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Crystallization kinetics, spherulitic morphology, mechanical properties and heat resistance of β-nucleated impact-resistant propylene-ethylene copolymer

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ABSTRACT

β-nucleated impact-resistant propylene–ethylene copolymer (IPC) samples were prepared via melt compounding. The isothermal and non-isothermal crystallization and melting behaviors of the samples were investigated by means of differential scanning calorimetry (DSC). Avrami equation was used to analyze the isothermal crystallization kinetics of the samples. The Lauritzen–Hoffman theory was applied and the nucleation constant K_g and the surface free energy σ_e was calculated. Jeziorny's and Mo's methods were used to analyze the non-isothermal crystallization kinetics of the samples. The activation energy (ΔE) of non-isothermal crystallization and the nucleating activity of the samples were calculated by Friedman's formula and Dobreva's method, respectively. The results show that the addition of β-nucleating agent (NT-A and NT-C) decreases the K_g and σ_e, so that the nucleation and crystallization rate of IPC is increased greatly under isothermal condition. Jeziorny's and Mo's methods well describe the non-isothermal crystallization kinetics of the samples. NT-C is more effective than NT-A as a β-nucleating agent. It is also found that the addition of nucleating agent decreases the size and increases the number of spherulites significantly. The Izod notched impact strength and heat deflection temperatures (HDT) of IPC are also improved by the nucleating agents.

1. Introduction

Isotactic polypropylene (iPP) is one of the most important thermoplastic polymers, owing to its low manufacturing cost and versatile properties. But its application in some fields is limited due to its relatively poor fracture resistance, especially at low temperature. Thus, several routes have been developed to improve the fracture toughness of iPP, namely, blending with elastomeric material (e.g., ethylene–propylene–diene copolymer, ethylene–vinyl acetate copolymer) [1,2], copolymerization with ethylene or other olefins [3,4], and addition of β nucleating agents (β-NA) [5]. Among these routes, in situ copolymerization with ethylene is an effectively industrial method to obtain the impact-resistant propylene–ethylene copolymer (IPC) [6]. As a promising material, IPC has been extensively used as matrix component in pipes, automobile parts, furniture, and other industrial uses owing to its outstanding comprehensive properties.

β-NA is used as an impact additive for improving the fracture toughness of iPP. Lu and Dou [7] reported that the maximum β content in iPP specimen reached 79.1% with addition of 0.05 wt% *N*, *N*'-dicyclohexylsuccinamide. Shi and Dou [8] prepared β-iPP samples by adding a β-NA 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. If both of β nucleation and rubber modification were utilized, a synthesized effect on the resulting toughness was detected at low temperature due to higher stiffness of the rubber inclusions at the cryogenic temperature and additional orientation of the β-crystalline phase [9]. Luo et al. [10] prepared β-nucleated IPC by adding a β-NA WBG, and the impact strength at 0 °C reached the maximum (4 times greater that of neat IPC) after adding 0.5 wt% WBG. Liu et al. [11] reported calcium tetrahydrophthalate was a high efficient β-NA for IPC and found the β-NA also greatly accelerated the crystallization rate of IPC.

Mechanical and physical properties of semi-crystalline polymers are decided by crystal structures and morphology, which in turn are influenced by crystallization behaviors of polymers. Thus, it is essential to study of the crystallization kinetics of polymeric products. Many models, such as Jeziorny model [11–14], Ozawa model [15,16], Mo model [12–13,17–19], and so on [20–22] were

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used to describe the non-isothermal crystallization kinetics of nucleated PP and PP composites.

The crystallization behavior of IPC has attracted much attention in recent years because of its complex multiphase structure. Study on the non-isothermal crystallization of IPC has become technologically important since it is close to the real processing situation and can provide helpful information for the determination of processing parameters [4,23]. Li et al. [24] introduced a highly effective β-NA into IPC and found that the multiple melting behaviors were greatly dependent on both the concentration of β-NA and the cooling rate applied during the non-isothermal crystallization process. Motsoeneng et al. [25] revealed that the non-isothermal crystallization kinetics of neat IPC and nucleated IPC followed a three-dimensional growth with a thermal nucleation mechanism.

In this study, isothermal and non-isothermal crystallization and melting behaviors of IPC nucleated by two commercial β-NAs (NT-A and NT-C) were investigated by means of differential scanning calorimetry (DSC). Isothermal crystallization kinetics was analyzed by Avrami equation and Lauritzen–Hoffman theory. The kinetic parameters of the non-isothermal crystallization were analyzed by Jeziorny and Mo models. The effective activation barrier for the non-isothermal crystallization process was calculated by the isoconversional method. Moreover, the nucleation activity was calculated by the method proposed by Dobreva and Gutzow. In addition, the spherulitic morphology, mechanical properties and heat resistance of the nucleated IPC specimens were also investigated.

