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Effect of nano-scaled styrene butadiene rubber based nucleating agent on the thermal, crystallization and physical properties of isotactic polypropylene

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ABSTRACT

The influence of a specific nano-scaled styrene butadiene rubber based β-nucleating agent (β-NA) on the properties of isotactic polypropylene (iPP) was investigated in the current research. β-NA was applied at the concentration ranged from 0.05 to 0.50 wt%. Microscopic observation revealed that the neat iPP crystals grew very slowly; they ranged in size from 100 to 200 μm. The addition of β-NA led to higher population of nuclei and smaller spherulites than those found in neat iPP. The addition of only 0.05 wt% β-NA significantly decreased the sizes of the spherulites down to 5 μm; the crystal grew very rapidly, leading to extremely fine morphology. Analysis by X-ray diffraction (XRD) confirmed that iPP/β-NA constituted mainly of β-crystal structure. The transformation of β to α phase was observed upon re-extrusion, it was verified by the lowered fraction of the β-crystalline phase (K_β) although the total degree of crystallinity remained unchanged. A significant improvement in the impact strength of the iPP/β-NA was observed when the β-NA was employed from 0.10 to 0.20 wt%, leading to the formation of tough β-crystals in the β-NA nucleated iPP. The color measurement implied that the iPP nucleated with β-NA was superior in terms of whiteness but it was less transparent, as was evident by the increased haze.

1. Introduction

Isotactic polypropylene (iPP) is one of the most important commercial plastic due to its relatively low-cost, recyclability, good mechanical properties and good processability [1–11]. The crystal morphology, spherulite size and the degree of crystallinity are widely known to directly affect the mechanical and the thermal properties and the processing time of iPP [12–16]. Upon cooling, the iPP chains can crystallize to form crystals of different spatial arrangements namely monoclinic (α), trigonal (β), orthorhombic (γ) and smectic [4,12].

Generally, the α-form is the most stable crystal with excellent tensile strength but inferior toughness [17–20] while the β-form has greater toughness but lower thermal stability. Several advantages of the β-NA has been reported including lower crystalline density, lower melting point [15,21,22] and higher toughness [23–25]. It was believed that the β-crystal can be achieved under stipulated conditions such as a temperature gradient, under shearing or by using a specific nucleating agent [4,15,20]. Among these approaches, the addition of β-nucleating agent (β-NA) to iPP is the easiest method for the preparation of iPP rich in β-phase [4].

Many researchers have attempted to produce iPP with high fraction of β-crystal form. Jiang et al. [12] found a dramatic increment of the impact strength by 191% when rare earth organic coordination compound (WBG) was added. They reported that the spherulite size was significantly decreased compared with that observed in the neat iPP when WBG was incorporated at only 0.135 wt% [4]. Xiao et al. [26] utilized a hetero-nuclear dimetal complex of lanthanum and calcium as a β-nucleating agent for iPP and concluded that the optimum concentration of β-nucleating agent was only 0.08 wt%. Wang et al. [27] promoted the β-phase in iPP by utilizing multi-walled carbon nanotube supported calcium pimelate and found excellent impact toughness compared with that of the neat iPP.

It is widely known that the degree of crystallinity of PP is usually restricted when rubber was added for toughening purpose [8,9]. Thus, many researchers have attempted to produce the nucleated iPP with high impact resistance. Fanegas et al. [10] investigated the effect of poly(styrene-*b*-ethylene butylene-*b*-styrene) (SEBS) and a metallocenic ethylene–octene copolymer (EO) on the toughening and the crystallization performance of the nucleated PP. They found that the degree of crystallinity remain

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unchanged with the presence of both SEBS and EO. Choudhary et al. [11] concluded that the addition of 10 wt% ethylene propylene diene monomer (EPDM) to iPP increased the spherulite size and significantly decreased the degree of crystallinity.

