



Effect of annealing temperature on the mechanical properties, thermal behavior and morphology of β -iPP/PA6 blends

Jie Li, Rui-Ying Bao, Wei Yang*, Bang-Hu Xie, Ming-Bo Yang

College of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu, 610065 Sichuan, People's Republic of China

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ABSTRACT

The correlations between the mechanical properties and microstructures of annealed pure polymers after annealing have been investigated extensively. However, the effect of annealing on the microstructures and properties of polymer blends were rarely studied. In this work, the effect of annealing temperatures (T_a) on the blend of β -form isotactic polypropylene (β -iPP) and polyamide 6 (PA6) was investigated by scanning electron microscope (SEM), differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). Both DSC and WAXD results showed that low content of β nucleating agent induced both β_1 and β_2 melting peaks of β -iPP; the melting peak of β_2 -iPP disappeared at the T_a of 130 °C; at even higher T_a (above 150 °C), β -iPP disappeared because of the β to α transition. The flexural modulus and yield strength of β -iPP/PA6 blends increase at high T_a (above 130 °C), but the impact strength does not improve distinctly at the whole range of T_a studied due to the poor interfacial interaction between iPP and PA6.

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1. Introduction

In polymer processing, polymer melt is generally cooled down from the melt temperature rapidly to room temperature, so it is difficult for polymer chains to achieve the equilibrium state and generally imperfect packing structures are formed and this is especially true in semicrystalline polymers. A great amount of work has been carried out to study the effect of annealing on the development of microstructures and the comprehensive properties of isotactic polypropylene (iPP) [1–5]. The results showed that at moderate annealing temperature (T_a) between the glass transition temperature (T_g) and melting temperature (T_m), annealing could promote the chain relaxation and lead to a more thermodynamically stable state [3,4,6]. As a result, microstructures change such as the perfection of defective crystals, thickening of crystal lamella and partial melting–recrystallization can be adjusted by selecting annealing conditions [7–9] and the iPP annealed at proper conditions can notably improve its toughness [1–4,10].

Until now, the effects of annealing on the microstructures and properties of iPP and the mechanisms have been systematically investigated [2–4,11]. However, in practical applications, pure iPP cannot always meet various requirements in different areas, so iPP based multiphase materials, such as iPP/polyamide 6 (PA6) blends [12–14], have already been extensively used owing to the

good combination of mechanical properties from PA6 and the inertness to humidity and ease of processing from iPP.

It is well-known that iPP is a polymorphic material which has four main crystal modifications including monoclinic (α), trigonal (β), orthorhombic (γ) and smetic [11,15]. The α form, the most thermodynamically stable phase of iPP, shows a typical cross-hatched lamella structure and compact stacking of molecular chains, which endows excellent modulus and tensile strength to iPP. The β form of iPP (β -iPP) is a thermodynamically metastable phase. The β - α polymorphous transition and the loose structure in β -crystals endow β -iPP with excellent toughness [11]. Generally, β -iPP can be obtained by (1) directional crystallization in a temperature gradient field; (2) shear or elongation-induced crystallization and (3) the introduction of specific nucleating agent, i.e., β nucleating agent (β -NA), which is the most effective and accessible method to obtain iPP with high content of β crystals [16–19].

PA6, a semicrystalline polymer with excellent mechanical properties, exhibits two main crystalline structures of α and γ phases. The α form phase is more thermodynamically stable and has a monoclinic structure with fully extended PA6 chains. The γ phase is composed of pleated chains, where the hydrogen bonds are formed between parallel chains and the direction of intermolecular hydrogen bonds is perpendicular to the plane of the carbon framework [20,21]. Phase transition happens between α phase and γ phases via melting–recrystallization, annealing and the application of stress at room temperature [20]. When iPP/PA6 blends are rapidly cooled to room temperature during processing, a metastable structure is obtained because iPP and PA6 are both semicrystalline

* Corresponding author. Tel./fax: +86 28 8546 0130.

E-mail address: weiyang@scu.edu.cn (W. Yang).

polymers. This structure is stable at room temperature, but it can transform into more stable structures on heating or by plastic deformation under external loads [11,22].

We have proved that the introduction of β nucleating agent (β -NA) into iPP/PA6 blends can improve the toughness of the blends [23]. In this work, we focus on the effects of evolution of microstructures of β nucleated iPP/PA6 blends without compatibilizer during annealing at different temperatures on the changes of morphologies, mechanical properties and thermal properties.

2. Experimental details

2.1. Materials

Commercial grade iPP (trademark T30S) with a melt flow rate (MFR) of 2.6 g/10 min (230 °C, 2.16 kg load) and the isotactic index of 98%, was purchased from Lanzhou Petroleum Chemical Co., China. PA6 (trademark M2800), commercially available, with a MFR of 11.0 g/10 min (230 °C, 2.16 kg load) and a density of 1.14 g/cm³ was purchased from Guangdong Xinhui Meida Nylon Co., Ltd., China. The aryl amide nucleating agent (trademark TMB-5) with a thermal decomposition temperature of 348.9 °C was purchased from Fine Chemicals Department of Shanxi Institute of Chemical Industry, China, and used as received. The diameter of particles was in the range of 120–150 nm and the length was around 400 nm.

