



Synergistic improvement of toughness of isotactic polypropylene: The introduction of high density polyethylene and annealing treatment

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ARTICLE INFO

Article history:

Received 11 October 2012

Accepted 27 January 2013

Available online 13 February 2013

Keywords:

Polypropylene

High density polyethylene

Blend

Annealing

Toughness

ABSTRACT

The effects of introduction of high density polyethylene (HDPE) and further annealing treatment on the toughness of isotactic polypropylene (PP) were systemically investigated. The introduction of HDPE can improve the toughness of PP at no expense of the stiffness. For the PP containing 10 wt% of HDPE, the notched Izod impact strength is increased by approximately 16.3%. After annealed at 130 °C for 12 h, the impact strength of PP alone is increased by 336.7% compared to pristine PP, while this value is dramatically increased by 1107% for the PP containing 10 wt% of HDPE, which suggests that the introduction of HDPE and further annealing treatment have significant synergistic effect on the toughness improvement of PP. Characterization of microstructure evolution of PP with and without HDPE upon annealing reveals that the dramatic improvement in toughness of PP may be attributed to at least three aspects: (1) the prominently reduced spherulite size of PP induced by the introduction of HDPE, (2) the changes of crystallinity and molecular mobility upon the annealing treatment, which would promote the cavitation process during deformation, and (3) the enhanced interface in PP/HDPE blend upon the annealing treatment.

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1. Introduction

Isotactic polypropylene (PP) is a kind of versatile commodity plastic with numerous advantages, such as low density, ease of processing, recyclability, and relatively low cost. However, the poor impact resistance of PP and its sensitivity to notch, disenable it to be used as an engineering plastic. Numerous methods have been proposed to improve the toughness of PP in the past several decades, mainly including copolymerization [1,2] and blending [3,4]. Among these methods, the copolymerization with other comonomer is one of the most effective methods. By randomly copolymerizing of propylene with small proportion of ethylene or other α -olefins, various high-performance polypropylene random copolymers (PPR), which are featured by long propylene sequences and occasional ethylene units along its polymer backbone, have been developed [1]. PPR has excellent mechanical properties and its properties can be easily tailored by tuning the comonomer content and chain sequences, which make it widely used in package and pipe applications. With the development of catalyst technology and polymerization process, PP in-reactor alloys have also been synthesized by multi-stage polymerization of propylene and propylene/ethylene mixture over a porous spherical

TiCl₄/MgCl₂ catalyst with so-called “reactor granule technology” [2]. These in-reactor alloys are known as impact-resistant polypropylene copolymer or high impact polypropylene due to excellent rigidity-toughness balance. Up to now, the PP materials prepared by copolymerization have been widely used in both domestic and industrial applications. Compared with copolymerization, blending with a variety of elastomers has been recognized as the most versatile and economical method for its much more simple preparation process. Currently, the introduction of elastomers such as ethylene-propylene-diene monomer rubber (EPDM) or ethylene-propylene rubber (EPR) into PP has been one of the most widely utilized techniques to produce PP blend with improved toughness [3,4]. Nevertheless, this enhancement in toughness is always accompanied by sharp decreases in flexural modulus and thermal performance of the resulting materials [3,4], which are also extremely important in practical applications. Since Kurauchi and Ohta [5] proposed the “cold drawing toughening mechanism”, improving the toughness of a thermoplastic matrix by blending with another non-elastomeric thermoplastic has drawn much attention and provided a promising approach to toughen plastics without serious sacrifice of other mechanical properties [6].

Polyethylene (PE) is another family of widely used commodity thermoplastic that is commercially available in different grades, including low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), and ultra

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high molecular weight polyethylene (UHMWPE). Due to the massive production and cheapness of PE, improving the mechanical properties of PP by blending with PE has drawn particular interest [7–13]. Although it is widely reported by many investigations that the introduction of PE can toughen or stiffen PP, there still remains disputation in these investigations. Even opposite effects on toughness and stiffness were reported [7–13]. The discrepancy in effect of PE might be ascribed to two aspects. One is the different miscibility of PE and PP. According to Li et al. [14] PP is immiscible with HDPE and LDPE, while it is miscible with LLDPE. Madi [8] reported that the miscibility of PP and PE is limited, and HDPE exhibits better miscibility with PP than other sort of PE. Blom et al. [15] reported that PP is partially miscible with HDPE. They attributed the discrepancy in miscibility to the different sorts of PE utilized. Actually, the difference in molecular structure would lead to discrepancy in miscibility even for the same sort of PE utilized. On the other hand, the microstructure, such as crystallization structure and phase morphology, is also determining to the mechanical properties of PP. As has been confirmed by Nolley et al. [16], different processing conditions lead to discrepancy in microstructure of PP/LLDPE blend. Thus, investigations on the structure–property relationship of PP/PE blends under different processing conditions are essential, and these investigations will in return be helpful for the production of high-performance PP-based materials.