Thus, the combination of toughening as well as nucleating was proposed in the current research by using a styrene butadiene rubber (SBR) based material to simultaneously acted as a toughening agent and a crystallization facilitator. In this paper, a nano-scaled SBR-based β-NA was employed to induce the trigonal β-crystal form in iPP. The investigation was conducted by varying the β-NA content from to 0.5 wt%. The study focused on the influences of the β-NA content on the morphological changes, crystalline transformation, crystallization behavior, mechanical and thermal properties of iPP.

2. Materials and methods

2.1. Materials and processing

Powder of iPP homopolymer (PP1100 NK, IRPC Public Company Limited, Thailand) was used as raw material. Its melting temperature and melt flow rate were 165 °C and 11 g/10 min respectively. The iPP powder contained no additives as it was collected immediately after polymerization. A nano-scaled β-NA (VP101T, BRI-CI China) was incorporated as a nucleating agent to induce the β-crystal in the iPP. It is composed of SBR, sodium salt and sodium benzoate. The β-NA has an average particle size of 55 nm.

A series of the β-NA nucleated iPP was prepared with various β-NA contents of 0.05, 0.10 0.15, 0.20, 0.30, 0.40 and 0.50 wt%. The β-NA was firstly dry mixed with the iPP powder by using a high speed mixer (Labtech Engineering model 5VS, Thailand) at the impeller speed of 1000 rpm to disperse the β-NA particles in the iPP powder. Each of the β-NA nucleated iPP composition was then melt-blended by using a co-rotating twin screw extruder (Labtech Engineering model LTE16-40, Thailand), the screw temperatures were set at 200–220 °C. Each formulation of the nucleated iPP extrudate was pelletized and injection molded to obtain the test specimens for subsequent mechanical, thermal tests and morphological characterizations. The injection molding was conducted at the temperature range of 200–220 °C and the injection feed pressure at 80 bar respectively.

2.2. Testing and characterizations

2.2.1. Thermal characterizations

The crystallization temperature (T_c) and the melting temperature (T_m) of the β-NA nucleated iPP were evaluated by using a Differential scanning calorimeter (DSC, Perkin Elmer, DSC6000). The test condition covered a broad range of temperature from −70 to 210 °C at the heating rate of 10 °C/min under nitrogen atmosphere.

An X-ray Diffractometer (XRD) (Bruker AXS model D8 Advance, Germany) was employed to characterize the crystal morphology of the neat iPP and the β-NA nucleated iPP. The continuously scanning angle in this study ranged from 5° to 35° at 40 kV and 30 mA. In the XRD pattern of iPP, the principal indices of the fraction of the α-crystal form were (110), (040) and (130) while the major reflection of the β-crystal was (300) [4,28–31]. The fraction of the β-crystalline phase (K_β), the overall degree of crystallinity (X_{all}), the degree of β-crystallinity (X_β) and the degree of α-crystallinity (X_α) were calculated by using the following equations [6].

$$K_\beta = \frac{\beta_{(300)}}{\beta_{(300)} + \alpha_{(110)} + \alpha_{(040)} + \alpha_{(130)}} \quad (1)$$

$$X_{all} = 1 - \frac{A_{amorphous}}{\sum A_{amorphous} + A_{crystallization}} \quad (2)$$

$$X_\beta = K_\beta X_{all} \quad (3)$$

$$X_\alpha = (1 - K_\beta) X_{all} \quad (4)$$

where $\alpha_{(110)}$, $\alpha_{(040)}$ and $\alpha_{(130)}$ were the integral intensities of the (110), (040) and (130) reflections of the α-PP respectively. $\beta_{(300)}$ was the integral intensity of (300) reflections of β-iPP. K_β represents the relative amount of the β-crystal phase with respect to the α-crystal phase. $A_{amorphous}$ refers to the area of the amorphous peak. The X_{all}, X_β and X_α are the overall degree of crystallinity, the degree of β-crystallinity and the degree of α-crystallinity respectively.

