Toughening with little rigidity loss and mechanism for modified polypropylene by polymer particles with core–shell structure

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ABSTRACT

Toughening with little rigidity loss was achieved by adding high density polyethylene (HDPE) into polypropylene/ethylene-propylene random copolymer (PP/EPR) blends to fabricate a series of PP/EPR/HDPE ternary blends with core–shell dispersed particles. Morphology observations revealed that the addition of HDPE leads to the appearance of core–shell dispersed particles in PP matrix, *i.e.*, HDPE core encapsulated in EPR shell. Dynamic mechanical analysis results showed that the introduction of HDPE could increase glass transition temperature (T_g) and loss factor peak area of EPR in PP/EPR/HDPE blends, which is similar to the effect of adding EPR in PP/EPR. The shrinkage behavior results suggested that the increase of glass transition temperature of EPR was induced by the mismatch of thermal expansion coefficients of components and the larger peak area was ascribed to the stronger relaxation friction of EPR. According to percolation of stress volumes, the interparticle distance was proposed to be a key factor of toughening effect of rubber particles in thermoplastic and thereby a toughening mechanism about the equivalent rubber content was established to explain balanced toughness-strength improvement of PP/EPR/HDPE blends with core–shell particles. The rubber particles with core–shell structure lead to the increase of particle size and the decrease of interparticle distance on the premise of not increasing actual rubber content, resulting in a notable improvement of toughness, while the 'hard' core made from HDPE component provides a satisfied rigidity.

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1. Introduction

In order to improve the impact strength of polypropylene (PP), various polymer blends have been fabricated by adding different elastomers [1–5] and nanofillers [6,7] in PP matrix, and different toughening mechanisms have been investigated in past years [1,8–12]. Besides the blending technique, copolymerization of propylene with some other monomers provides another effective toughening approach [13]. Due to the copolymerization-induced good distribution of dispersed phases in matrix, the copolymer products exhibit a higher toughness compared with the homopolymer material. Consequently, up to now the impact polypropylene copolymer (IPC) exhibiting an excellent toughness has been one of the most successful market products [14]. IPC is a multi-phase and multi-component polymer alloy produced by two-step polymerization comprised of bulk polymerization of propylene and subsequent gas-phase copolymerization of ethylene and propylene [15–17]. Due to the special polymerization method, IPC mainly contains three 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) [18–22]. The previous works revealed that ethylene-propylene block copolymers with long ethylene sequences (or *h*PE) wrapped by EPR forms the core–shell particles, dispersing in PP matrix [15,23–26]. Though many researchers believe in that the excellent toughness of IPC comes from the unique core–shell particles [27,28], the reason for the higher toughening efficiency of core–shell particles than common rubber particles is still unclear.

On the other hand, ternary polymer blend comprised of PP/EPR/ high density polyethylene (HDPE) was reported to exhibit a significant higher toughness than PP/EPR binary blend with the same rubber content [29]. Krulis [30] found the ternary blend containing an appropriate polyethylene (PE) content showed an improved

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impact strength, more than twice of PP/ethylene-propylene-diene monomer (EPDM). They proposed a synergistic toughening effect of PE and EPDM and attributed it to the finer dispersion of ternary blend PP/EPDM/PE than the EPDM rubber alone. D'orazio [31] believed that EPR might act as "interfacial agents" in PP/EPR/PE blends and therefore improved the adhesion between PE dispersed phase and PP matrix. Zoran [32] found that EPR containing PE was much more efficient in improving impact strength of PP/EPR blends than neat EPR, but had little effect on other mechanical or rheological properties. In addition, other researchers [33,34] also found that partial replacement of EPR with PE in the dispersed phase could enhance the impact strength of PP blends. However, the exact mechanism of toughening PP with EPR in the presence of PE is still unclear.

It is noted that the dispersed phase in PP/EPR/HDPE mentioned above [30–32] occurred in core–shell structure, i.e., HDPE core wrapped by EPR shell under certain conditions [35–37]. Hemmati et al. [36] illustrated the driving force of core–shell particles by using models based on the interfacial free energy and spreading coefficient, revealing that interfacial interaction between phases plays a significant role in morphology formation of PP/EPR/HDPE blend. They also pointed out that viscosity ratios of components and the composition only affected the size of core–shell particles and had no appreciable influence on the type of morphology. Noted that the primary components of IPC are PP, EPR and EbP with different sequence lengths of ethylene and propylene, the formation mechanism of core–shell particles in IPC should be similar to that in PP/EPR/HDPE ternary blend. Based on the important structure–properties relationship [38–40], we argue that both IPC and PP/EPR/HDPE have similar toughening mechanism related with the core–shell dispersed particles due to the similar high toughness as well the dispersed phase structure. Furthermore, this unknown toughening mechanism results in the significant difference in toughening efficiency between core–shell particles and pure rubber particles.

Considering the great advantages of core–shell particles, i.e., HDPE core (or long PE-sequence core) encapsulated in EPR shell, for PP toughening, it is important and necessary to probe the toughening mechanism of multicomponent systems containing polymer particles with core–shell structure. In this paper, a series of PP/EPR/HDPE ternary blends with core–shell dispersed particles were prepared. According to a systematical investigation about their impact strength, crystallization behavior, morphology structure and dynamic mechanical behavior, a new insight into toughening mechanism of toughened PP with core–shell polymer particles was established.

2. Experimental section

2.1. Materials and sample preparation

Commercial available isotactic polypropylene (PP, T300, $M_w = 3.6 \times 10^5$, $M_w/M_n = 4.23$, Shanghai petrochemical, China), 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) and HDPE (5000S, $M_w = 1.3 \times 10^5$, $M_w/M_n = 5.9$, Daqing petrochemical, China) were adopted to prepare PP/EPR, PP/EPR/HDPE and PP/HDPE blends. The components are weighed as the designed mass ratio and blended in a torque rheometer (XSS-300, KCCK, Shanghai, China) at 180 °C and 60 rpm (revolutions per minute) for 10 min. A PP/EPR (81/19 w/w) blend sample containing α-nucleating agent (NAP-71, GCH technology Co. Ltd., China) with mass percentage of 0.01% was prepared and named as PP/EPR-NA. Finally, the specimens for Charpy impact and tensile test were prepared by compression molding at 180 °C under 10 MPa for

8 min. During the processing, a small amount of antioxidant (Irganox 1010) was added for all samples.

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. A 45° V shaped notch was made (depth 2 mm) before measurement. The specimens were kept in an environment container at −20 °C and 23 °C for 12 h before 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 by using an S-type load cell. Mechanical properties were determined from five replicates for each sample.

2.4. Scanning electron microscope observation

The fracture surface of specimens obtained at liquid nitrogen for 30 min was etched in 50 °C n-octane for 4 h, and observed using scanning electron microscope (SEM, S-4800, Hitachi, Japan) after being coated with gold–palladium. The operating voltage and current were 3 kV and 10 μA, respectively.

2.5. Polarized optical microscopy observation

Polarized optical microscopy (POM) observations were carried out using an optical microscope (BX51, Olympus) equipped with an Olympus camera and the temperature was monitored with a temperature controlled hot stage (THMS600, Linkam Co.). The specimens were sandwiched between two microscope cover slips for observation. All specimens were first heated to 190 °C and held for 5 min to eliminate previous thermal history. Isothermal crystallization experiments were conducted at 140 °C. Non-isothermal crystallization experiments were conducted from 190 °C to 40 °C at a cooling rate of 10 °C/min. All observations proceeded under nitrogen atmosphere.

2.6. Differential scanning calorimetry measurement

The thermal behavior was examined by using a Q100 differential scanning calorimetry (DSC, TA Instruments Corporation, USA) with nitrogen as purge gas. The samples were first heated to 190 °C and held for 5 min to eliminate previous thermal history, and then cooled down to 40 °C and maintained for 5 min. Finally, the samples were heated to 190 °C again. The cooling and twice-heating flow curves were recorded as the thermal behavior. Both the heating and cooling rates in all tests were 10 °C/min.

2.7. Dynamic mechanical analysis measurement

Dynamic mechanical analysis (DMA) measurements were carried out on a Q800 analyzer (TA Instruments Corporation, USA). Single cantilever mode was used, and the measurement was carried out from −140 °C to 130 °C at a heating rate of 3 °C/min and an oscillatory frequency of 1 Hz.

The influence of temperature drop on shrinkage behavior of specimens can be characterized under thermomechanical analysis (TMA) mode with a controlled force of 5 mN. The cooling rate was 3 °C/min from 180 °C to −140 °C. The thickness change of