As a commonly utilized processing method, annealing implies heating a polymer solid to temperatures approaching its melting point and holding the condition for a period of time, it is frequently used in both fundamental research and industrial processing to improve mechanical properties of polymers [17–20]. The effect of annealing on the structure and properties of polymers has been studied extensively. Many structure changes were reported as a result of annealing, including the perfection of defective crystals, thickening and lateral growth of primary lamellae, partial melting-recrystallization, phase transition of different polymorphs, and rearrangement of constrained molecular chains in amorphous phase [21–26]. Hedesiu et al. [21] recently demonstrated that annealing reduces the fraction of the amorphous phase, maintains the fraction of the semi-rigid phase, and increases the fraction of the crystalline phase in PP. Chan et al. [17,18] and Bai et al. [19,20] reported that the impact strength of PP blend gains increment by more than 100% upon annealing. They found that the annealing treatment greatly promotes cavitations, which is suggested to be responsible for the toughening effect of annealing. According to our previous investigations [22], annealing can also improve the heat distortion temperature of PE, this improvement is related with promoted crystallinity as well as the relaxation process involving the intralamellar slipping of crystalline blocks and diffusion of crystallites. Gross and Peterman [23] reported that the annealing treatment leads to an increment in the stiffness of highly oriented PP/HDPE blend, owing to the epitaxial crystallization of HDPE on the fibre texture of the PP film, but they did not investigate the annealing effect on the toughness. Although these pioneered studies have paid much attention to the effects of annealing treatment on the structures and properties of PP or PP blends, the effect of annealing on the toughness improvement of PP/PE blend has not been specially investigated up to now.

In this work, considering the significance of toughening in the development of PP based materials, we systemically investigated the effect of the introduction of HDPE and further annealing treatment at 130 °C on the toughness of PP. Moreover, the corresponding microstructural evolution upon annealing treatment was investigated. It was found that the existence of HDPE and annealing treatment have significant synergistic effect on the toughness improvement of PP. This work may be helpful in developing a simple and effective method to toughen PP, as well as in deepening the

understanding of the structure–property relationship of PP based materials.

2. Experimental

2.1. Materials

The PP employed in this work was F401, which was supplied by Sinopec Yangzi Petrochem Co. (Nanjing, China); it has a M_w of 2.2×10^5 g/mol, $M_w/M_n \sim 4.85$, a melt flow rate (MFR) of 2.5 g/10 min (230 °C, 2.160 kg), a density of 0.91 g/mL and a tacticity of 96.5%. The HDPE employed in this work was 5200B, which was supplied by Sinopec Yanshan Petrochem Co. (Beijing, China); it has a M_w of 2.0×10^5 g/mol, $M_w/M_n \sim 16.03$, a melt flow rate (MFR) of 0.35 g/10 min, a density of 0.96 g/mL.

2.2. Sample preparations

A two-step process was utilized to prepare mechanical test specimens. PP and HDPE were firstly melt blended in a CET-35 twin-screw extruder (Nanjing, China) at a temperature profile of 170–200 °C and then pelletized. The dried pelletized blends were subsequently injection molded into standard specimens for notched Izod impact, flexural, and tensile tests in an 80A injection molding machine (Wuxi, China) at barrel temperature of 200 °C and mold temperature of 25 °C. The pristine PP and HDPE specimens were also prepared in identical procedures for comparison. Specimens for other characterizations were prepared by melt blending of PP and HDPE on an XSS-300 torque rheometer (Shanghai, China) at 200 °C. The roller speed was set as 75 rpm and the mixing time was set as 10 min. A small amount of antioxidant (Irganox 1010) existed in the as-received PP and PE; therefore no additional antioxidant was used. The blends were subsequently molded to 1.5-mm thick and 0.5-mm thick sheets at 200 °C in a press under a pressure of 15 MPa for 5 min.

The prepared PP and PP blend containing 10 wt% of HDPE were annealed in a fan-assisted oven for 12 h at 80, 100, 120, and 130 °C, respectively. After annealing, the samples were cooled in the ambient air. For convenience, the unannealed PP and PP blend containing 10 wt% of HDPE were denoted as PP-U and 10PE-U, while their counterparts annealed at 130 °C were denoted as PP-A and 10PE-A, respectively.

2.3. Mechanical test

The notched Izod impact strength was tested on an XJJ-5 impact tester (Changchun, China) with hamper energy of 4.9 J according to GB/T 1043-93 [27]. An SANS universal testing machine (Shenzhen, China) was used to test the tensile properties according to standards of GB/T 1040-92 [28] at a crosshead speed of 50 mm/min, and to test the flexural performances according to GB/T 9341-2000 [29] at a crosshead speed of 1 mm/min. All the measurements measured out at 23 ± 0.5 °C. For each sample, the average value reported was derived from at least five specimens.

2.4. Dynamic mechanical analysis (DMA)

DMA testing was performed using a NETZSCH 242C dynamic mechanical analyzer (Netsch, German). Specimens with approximate dimensions of $10 \times 5 \times 1.5$ mm³ were carefully surface polished to eliminate shrinkage and were then used to perform the test under dual cantilever mode at a vibration frequency of 1 Hz in nitrogen atmosphere. The testing was carried out from –80 to 120 °C, at a heating rate of 3 °C/min.

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