2.2. Sample preparation

The PA6 resin was dried for 12 h under vacuum at 80 °C prior to processing to avoid heat oxidation degradation. To obtain a fine dispersion of β -NA in iPP/PA6 blends, a two-step blending process was adopted to prepare the iPP/PA6 blends nucleated by TMB-5. Firstly, a master batch of iPP with 5 wt.% TMB-5 was produced within an internal mixer (XSS-300, Shanghai Kechuang Rubber Plastic Mechanical Equipment Co., Ltd., China). Then, in an SHJ-20 co-rotating twin-screw extruder (Nanjing Giant Machinery Co., Ltd., China) with a screw diameter of 25 mm, a length/diameter ratio of 32 and a temperature profile ranging from 195 to 230 °C from the feeding zone to the die, the master batch was melt blended with iPP and PA6 at a weight proportion of iPP/PA6 of 90/10 to obtain desired content of TMB-5 in the blends, 0.1 wt.% and 0.5 wt.%. The nucleated blends were named as P1 and P5, respectively. Simple iPP/PA6 blends, marked as P0, was also prepared for comparison. The extrudate was then quenched into water and pelletized. After drying to remove the moisture for 12 h under vacuum at 80 °C, the pellets were injection-molded into dumb-bell tensile samples and rectangular impact samples on a PS40E5ASE precise injection-molding machine (Nissei NDK, Japan), with a temperature profile of 220–255 °C from the feeding zone to the nozzle.

The annealing of the samples at selected annealing temperature (T_a) for 12 h was performed in a temperature-controlled vacuum. After annealing, the samples were cooled in the ambient air and kept at 23 °C for at least 48 h before testing.

2.3. Tests and characterization

The tensile test was performed on an Instron-5567 testing machine (Instron Corporation, USA) at ambient temperature (about 23 °C) according to ASTM D 638-10 [24] and the flexural test was conducted on an AGS-J universal materials testing machine (Shimadzu Scientific Instruments, Japan) according to ASTM D 790 [25]. The yield strength (σ_y) and elongation at break (EB) were obtained from the tensile stress–strain curves of the blends at a

crosshead speed of 50 mm/min. Notched Izod impact strength (σ_I) was obtained by using a UJ-40 impact testing machine (Chengde Jinjian Testing Instrument Co. Ltd., Hebei, China) at ambient temperature (about 23 °C), according to ASTM D 256-05 [26]. The flexural modulus (E_f) was measured with a loading speed of 2 mm/min. At least seven specimens were tested and the average values were reported.

The samples for DSC tests were taken from the core layer of the injection molded bars. DSC scanning of the samples was performed on a TA DSC Q20 differential scanning calorimeter (TA Corporation, USA) in a nitrogen atmosphere. The calibration of the temperature and heat flow scales at the same heating rate was performed with standard indium. Samples were heated from 50 to 240 °C at a rate of 10 °C min⁻¹, and then cooled to 80 °C at a rate of 10 °C min⁻¹ to determine the crystallization behavior. Thermograms were evaluated by means of Universal V2.6D (TA Instruments) software.

The degree of crystallinity, X_c (%), for each sample was calculated by

$$X_c = (\Delta H_m / \Delta H_{m-100\%}) \times 100\% \quad (1)$$

where $\Delta H_{m-100\%}$ is the melting enthalpy of perfect crystals and ΔH_m is the melting enthalpy of the samples. Here, the values of $\Delta H_{m-100\%}$ for α -iPP, β -iPP and PA6 were selected as 177.0, 168.5 [27] and 185.8 J/g [22] respectively.

The fraction of β -iPP (f_β) was calculated by

$$f_\beta (\%) = X_{c\beta} (\%) / (X_{c\alpha} (\%) + X_{c\beta} (\%)) \times 100\% \quad (2)$$

where $X_{c\alpha}$ (%) and $X_{c\beta}$ (%) are the degree of crystallinity of α -iPP and β -iPP, respectively.

All the samples used for XRD characterization were cut from the core layer of the injection molded bars by an ultrathin semiautomatic microtome (KD-3358, Zhejiang Jinhua Kedi Instrumental Equipment Co., Ltd., China), 1 mm away from the surface layer. Patterns of the specimens were recorded in a range of $2\theta = 12$ –30° with a step scanning rate of 2°/min at ambient temperature (about 23 °C) with an X'Pert Pro MPD DY1291 (Philips, Netherland) apparatus, equipped with Ni-filtered Cu K α radiation with a wavelength of 0.154 nm, in the reflection mode. The operating condition of the X-ray source was set at a voltage of 40 kV and a current of 35 mA. The β -iPP fraction (K_β) was calculated from XRD diffractogram according to the Turner–Jones formula: [28]

$$K_\beta = H_{300}^\beta / (H_{110}^\alpha + H_{040}^\alpha + H_{130}^\alpha + H_{300}^\beta) \quad (3)$$

where H_{110}^α , H_{040}^α and H_{130}^α are the intensities of (110), (040) and (130) reflections of α -iPP, respectively, and H_{300}^β is the intensity of (300) reflection of β -iPP.

For morphology observation, injection-molded specimens were firstly cryogenically fractured in liquid nitrogen. The fracture surfaces were etched by formic acid to remove PA6 phase, and then a mixed acid solution containing 33 wt.% concentrated sulfuric acid (H₂SO₄), 66 wt.% concentrated phosphoric acid (H₃PO₄) and 1.3 wt.% potassium permanganate (KMnO₄) [29] was used to etch the amorphous region of iPP on the fracture surface at ambient temperature (about 23 °C) for 16 h. The samples were gold-coated and examined with a JSM-5900LV scanning electron microscope (SEM, JEOL, Japan) at an acceleration voltage of 30 kV.

3. Results and discussion

3.1. Mechanical properties

Fig. 1 shows the strength and stiffness of unannealed iPP/PA6 simple blends and β -nucleated iPP/PA6 blends and the samples annealed at different temperatures. The results indicated that annealing at proper temperatures could improve the flexural modulus (E_f)

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