2.2.2. Polarizing optical microscopy (POM)

The crystal morphology of the neat iPP and the β-nucleated iPP was investigated microscopically by using a POM (Nikon model Eclipse 50i Pol, Japan) coupled with an image processing facility and a heating/cooling unit (Linkam model LTS420, UK). Thin sections of the neat iPP and each modified-iPP for the POM observation were prepared by using a hydraulic press (Labtech Engineering model LP50, Thailand) to obtain films of 35 μm in thickness. Each specimen was heated from 50 to 200 °C at the rate of 10 °C/min. The temperature was then held constant at 200 °C for 5 min in order to remove the thermal history of the neat iPP and all the modified iPP. After isothermal holding, each specimen was cooled at identical rate down to 50 °C. The specimen was then re-heated to 200 °C. Finally, the specimen was cooled down again to the crystallization temperature (T_c) of 135 °C and they were kept isothermally in order to observe the crystallization behavior of the nucleated iPP.

2.2.3. Impact strength

The notched Izod impact strength was measured according the method and procedure described in ASTM D 256. The test was conducted by using an impact tester (Yasuda model 258PC, Japan). Ten replicate samples were tested for each formulation to determine the average impact strength.

2.2.4. Haze and color measurements

A haze measurement was conducted in accordance with ASTM D1003 procedure A by using a haze meter (Haze-gard plus, Germany). The test was conducted by detecting the scattered-light on five test specimens. The color changes of the nucleated iPP were evaluated by using a color meter (Hunter Lab model Colorflex 45/0, USA) in CIE L^* a^* b^* color system. Maximum L^* represents perfect reflecting diffuser or lightness. Minimum L^* is 0, it represents black. The a^* and b^* have no numerical scale limit, a positive a^* indicates red and the negative one represents green. The positive b^* is yellow and the negative one is widely known as blue. In the current research, L^* and b^* were employed to indicate the whiteness and the yellowness of the iPP and all the nucleated iPP.

3. Results and discussion

3.1. Effect of β-nucleating agent on the transition temperatures of iPP

Fig. 1a illustrates the DSC heating thermogram of the iPP and the SBR-based β-NA modified iPP. Single melting peak was observed in the neat iPP. With the presence of β-NA, the nucleated iPP exhibited two distinct melting peaks at around 150 °C and 168 °C. The lower melting peak (the left one) corresponded to the melting temperature of the β-phase while the higher one represented that of the α-phase in the nucleated iPP [4,30,31–36]. The DSC results evidently showed that the β-NA was capable of inducing two different crystal phases in the iPP, which were subsequently verified by XRD to be α- and β-crystals.

Fig. 1b shows the crystallization temperatures (T_c) of the iPP with various contents of β-NA. The T_c was obtained under non-isothermal cooling at the rate of 10 °C/min after melting at 210 °C. The iPP showed a T_c at 108 °C while the β-NA modified iPP exhibited a slightly higher T_c in the presence of β-NA. The T_c was raised to about 120 °C when β-NA was added by 0.20 wt% and beyond. This increment was attributed to the heterogeneous nucleation induced by the β-NA. It was further observed that the maximum increment of T_c was found when the content of β-NA was at 0.30 wt% and beyond, implying that the amount of β-NA nucleating agent by more than 0.30 wt% would not raise the crystallization temperature any further. Numerous research reported similar behavior for iPP modified with a compound of stearic acid and stearate lanthanum [4], WBG [12], MWCNT-supported β-NA [27], cadmium bicyclo hept-5-ene-2,3-dicarboxylate [30] and sodium benzoate [32].

3.2. Effects of nucleating agent on the fraction of β-crystals and the degree of crystallinity of iPP

A comparison of the XRD patterns of iPP with various β-NA contents was illustrated in Fig. 2. The neat iPP demonstrated a diffraction characteristic of the α-phase at 2θ of 14.1°, 17.0°, 18.5°, 21.1° and 22.0° Corresponding to the (110), (040), (130), (131) and (111) [4,20,21,30] reflections respectively. Only the α-crystal phase was found in the neat iPP; this implies that