2. Experimental

2.1. Materials

The IPC pellets (Grade B8101, ~9 wt% ethylene content, MFR = 0.45 g/10 min at 2.16 kg and 230 °C) is a commercial product of Sinopec Yanshan Petrochemical Company Ltd. (Beijing, China); β-NAs (NT-A and NT-C, carboxylates) were supplied by Nanjing Chengkuan Trade Co., Ltd. (Nanjing,China), their FTIR spectra and applications were shown in the literatures [8,14,26]; liquid paraffin (Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) was used as received.

2.2. Preparation of samples

The IPC pellets were premixed with 0.1 mass% liquid paraffin and 0.2 mass% β-NA. The mixtures were compounded in an internal mixer (HL200, Jilin University Science & Technology Equipment Factory, Changchun, China) at 220 °C and 40 rpm for 5 min. The melt was cooled and cut into small pieces. Standard test specimens for mechanical and heat resistance tests were injection-molded with a micro-injection molding machine (SZ-15, Wuhan Rui Ming Plastics Machinery Company, Wuhan, China).

A small piece was placed between two glass slides on a hot stage and kept at 210 °C for 5 min to allow the sample to melt completely and to remove its thermal history. It was squeezed on the top slide to form a film and was quickly transferred onto a hot stage and kept at 120 °C for 30 min. The thickness of the samples after isothermal crystallization was approximately 0.5 mm for DSC characterization, and 10–20 μm for polarized light microscopy (PLM) observation, respectively.

2.3. DSC measurements

Isothermal and non-isothermal crystallization exotherms and subsequent melting endotherms were recorded using a ZF-DSC-D2 DSC instrument (Shanghai Zufa Industry Co., Ltd., Shanghai, China) under a dry nitrogen atmosphere. The temperature and heat flow were calibrated with indium, tin and zinc. Samples were heated from room temperature to 210 °C at 10 °C/min and held at 210 °C for 5 min to eliminate their thermal history. After the first scan, the melted samples were rapidly cooled at 50 °C/min to the predetermined crystallization temperature T_c and maintained for the time necessary for isothermal crystallization. In the case of non-isothermal crystallization, the melted samples were cooled to 50 °C at the constant cooling rate (Φ) of 3, 5, 10 and 15 °C/min, respectively, and held at 50 °C for 5 min, then reheated to 210 °C at 10 °C/min.

The melting and cooling curves were recorded. The melting temperatures of α-form ($T_{m,\alpha}$) and β-form ($T_{m,\beta}$) were obtained from the melting curves. The melting enthalpies of α-form ($H_{m,\alpha}$) and β-form ($H_{m,\beta}$) were obtained from the separation of the areas of α and β melting peaks by a "vertical line" method [27,28]. The peak crystallization temperatures (T_{cp}) were obtained from the cooling curves. The content of β crystalline form (K_{DSC}) was calculated as follows:

$$X_\alpha = \frac{H_{m,\alpha}}{H^\circ_{m,\alpha}} \times 100\% \quad (1)$$

$$X_\beta = \frac{H_{m,\beta}}{H^\circ_{m,\beta}} \times 100\% \quad (2)$$

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

where $H^\circ_{m,\alpha}$ and $H^\circ_{m,\beta}$ are the enthalpies of fusion of α-iPP with 100% crystallinity (177 J/g) and β-iPP with 100% crystallinity (168.5 J/g) [29].

2.4. PLM observations

Spherulitic morphologies of the isothermally crystallized samples were observed in a polarized light microscope (LW-200-4JS, Shanghai LW Scientific Co., Ltd., Shanghai, China) equipped with a cross polars and a CCD camera. PLM photographs were captured and stored in a computer.

2.5. Mechanical tests

The tensile tests were carried out using an electromechanical universal testing machine (SANS5254, Shenzhen SANS Testing Machine Co., Ltd., Shenzhen, China) according to ISO 527-2/1BA/50. 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/A.

2.6. HDT tests

Heat deflection temperatures (HDT) of the specimens were measured according to ISO 75 using a HDT-VICAT tester (ZWK1302-B, Shenzhen SANS Testing Machine Co., Ltd., Shenzhen, China). The flexural stress was 0.45 MPa and the heating rate was 120 °C/h.

3. Results and discussion

3.1. Isothermal crystallization kinetics

The isothermal crystallization kinetics of a material can be analyzed by evaluating its degree of crystalline conversion as a