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Largely enhanced fracture toughness of the PP/EPDM blends induced by adding carbon nanofibers

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ABSTRACT

In this work, a small quantity of carbon nanofibers (CNFs) were incorporated into polypropylene/ethylene-propylene-diene terpolymer (PP/EPDM) blends. The effects of CNF content on the processing flowability, the microstructure of PP matrix and the morphology of elastomer particles were investigated. The results showed that the processing flowability of the material was not apparently influenced. The straight CNFs selectively located in the PP matrix and exhibited oriented dispersion along the flow direction of melt during the injection molding processing. CNFs exhibited nucleation effect on crystallization of PP. Homogeneous EPDM particles with smaller particle diameters were obtained in the blend composites. Mechanical properties measurements showed that the largely enhanced fracture toughness was achieved for the blend composites and the brittle-ductile transition was induced at lower EPDM content. Specifically, incorporating only 0.2 wt% CNFs into the PP/EPDM (85/15), the impact strength was enhanced about 246%. Further results showed that for the blend which exhibited brittle-fracture feature, the brittle-ductile transition could also be induced with increasing CNF content. The toughening mechanisms were then proposed.

1. Introduction

Incorporating elastomers is demonstrated a highly efficient method in improving the fracture toughness of the brittle polymers. The toughening efficiency of elastomers is influenced by many factors, such as the compatibility between elastomer and polymer matrix which determines the particle size of elastomer in the blend and the interfacial interaction between components, the content of elastomer which is usually related to the matrix ligament thickness, and the intrinsic characteristic of matrix which usually determines the energy absorption mode under the load condition. Generally, elastomers, which exhibit better compatibility, smaller particle size and matrix ligament thickness, show better toughening effect in ductile and/or quasi-ductile polymer matrix [1]. However, it is worth noting that in most of elastomer-toughened blends, high impact strength can be only obtained at high elastomer content, which not only induces the great deterioration of tensile strength and modulus but also results in the deterioration of processing flowability because of the great increase of melt viscosity. Therefore, much effort has been carried out to amplify the toughening efficiency of elastomer at relatively low content.

The common strategy is introducing the third polymer component which acts as the compatibilizer to enhance the interfacial adhesion between components [2]. The compatibilizer may be introduced through physical method such as melt compounding processing [3] or through chemical method such as *in-situ* grafting reaction [4]. Another strategy is incorporating nanofillers and the toughening mechanisms are suggested to be related to the dispersion states of the nanofillers. The first scenario is that nanofillers locate at the blend interface and show the role of compatibilizer, which enhance the interfacial adhesion between component under the load condition [5]. The second scenario is that nanofillers selectively locate in the elastomer component and in this condition, nanofillers and elastomer component form the 'core-shell'-like structure [6,7], which not only results in morphological change but also induces the change of stress field in the sample under the load condition, and finally leads to the enhancement of the toughening effect.

As one of the allotropes of carbon-based material, carbon nanotubes (CNTs) exhibit excellent toughening effect in the immiscible polymer blends and the toughening efficiency is greatly dependent upon the selective location of CNTs in the blend composites [8]. For example, the selectively located CNTs at the blend interface exhibit bridging effect, which improves the interfacial adhesion and weakens the crack initiation and propagation ability at the blend interface and consequently, samples exhibit enhanced tensile ductility [9]. Once CNTs selectively

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locate in one component, they can greatly enhance the impact strength of the blend composites through inducing morphological change and stress field superposition [10]. However, it is worth noting that the homogeneous dispersion of CNTs is challenging and in most cases, CNTs form the aggregates or bundles, which is factually weakens the toughening effect of CNTs in the blend composites [11,12].

Carbon nanofibers (CNFs) are also one of the carbon-based materials and they usually exhibit the diameter of about 200 nm and the aspect ratio of about 100 [13]. CNFs usually exhibit larger diameter but smaller aspect ratio than those of CNTs [14,15]. On the one hand, different from the poor dispersion of CNTs in the polymeric composites, CNFs exhibit relatively homogeneous dispersion in the polymeric composites. On the other hand, most of CNFs are presented in the straight morphology rather than the coiled morphology [16]. This indicates that the dispersion of CNFs in the blend composites is possibly much different from the dispersion of CNTs in the blend composites. However, to date, little work has been carried out to investigate the dispersion of CNFs in the blend composites and the resultant mechanical properties.

In this work, a small quantity of CNFs have been incorporated into the typical elastomer-toughened plastic system, i.e. polypropylene/ethylene-propylene-diene terpolymer (PP/EPDM) blends. The brittle-ductile transition behaviors of the blend composites induced by varying EPDM and CNF contents are comparatively investigated. The brittle-ductile transition is a common phenomenon occurred in the elastomer-toughened plastic system, which usually represents the fracture behavior changes of materials from a brittle fracture mode with low energy absorption to ductile fracture mode with high energy absorption. It is interesting to observe that incorporating only 0.2 wt% CNFs results in the great enhancement of impact strength of the blend composites. Furthermore, compared with the blank blends, the brittle-ductile transition of the blend composites occurs at lower EPDM content.

