig.1 DSC Curves of Isothermally Crystallized Samples (1 Pure iPP; 2 NT-C 0.05%; 3 NT-C 0.10%; 4 NT-C 0.20%; 5 NT-C 0.30%; 6 NT-C 0.40%; 7 ST-C 0.05%; 8 ST-C 0.10%; 9 ST-C 0.20%; 10 ST-C 0.30%; 11 ST-C 0.40%)

Mechanical Measurements

The tensile and flexural tests were carried out by using an electromechanical universal testing machine (SANS5254, Shenzhen SANS Testing Machine Co., Ltd., Shenzhen, China) according to ISO 527 and ISO 178, respectively. The Izod notched impact strength was measured using a pendulum impact testing machine (MZ2056, Jiangdu Mingzhu Testing Machine Factory, Jiangdu, China) according to ISO 180.

Results and Discussion

DSC Measurements

The melting and cooling curves of the isothermally crystallized samples are shown in Fig.1. The relevant parameters are presented in Table 2. It is shown that pure iPP has predominant α-crystals, while the nucleated iPP has both α and β-crystals. Fig.1(a) shows the first melting curves of the samples. In general, with the addition of nucleating agents, β contents are enhanced firstly and then are weakened. Table 2 shows the maximum β contents are obtained at 0.20wt% nucleating agents for both nucleators. Compared with iPP/NT-C, iPP/ST-C has greater K_{DSC}, which reflects the better β nucleation efficiency of ST-C.

Figure 1(b) shows the second melting curves of the samples. Compared to the first melting curves, the second melting curves have weaker β melting peaks. The first and second heating curves are different due to the different thermal history that the samples experienced. The formation of pure β-iPP has a restricted temperature range, i.e., upper [T (β, α) =140–141 ℃] and lower limit temperatures [T $(\alpha, \beta) \sim$ 105 ℃][8]. The samples evaluated in the first melting undergo isothermal crystallization at 120 ℃, which facilitates the formation of β-crystals. Then the melted samples were cooled to 100 ℃, i.e., below T (α, β), which is adverse to the formation of β-crystals.

As shown in Fig.1(c) and Table 2, T_c^{on} and T_c^p shift to higher temperatures after the addition of the β nucleators and T_c^{on} and T_c^p of iPP/ST-C are greater than those of iPP/NT-C. This indicates that both NT-C and ST-C promotes the crystallization rate of iPP, but the crystallization ability of iPP/ST-C is superior to that of iPP/NT-C. Steps, ridges, cracks, holes, etc., which are on the surface of the nucleating particle offer active sites for the nucleation[9]. At the same weight percentage, ST-C has smaller particle size and larger surface area than those of NT-C. Therefore ST-C offers more active sites for the nucleation and enhances the crystallization of iPP greatly.

Tab.2 Thermal Parameters of the Isothermally Crystallized Samples

β nucleator [wt%]	First melting			Second melting			Cooling	
	$T_{m,\alpha}$[℃]	$T_{m,\beta}$[℃]	K_{DSC} [%]	$T_{m,\alpha}$[℃]	$T_{m,\beta}$[℃]	K_{DSC} [%]	T_c^{on}[℃]	T_c^{p}[℃]
-	165.5	-	-	165.8	-	-	117.9	110.7
NT-C 0.05	164.1	151.1	30.35	164.8	150.8	29.10	120.3	112.0
NT-C 0.10	164.5	150.8	50.99	164.6	151.6	35.15	121.1	112.8
NT-C 0.20	165.1	151.5	51.26	165.2	152.4	39.76	121.9	113.8
NT-C 0.30	165.3	152.1	42.54	165.0	152.2	51.06	122.1	113.6
NT-C 0.40	165.1	151.6	50.22	165.2	152.2	53.54	123.2	114.9
ST-C 0.05	165.0	151.5	54.74	165.2	151.7	40.98	120.5	111.9
ST-C 0.10	164.6	150.5	53.95	164.8	151.5	47.44	121.5	113.2
ST-C 0.20	164.2	151.0	56.52	164.7	151.5	45.92	122.7	114.8
ST-C 0.30	164.8	150.6	48.12	164.9	151.6	45.36	122.4	114.2
ST-C 0.40	165.4	151.4	46.53	165.7	152.0	38.30	122.9	115.5

Mechanical Properties

Table 3 shows the mechanical properties of the nucleated iPP specimens. In contrast to pure iPP, tensile strength and flexural modulus decrease, while tensile strain at break and notched impact strength increase for the nucleated iPP. Izod notched impact strength reaches the maximum value with the addition of 0.30wt% nucleating agents. The maximum notched impact strength of iPP/NT-C and iPP/ST-C is 3.71 and 4.60 times greater than that of the pure iPP, respectively. NT-C and ST-C are incompatible with iPP and the particle size of nucleating agent has great influence on toughening effect. With the decrease of particle size, interface bonding between particle and matrix is enhanced[10]. The relatively large particle size and wide distribution of NT-C might cause stress concentration in the matrix. On the contrary, the fine size and narrow distribution of ST-C lead to the superior toughness of iPP/ST-C specimens.

Tab.3 Mechanical Properties of the Nucleated iPP Specimens

β nucleator [wt%]	Tensile strength [MPa]	Tensile strain at break [%]	Flexural modulus [MPa]	Izod notched impact strength [kJ/m^2]
-	49.0±0.7	10.5±2.1	1859±14	18.60±2.38
NT-C 0.05	44.7±2.0	35.2±4.1	1638±14	43.48±6.58
NT-C 0.10	43.3±0.7	55.8±0.3	1644±12	60.99±2.64
NT-C 0.20	45.5±3.9	56.6±13.9	1676±26	64.32±3.60
NT-C 0.30	45.1±0.6	48.2±4.6	1574±16	69.07±5.59
NT-C 0.40	46.6±0.8	58.5±13.9	1706±10	63.39±2.53
ST-C 0.05	47.0±0.1	149.1±27.6	1603±17	71.64±4.42
ST-C 0.10	44.5±1.4	128.2±12.5	1582±7	81.32±7.32
ST-C 0.20	45.5±1.0	146.5±13.2	1547±28	78.21±2.42
ST-C 0.30	43.5±0.9	179.1±7.1	1616±10	85.47±4.49
ST-C 0.40	45.6±0.2	144.9±10.5	1621±14	82.54±3.88

Conclusions

DSC results show that the addition of nucleating agents (NT-C and ST-C) can effectively improve the formation of β-modification. The maximum β contents are obtained with the addition of 0.20wt% nucleating agents. ST-C has more efficient β nucleation efficiency, which may relate to its fine particle size and large surface area.

Mechanical tests indicate that the toughness is influenced by the particle size of the nucleating agent. The superior toughness is obtained for iPP/ST-C specimens.

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