



## Improving interfacial adhesion between immiscible polymers by carbon nanotubes

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### ABSTRACT

Although previous work has already shown that the presence of functionalized multiwalled carbon nanotubes (FMWCNTs) induced the great improvement of fracture toughness of an immiscible polymer blend, there is not exact evidence to show that the improvement of fracture toughness is only attributed to the improvement of interfacial adhesion resulting from the selectively distributed FMWCNTs at the interface of the immiscible polymer blend. In this work, we design several samples by compressing different polymer sheets to merge together and measure the peel adhesion strength between polymer sheets to evaluate the interfacial adhesion of different samples. The results show that with the presence of FMWCNTs in the high density polyethylene (HDPE) or in the maleic anhydride grafted HDPE (HDPE-g-MA), the peel adhesion strength between HDPE and polyamide 6 (PA6) or between HDPE-g-MA and PA6 is greatly improved, showing the positive effect of FMWCNTs in improving the interfacial adhesion between immiscible polymers. Further results obtained from scanning electron microscope (SEM) indicate that the presence of FMWCNTs induces the severe plastic deformation of sample during the peel adhesion test. The mechanisms for the improvement of interfacial adhesion are attributed to the enhancement of polarity of HDPE or HDPE-g-MA sample induced by FMWCNTs which facilitate the chain segments diffusion across the interface, and the bridge effect of FMWCNTs at the interface which prevents the propagation of crack along the interface.

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### 1. Introduction

Polymer blending is believed to be one of the most efficient ways to obtain new materials with excellent comprehensive properties. However, most of polymer blends are immiscible in thermodynamically, which results in the clear interface between the two components. Generally, the chain segments diffusion at the interface greatly depends on the degree of the miscibility between the two components. Obviously, the density of chain entanglement at the interface is much smaller than that of bulk polymer in the immiscible polymer blend. Therefore, it can be deduced that the crack first initiates at the interface and propagates along the interface plane under the load condition, leading to the failure of the material. So, enhancing the interfacial adhesion in the immiscible polymer blend is the prerequisite to improve the mechanical properties of the material.

Compatibilizer, consisting of block copolymer or graft copolymer which exhibits the similar chain structures to the

components of the immiscible polymer blend, has a tendency to selectively distribute at the interface, reducing the interfacial tension of the material and promoting the chain segments diffusion across the interface. Consequently, compatibilized polymer blend exhibits improved fracture toughness compared with uncompatibilized polymer blend [1]. However, the degree of improvement of interfacial adhesion depends on the content of compatibilizer. For the immiscible polymer blend with rather poor interfacial adhesion, a large quantity of compatibilizer must be used. This results in a negative effect on the tensile strength and tensile modulus of the material [2,3]. Therefore, it is very essential to seek other method to enhance the interfacial adhesion of the immiscible polymer blend.

It is well known that carbon nanotubes (CNTs) is one of the best reinforcement agents for polymers due to their extremely high tensile strength, modulus [4–8] and similar chain structure to polymers, which insures the relative stronger interfacial interaction between CNTs and polymers compared with other short fibers such as glass fiber or short whisker. The other interesting result is that CNTs also improve the fracture toughness of polymers. Coleman JN et al. [9] introduced CNTs into poly(methyl methacrylate) (PMMA) and found that the toughness and ductility were enhanced by 1282% and 526%, respectively. Morphology characterization

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showed a number of one dimensional objects containing CNTs bridging the crack. Dickey EC et al. [10] investigated the crack initiation and propagation in CNTs reinforced polystyrene (PS) composites through in situ transmission electron microscope (TEM) characterization and found that CNTs aligned perpendicularly to the crack initiation and bridged the crack face in the weak, thus providing closure stresses across the crack faces. Furthermore, they observed that about half of the aligned CNTs had been broken and subsequently pulled out from the matrix. Hubert P et al. [11] used the Elastic Plastic Fracture Mechanics to model the effects of aligned and randomly oriented CNTs, with respect to the crack growth plane. The results also showed that aligning relative long CNTs perpendicular to the crack growth plane had great potential to enhance the toughness of brittle polymer. Other researches also proved that the orientated CNTs exhibited determinable role in improving the fracture toughness of the nanocomposites [12–15].

Illuminated by the toughening mechanism of CNTs in homogeneous polymer, we therefore attempted to introduce CNTs into the immiscible polymer blend and we expected that the selectively distributed CNTs at the interface could prevent the initiation and propagation of crack. Three different types of the immiscible polymer blends including apolar/weak-polar, polar/polar and apolar/strong-polar were selected. In polypropylene/ethylene-co-vinyl acetate (PP/EVA) blends (apolar/weak-polar), CNTs were introduced into the interface of the blends, and the notched Izod impact strength was improved from 10.2 kJ/m<sup>2</sup> of blank PP/EVA to 63.2 kJ/m<sup>2</sup> of ternary blends containing 2.0 wt% CNTs [16]. Specifically, the improvement of the fracture toughness was proved to be greatly dependent on both the phase morphologies of the blends and the processing procedures which influence the number of CNTs at the interface [17]. In poly(L-lactide) (PLLA)/EVA blend (polar/polar), selectively distributed CNTs at the interface were also achieved. The ductility of reinforced PLLA/EVA blends was higher than that of blank PLLA/EVA blends [18]. Even for high density polyethylene/polyamide 6 (HDPE/PA6) blend (apolar/strong-polar) which shows the rather poor interfacial adhesion, the presence of CNTs in the material also promoted the great improvement of elongation at break from 39.9% of blank HDPE/PA6 to 106.9% of ternary blend containing 2.0 wt% CNTs [19].