2. Experimental part

2.1. Materials

PP (T30S) was purchased from Lanzhou Petroleum Chemical Co., Ltd (China). It has a melt flow rate of 2.5 g/10 min (230 °C/2.16 kg). EPDM (JSR EP35) was purchased from Japan Synthetic Rubber Co. CNFs were obtained from Beijing Xinjincheng Electronics Co., Ltd (China). CNFs have an outer diameter of about 150–200 nm and a length of about 10–20 μm, and the purity is above 99.9%.

2.2. Sample preparation

Before sample preparation, all the materials were dried in an oven set at 50 °C for 8 h. The samples were prepared through a two-step processing procedure. The masterbatch of EPDM/CNF (90/10, wt/wt) was first prepared, then the masterbatch was further compounded with PP and EPDM to prepare the blend composites. The melt compounding was conducted on a twin-screw extruder (Nanjing Ruiya, China). The melt temperatures from hopper to extrusion head were set at 150-160-170-180-190-190-185 °C and the screw speed was maintained at 130 rpm. After being granulated, the pellets were further dried at 50 °C for 8 h, and then the pellets were injection-molded to obtain the standard specimen that has a width and a thickness of 10 and 4 mm, respectively. The injection molding was conducted on an injection molding machine (Chen Hsong Machinery, China). The melt temperatures were set at 190-195-190 °C from hopper to nozzle and the mould temperature was 23 °C. Here, the ternary blend composites with different CNF contents (0.05, 0.1, 0.2, 0.5 and 1.0 wt%) were prepared, and the sample notation was defined as P*x*E*y*C*z*, where *x*, *y* and *z* represent the weight fraction of PP, EPDM and CNFs, respectively. For example, P85E15C0.2 means that the weight ratio between PP and EPDM is 85/15 while the content of CNTs in the blend composite is about 0.2 wt%.

2.3. Microstructure and morphology characterizations

The processing flowability of sample was measured through using a rotational rheometer DHR-1 (TA Instrument, USA). The plate sample was prepared through compression-molding processing and it had a diameter of 20 mm and a thickness of 2 mm. The measurements were carried out at melt temperature of 190 °C and a frequency range of 0.01–100 Hz. The crystallization and melting behaviors of samples were investigated using a differential scanning calorimeter (DSC) STA449C (Netzsch, Germany). About 5 mg sample was firstly heated from 30 °C to 200 °C at a heating rate of 10 °C/min and maintained at 200 °C for 5 min to eliminate thermal history, and then it was cooled down to 30 °C at a cooling rate of 5 °C/min. Sample was protected in nitrogen atmosphere. The isothermal crystallization morphologies of samples obtained at crystallization temperature of 142 °C were characterized using a polarized optical microscope (POM) DM2700P (Leica, Germany) with a hot stage LTS 420 (Linkam Instrument, UK). The morphologies of the samples were also characterized using a scanning electron microscope (SEM) Fei Inspect (FEI, the Netherlands). To observe the morphology of the rubber particles, the sample was cryogenically fractured in liquid nitrogen and then the fractured surface was etched in xylene to remove EPDM. Samples were fractured perpendicularly to or parallel with the flow direction of the melt. The impact-fractured surface morphology was also characterized. Before SEM characterization, the surface was coated with a thin layer of gold.

2.4. Mechanical properties measurements

An impact tester XC-22Z (Chengde Jinjian, China) was used to measure the notched Izod impact strength according to ASTM D 256-04 using a rectangular sample that was firstly pre-fabricated a notch of about 2 mm. Tensile properties were measured using a dumbbell specimen, and the measurements were conducted on a universal tensile machine AGS-J (SHIMADZU, China) at a cross-head speed of 50 mm/min according to ASTM D638. All the measurements were carried out at 23 °C, and the average value of 5 specimens was reported.

3. Results and discussion

3.1. Rheological properties

The processing flowability of the blend composites was firstly evaluated through rheological measurements. Fig. 1 shows the storage modulus (G') and viscosity (η) of the blend composites with increasing CNF content. Interestingly, incorporating CNFs does not induce the apparent change of G' and η, which is much different from the phenomena observed in the CNT-incorporated blend composites, in which a small quantity of CNTs induce the great enhancement of G' and η due to the formation of the percolated CNT network structure, especially when CNTs selectively locate in the matrix [17]. Herein, the invariant G' and η indicate that the processing flowability of the blend composites is not influenced at CNF content lower than 1 wt%. In other words, CNFs do not form the percolated network structure in the composites [12].

3.2. Microstructure and morphology

The crystallization behaviors of PP in the blend composites were comparatively investigated using DSC and POM. Fig. 2a and Fig. 2b show the effects of CNF content on the melting and crystallization of the P85E15 blend. Compared with the blank P85E15 sample, the melting point (T_m) of PP in the blend composites is nearly invariant with increasing CNF content. The degree of crystallinity (X_c) is calculated according to the following relation: