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Correlation between impact properties and phase structure in impact polypropylene copolymer

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ABSTRACT

The influence of the dispersed phase on impact properties of impact polypropylene copolymer (IPC) was systematically investigated by preparing a series of samples with different self-structure and size of dispersed particles. The impact test results at room temperature revealed that in case of rubber size below the critical value, the core–shell structure was dominant in the excellent impact strength though the impact strength was also affected by the size. For the impact strength at lower temperature, it seemed to be independent of the core–shell structure of dispersed particle and only dropped with the increase of rubber size. Compared with common polypropylene/ethylene–propylene rubber (PP/EPR) binary blend, IPC samples presented larger rubber sizes but higher impact strength at lower temperature, which was ascribed to the presence of ethylene propylene block copolymers (E*b*P) component. For describing the toughening mechanism of IPC at room temperature determined by size and self-structure of dispersed phase, a quantity linear relationship between toughness and rubber size was proposed.

1. Introduction

The excellent impact property, especially at low temperatures has made impact polypropylene copolymer (IPC) be an important commercial polyolefin used in many applications [1–4]. Due to the special polymerization method, IPC is a multi-phase and multi-component polymer alloy containing three main components, *i.e.*, ethylene–propylene random copolymer (EPR), a series of ethylene propylene block copolymers with different sequence lengths (E*b*P) and propylene homopolymer (*h*PP), and maybe a small amount of ethylene homopolymer (*h*PE) [5–8]. In past years, the composition [9], morphology and structure [10,11], crystallization behavior [11–13], mechanical properties [2,3], and rheological behavior [14,15] of IPC have been investigated. The previous works have revealed that the morphology structure of IPC could be well described by a dispersed phase model with multilayer core–shell structure [12,13,16–18]. Furthermore, it is suggested that the excellent properties, especially the toughness, of IPC come from the unique core–shell particles dispersed in it [12,19,20]. However, the details about structure–property relationships of IPC are indistinct.

As for polypropylene (PP), different elastomers have been added for the purpose of improving impact properties in past years [21–24]. Up to now the elastomers are believed to enable promoting multiple crazing, inducing shear yielding of the matrix and ending the propagation of cracks [25–27]. It is accepted that the toughening efficiency is related to rubber content, particle shape, particle size and size distribution, interfacial adhesion and compatibility between rubber and matrix [23,28–32]. When the rubber and matrix are determined, rubber size is the most important factor affecting the toughening efficiency. Wu [33–35] have studied the effects of rubber size and rubber-matrix adhesion on notched impact toughness of nylon/rubber blends, revealing a sharp brittle-tough transition occurring at a critical rubber size and proposing a quantitative formula to depict the correlation between the critical dimension of rubber particle and the critical matrix-ligament thickness. Jang [36] and Speri [37] also found that PP/ethylene–propylene–diene monomer (EPDM) blends with smaller rubber particles are more impact-resistant than the blends with larger ones.

In view of the similar components in IPC and PP/EPR (or PP/EPDM) blends, it is reasonable to suggest that the high toughness of IPC may also be correlative with the rubber size. However, the toughness of IPC is far higher than that of PP/EPR blends with the same rubber content and the size of dispersed particles is hardly regularly adjusted due to IPC is an *in-situ* polymer alloy, so how the rubber size affects the toughness is still unknown. In this paper, through preparing IPCs with different rubber sizes by melt processing, the correlation between impact property and rubber particle including the self-structure and size, was

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systematically studied and discussed. Subsequently, two different dominant factors in toughening mechanism of IPC were proposed.

2. Experimental details

2.1. Materials and sample preparation

The commercial IPC (SP179, molar percentage of ethylene component is about 13.5%) was purchased from SINOPEC Qilu Corporation Ltd., China with $M_w = 1.74 \times 10^5$, $M_w/M_n = 3.96$. The as-received IPC pellets were first annealed at 210 °C for 10, 20, 30 min in a nitrogen atmosphere oven to obtain the annealed pellet samples. Subsequently, the pellet samples annealed for 30 min were extruded in a co-rotating twin screw extruder (PRISM TSE 16 TC, Thermo Scientific, Waltham, UK) under the designated extrusion conditions for different frequencies, with adding a small amount of antioxidant (Irganox 1010, 0.2% content per extrusion). The annealing and extrusion are conducted for the purpose of regulating the rubber size and structure. Finally, the Charpy impact test specimens with the size 80 mm × 10 mm × 4 mm were prepared by compression molding at 180 °C under 10 MPa for 8 min using the original pellets, annealed samples and extruded samples.