The common feature of the microstructures of above ternary blends was that some CNTs were observed to be selectively distributed at the interface of the immiscible polymer blends. This was suggested to be the main reason for the improved fracture toughness. However, it is well known that the fracture toughness of the blend is determined by multiple factors, such as the phase morphology of the blend, the particle size distribution of minor phase and the distribution of nanofiller et al. Addition of CNTs, whether they distribute in one phase or at the interface, increases the viscosity of the component to a certain extent, leading to the change of viscosity ratio between the two components. This most likely induces the change of the morphology of the immiscible polymer blend. Therefore, further work is essential to be carried out to exclude the possible effect of phase morphology on fracture toughness and directly prove the positive effect of CNTs in enhancing interfacial adhesion of the immiscible polymer blend. To achieve this, in this work, we designed several different samples constituted with different polymer sheets through simple compression-molding procedures. The peel adhesion strength between polymer sheets was measured to evaluate the variation of the interfacial adhesion between different polymers. Interestingly, it was observed that greatly improved peel adhesion strength was obtained when CNTs were introduced into one of the polymer sheets, directly proving that selectively distributed CNTs greatly improved the interfacial adhesion in the immiscible polymer blend.

## 2. Experimental part

### 2.1. Materials

HDPE (5000S) with a melt flow rate (MFR) of 1.0 g/10 min (2.16 kg/190 °C) was purchased from Lanzhou Petrochemical Co, Ltd., P.R. China. PA6 (1013B) with an MFR of 15.49 g/10 min (2.16 kg/230 °C) was obtained from Shijiazhuang Chemical Fiber Co, Ltd., P.R. China. HDPE-g-MA (Fusabond MB-265D) with an MFR of 12.3g/10 min (2.16 kg/190 °C) was purchased from DuPont. Multiwalled carbon nanotubes (MWCNTs) were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Science (Chengdu, P.R. China). The outer and inner diameters of MWCNTs are 20–30 nm and 5–10 nm, respectively. The length of a single MWCNTs is about 10–50 μm. MWCNTs were washed and purified with concentrated hydrochloride acid, and the purity is more than 95%.

### 2.2. Sample preparation

In this work, the pristine MWCNTs were refluxed in concentrated nitric acid (98%) at 120 °C for 4 h to obtain functionalized MWCNTs (FMWCNTs) with carboxyl and hydroxyl groups on the outer surface of MWCNTs [19]. It is expected that the carboxyl and hydroxyl groups would not only favor the formation of hydrogen bonding between FMWCNTs and PA6, but also able to react with amidogen end groups of PA6, forming chemical interlinking, and thus facilitating the migration of FMWCNTs from HDPE phase to PA6 phase. Furthermore, it is also expected that FMWCNTs have a good dispersion in HDPE-g-MA material.

All the materials were dried at 80 °C for 8 h prior to extrusion and compression-molding. HDPE/FMWCNTs and HDPE-g-MA/FMWCNTs materials were prepared through melt extrusion which was carried out on a twin-screw extruder (SHJ-30, China) at a screw speed of 200 rpm and the temperatures of 140–175 °C from hopper to die. The contents of FMWCNTs in the HDPE/FMWCNTs and HDPE-g-MA/FMWCNTs materials were 1.0 wt% and 0.5–2 wt%, respectively. After being granulated, the pellets were compression-molded to obtain a sheet with a width of 20 mm, a thickness of 0.5 mm and a length of 150 mm. Furthermore, HDPE, HDPE-g-MA and PA6 droplets as obtained were also compression-molded to obtain the corresponding sheets with the same geometric parameters. The molding temperatures were set as 190 °C for sheets containing HDPE or HDPE-g-MA and 250 °C for PA6 sheet, respectively. Subsequently, the sheets were further compression-molded to merge together at molding temperature of 250 °C to obtain the different samples with different structures as shown in Fig. 1a. For sample 1 (shown as S1), it was assembled by HDPE and PA6 sheets; sample 2 (S2) showed the sandwich structure with HDPE-g-MA sheet between HDPE and PA6 sheets; sample 3 (S3) was assembled by HDPE/FMWCNTs and PA6 sheets, and sample 4 (S4) also showed the sandwich structure with HDPE-g-MA/FMWCNTs sheet between HDPE and PA6 sheets. Furthermore, the content of FMWCNTs in sample 4 was varied from 0.5 wt% to 2.0 wt% and therefore, the sample notation was further defined as S4-x, where x indicates the content of FMWCNTs in HDPE-g-MA.

### 2.3. Peel adhesion test

The schematic representation of peel adhesion test experiment is shown in Fig. 1b. The test was carried out on an SHIMADZU AGS-J tensile testing machine (Japan) according to EN ISO 6383-1 at room temperature. A cross-head speed of 5.0 mm/min was used.

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