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Study on synergistic toughening of polypropylene with high-density polyethylene and elastomer-olefin block copolymers under ultrasonic application

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ABSTRACT

In this study, we prepared the blends of polypropylene (PP) and high-density polyethylene (HDPE) with elastomer-olefin block copolymers (OBC) using an ultrasonic twin-screw extruder and investigated the mechanical, thermodynamic, and rheological properties of the blends. We examined the interfacial interactions among PP, OBC, and HDPE and observed that the PP/OBC/HDPE blends formed a core-shell structure with HDPE as the core and OBC as the shell. The crystallization temperature as well as the crystallinity of the blends were improved thanks to the heterogeneous nucleation between PP- and OBC-covered HDPE particles. Moreover, the impact strength of PP/OBC/HDPE blends was increased by three times as compared with PP because of the addition of 10 phr OBC and 15 phr HDPE; however, the viscosity increased slightly. Furthermore, it was evident from the fracture surface morphologies of PP/OBC/HDPE blends that the OBC-covered HDPE particles became smaller under the application of ultrasonic irradiation; hence, the interfacial interactions between the particles and the PP matrix were enhanced and the impact strength of the blends was improved.

1. Introduction

Polypropylene (PP) is one of the most widely used thermoplastics in the world due to its excellent mechanical properties, high corrosion resistance, remarkable electrical insulation capacities, and good processing performance. Its poor impact strength at low temperatures, however, is a primary concern for some special applications. Therefore, since the 1980s, studies on toughening modification of PP have been conducted to overcome this problem [1–6].

Some earlier literature reported that the impact strength of PP at low temperatures could be improved by the addition of polyethylene (PE). However, PP and PE are both highly immiscible, thus resulting in poor adhesion among its phases, coarse morphology, and terrible mechanical properties [7]. Bartlett et al. [8] found that for 25 wt% HDPE, the impact strength of PP/high-density polyethylene (HDPE) blends increased slightly and the tensile strength decreased simultaneously as compared with pure PP. The impact strength of the blends improved insignificantly for 50 wt% HDPE.

Multifarious rubbers or elastomers, such as ethylene-propylene-diene (EPDM) rubber and ethylene-octene copolymer (POE), also are employed to toughen PP because of their outstanding impact resistance and excellent aging resistance properties. The copolymers manifest good compatibility with the PP chain segments, and thus the interfacial tension becomes low and, consequently, a uniformly dispersed rubber phase in the PP matrix can be achieved. Lopez-Manchado et al. [9] noticed that the impact strength of PP/EPDM blends gradually increased with increasing EPDM content. For the EPDM content of 25 wt %, the impact strength of the blends increased by seven times; however, the tensile strength reduced by about 33%. It also was revealed that EPDM was distributed in the PP matrix in the form of droplets. According to Yang et al. [10], the impact strength of PP/POE blends increased significantly because of the rise in elastomer contents from 30 wt% to 35 wt% (a characterization of brittle-tough transition point); however, the decrease in rigidity of PP caused poor tensile properties.

In recent years, different approaches have been adopted for the synergistic toughening of PP with PE and rubber (elastomer). The main comonomer of elastomer is a propylene or octane, such as EPDM. The ethylene chains of elastomer are completely compatible with PE and the propylene chains or the octene chains are fully miscible in PP; thus, rubber (elastomer) acts as a compatibilizer between PP and PE and

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toughens PP. Stehling et al. [11] investigated the synergistic toughening of PP by poly (ethylene-*co*-propylene) (PEP)/HDPE and observed higher impact strength in PP/PEP/HDPE as compared with PP/PEP or PP/HDPE because of the formation of a core-shell structure with HDPE as the core and PEP as the shell. Souza and Demarquette [12] used EPDM, ethylene-vinyl acetate copolymer (EVA), and styrene-ethylene-butylene-stryrene (SEBS) as the compatibilizers of PP and HDPE and found that the blends with EPDM manifested the lowest interfacial tension.

In 2006, Dow Chemical reported a new type of elastomer-olefin block copolymers (OBC) composed of hard polymers (with more ethylene) and soft polymers (with more octene) [13–15]; thus, OBC has a higher melting temperature in comparison to olefin copolymers. The long ethylene sequences in the hard blocks of OBC crystallize in lamellar crystals of polyethylene with fewer defects and higher melting temperature; hence, OBC exhibits better impact resistance and higher heat resistance properties than other elastomers, such as EPDM, POE, and SEBS [16–19]. Liu et al. [16] analyzed the effects of OBC with different octene contents on the toughening of PP and found that the impact strength of PP/OBC blends increased with the increasing octene contents.

In spite of these favorable results, because of the viscosity difference, two polymers cannot be distributed evenly during the blending process to toughen PP. Speeding up the screw rotation has proved to be useful; however, the increase in shear force inevitably results in the degradation of polymers. The ultrasonic twin-screw extruder could be a feasible solution. Ultrasonic cavitation generates tremendous energy to uniformly disperse the polymers and, moreover, the short action time causes no serious degradation of polymers. Feng and Isayev [20] prepared the PP/EPDM melting blends using ultrasonic twin-screw extruder and found that the sizes of EPDM particles dispersed in PP were sharply reduced, thus causing improved toughness of the blends. Isayev and Chang Kook Hong [23] also proposed that the ultrasonic treatment enhanced the intermolecular interactions between dissimilar polymers because of the formation of in situ copolymers at the interfaces; hence, causing improved mechanical properties of the blends.

In the present work, we prepared the blends of PP, HDPE, and OBC using an ultrasonic twin-screw extruder. We studied the effects of OBC and HDPE on the mechanical, thermal, and rheological properties of the blends. In addition, we established a morphology-mechanical property relationship based on the morphologies of different composites. The interfacial interactions among PP, OBC, and HDPE were analyzed and the formation mechanism of core-shell structures in the blends was depicted.

2. Experiment

2.1. Materials

Polypropylene (PP, PPH-T03) with the melt flow rate (MFR) of 3.6 g/10 min (230 °C, 2.16 kg) and the weight-average molecular weight ($\overline{M}_w$) of 410 kg/mol was purchased from Sinopec Zhenhai Refining and Chemical Company Ltd (Ningbo, Zhejiang, China). Olefin block copolymers (OBC, 9100, 12 mol% octene) with MFR of 1 g/10 min (190 °C, 2.16 kg), $\overline{M}_w$ of 160 kg/mol, and the polymer dispersity index (PDI) of 2.4 were purchased from the Dow Chemical Company. High-density polyethylene (HDPE, YEM4902T, PE100 pipe material) with MFR of 10 g/10 min (190 °C, 2.16 kg) and $\overline{M}_w$ of 320 kg/mol was supplied by Sinopec Yangzi Petrochemical Company Ltd. The antioxidant IRGANOX1010 (pentaerythritol tetrakys 3-(3, 5-ditert-butyl-4-hydroxyphenyl) propionate) was purchased from the BASF (Ludwigshafen, Germany).

2.2. Preparation of blends

PP, HDPE, and OBC were dried at 75 °C under vacuum for 4 h to minimize the effects of moisture. We prepared PP-based blends with 0.2 wt% antioxidant (IRGANOX1010) and varying contents of HDPE and OBC (Table 1) using an ultrasonic twin-screw extruder (Fig. 1). The SHJ-20 co-rotating intermeshing twin-screw extruder with the screw diameter of 21.7 mm and the length to diameter ratio of 40 was produced by the Nanjing Jieya Company. The extruder was divided into eight segments and each segment was composed of a separated heating and water-cooling system. The temperature profiles were controlled at 170 °C, 180 °C, 190 °C, 200 °C, 200 °C, 195 °C, 190 °C, and 190 °C from feed to end. The feed rate was maintained at 10 rpm with the screw speed of 200 rpm and the flow rate of the die of about 7.4 g/min. We installed two ultrasonic launchers produced by the Shanghai Shengxi Instrument Company (China) at the head of the extruder with the frequency of 20 kHz and a power range of 0–600 W. The diameter of the ultrasonic horn tips was 16 mm, and the gap in the ultrasonic region was 8 mm with the width of 13 mm in the elliptical channel (FIG. S.1).

Table 1
Preparation parameters for PP/OBC/HDPE blends.

Sample	PP(phr)	OBC(phr)	HDPE (phr)	Ultrasonic Power(W)
PP	100	–	–	–
HDPE	–	–	100	–
P/H (90/15)	90	–	15	–
P/O/H(90/5/15)	90	5	15	–
P/O/H(90/10/15)	90	10	15	–
P/O/H(90/15/15)	90	15	15	–
P/O(90/10)	90	10	–	–
P/O/H(90/10/5)	90	10	5	–
P/O/H(90/10/10)	90	10	10	–
P/O/H(90/10/20)	90	10	20	–
P/O/H(90/10/15)-200	90	10	15	200
P/O/H(90/10/15)-400	90	10	15	400
P/O/H(90/10/15)-600	90	10	15	600

The ultrasonic power is the power of one launcher.

2.3. Mechanical properties

We carried out the tensile test according to the GB/T16421-1996 test method using an Instron 3367 test machine with a cross-head speed of 50 mm/min. We cut dumbbell-type samples with a thickness of 2 mm and length of 20 mm from the tablet samples for the tensile test. The tablet samples were pressed in a tableting machine (Model GT-7014-P, GOTECH Instrument Company, Taiwan) through the following process. First, the dried pellets were placed in the mold and preheated for 5 min at 200 °C. After 15 exhaust circulations at 5 MPa, the samples were pressed at 8 MPa for 5 min, and finally, the tablet samples were cooled by water circulation for 3 min.

We measured the impact strength of injection-molded samples according to the GB/T1843-2008 test method using an Izod impact test machine (Model 9050, CEAST Company, Pianezza, Italy). We prepared injection-molded samples in a micro-injection molding machine (Model Minijet, HAAKE Instrument Company, Germany) through the following process. The dried pellets were first placed in a cylinder and preheated for 5 min at 200 °C. The samples were then injected into the mold and maintained at 90 °C with the injection pressure of 1000 bar and the pressure keeping time of 20 s. We obtained an impact spline with a thickness of 4 mm, width of 10 mm, and notch-bottom radius of 0.25 mm after cooling the mold at room temperature.

2.4. Thermodynamic measurements

We employed a differential scanning calorimeter (Model DSC Q200, TA Instrument Company, New Castle, DE, USA) to test the