Commercial available isotactic polypropylene (PP, T300, $M_w = 3.6 \times 10^5$, $M_w/M_n = 4.23$, Shanghai petrochemical, China) and ethylene–propylene rubber (EPR, J-0030, $M_w = 1.5 \times 10^5$, $M_w/M_n = 2.03$, molar percentage of ethylene content is about 45%, Jilin chemical industrial company limited, China) were adopted to prepare PP/EPR blend in a torque rheometer (XSS-300, KCCK, Shanghai, China) at 180 °C and 60 rpm (revolutions per minute) for 10 min. The prepared PP/EPR sample was also annealed at 210 °C for 30 min first and subsequently extruded in extruder. Finally, the Charpy impact test specimens were prepared by compression molding at 180 °C. Meanwhile, the fractions of IPC were obtained through temperature-gradient extraction and the weight percentages of these fractions were confirmed as 19% EPR, 11.3% E*b*P and 69.7% *h*PP, as depicted in our previous papers [11,18]. A reference sample, PP/EPR-*f*, was prepared by blending the *h*PP and EPR fractions of IPC. The PP/EPR and PP/EPR-*f* samples were prepared at a rubber content of 19% in weight, both the same as that in IPC, in torque rheometer. During the processing above, a small amount of antioxidant (Irganox 1010) was added.

2.2. Impact strength test

The notched Charpy impact test was conducted on a Charpy impact test machine (MTS Systems Co. Ltd., China) according to ISO 179-1: 2000 [38]. A 45° V shaped notch was made (depth: 2 mm) before measurement, and the remaining width of the specimens was 8 mm. The specimens were kept in an environment container at −20 °C and 23 °C for 12 h before test, and then immediately subjected to test. The test result was an average of at least eight specimens.

2.3. Tensile properties test

Tensile tests at room temperature ((25 ± 3) °C) were performed to dumbbell-shaped specimens on a universal testing machine (CMT 4204, Shenzhen SANS Test Machine Co. Ltd., China) at 50 mm/min. Mechanical properties were determined from five replicates for each sample.

2.4. Morphology observation

The fracture surfaces of investigated samples were obtained at liquid nitrogen and then etched in 50 °C *n*-octane for 4 h. Samples were observed using scanning electron microscope (SEM, S-4800, Hitachi, Japan) after being coated with gold–palladium.

2.5. Dynamic rheological test

The dynamic rheological tests were conducted on an advanced rheometric expansion system (ARES, TA Instruments Corporation, USA) with parallel plate geometry of 25 mm diameter under air condition. The tests were performed as isothermal frequency sweeps from 100 to 0.01 rad s^{-1} for all samples at 180 °C. A strain of 1% which was ensured within the linear viscoelastic range was applied for frequency sweeps. The test specimens adding with a small amount of antioxidant (Irganox 1010) were prepared by compression molding at 180 °C under 10 MPa for 8 min.

3. Results and discussion

3.1. Comparison of IPC and binary PP/EPR blends

Fig. 1 gives the SEM images and toughness data of IPC, PP/EPR and PP/EPR-*f*. As mentioned in Experimental details section, these three samples have the same content of EPR. For all the three samples, the holes resulting from being etched in 50 °C *n*-octane for 4 h belong to rubber phase. In addition, the smaller granules in the holes and aggregate granules on the fracture surface are E*b*P component for IPC. The dispersed phase of etched IPC in Fig. 1A presents three different cases depending on the degree of wrapping E*b*P core in the EPR layer: (*i*) isolated holes marked as '*A*', (*ii*) the holes but containing a smaller granule marked as '*B*', and (*iii*) aggregate granules marked as '*D*'. In the case of E*b*P bridges only exist on the other side away from the viewer, an isolated E*b*P granule is left behind marked as '*C*' by removing the outer EPR layer. These morphologies of core–shell dispersed particles accord with the proposed phase model well [11,18]. However, for both PP/EPR and PP/EPR-*f* blends, only the usual holes induced by removing the rubber particles in matrix can be observed in Fig. 1B and C. There is a great difference in size distribution between PP/EPR and PP/EPR-*f* blends. Compared with PP/EPR-*f*, PP/EPR presents more uniform dispersion of rubber and smaller particle size. This fact is reasonably ascribed to the different disparities in viscosity ratio for the two blends shown as Fig. 2, since the difference in viscosity between components of PP/EPR-*f* is so larger than that for PP/EPR, leading to a bad dispersion [39–41]. In addition, Fig. 1D gives the impact strengths of different samples at low temperature and room temperature respectively. One can see from Fig. 1D that both impact strengths of PP/EPR-*f* at −20 °C and 23 °C are much lower than those of PP/EPR, while the impact strengths of PP/EPR are lower than those of IPC. These results indicate that the excellent toughness of IPC is influenced by the structure of dispersed particle. However, whether the impact strength of IPC is affected by the rubber size is still unknown.

3.2. Influences of rubber size and architecture of dispersed particles on toughness

To explore the origin of excellent toughness for IPC, the IPC samples with different architecture and size of dispersed particle were prepared by controlling annealing and extrusion conditions. Fig. 3 gives the morphology images of IPC samples subjected to different treatments. Since the EPR component has been etched in 50 °C *n*-octane for 4 h, the aggregations observed in SEM images are E*b*Ps [3,15]. The morphology evolution of the dispersed phase with a multilayered core–shell structure in IPC during molten-state annealing has been systematically studied in our previous paper [42]. That work revealed that during annealing period, the inner