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Shear enhanced interfacial interaction between carbon nanotubes and polyethylene and formation of nanohybrid shish–kebabs

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ABSTRACT

In this work, raw multiwalled carbon nanotubes (MWNTs) without any pre-treatment were blended with linear low density polyethylene (LLDPE), then molded via a so-called Dynamic Packing Injection Molding (DPIM) technique, in which oscillatory shear was exerted on the prepared composites during the stage of cooling solidification. The injection molded samples were extracted by xylene to remove LLDPE, and the remained MWNTs were collected and characterized. Shear enhanced interfacial adhesion between MWNTs and LLDPE was confirmed by dissolution experiment and Fourier transform infrared. The former a longer mixing time in xylene for remained MWNTs compared with raw MWNTs, while in the latter an increased intensity of characteristic LLDPE peak for MWNTs subjected to dynamic packing injection molding. More importantly, SEM images showed a formation of MWNTs/LLDPE nanohybrid shish–kebab, in which MWNTs served as shish, and LLDPE lamellae as kebab and periodically decorated on MWNTs. A simultaneously improved tensile strength and elongation of LLDPE have been achieved by adding the LLDPE-decorated MWNTs. Our work provides a new way for the modification of MWNTs, particularly a convenient way for the enhancement of interfacial adhesion in polymer/MWNT composites via realistic molding processing.

1. Introduction

Carbon nanotubes (CNTs) have an extremely high elastic modulus (about 1000 GPa) and strength (about 200 GPa). Furthermore, CNTs are extremely flexible when subjected to large strains and can be twisted and distorted without damage because of their deformation reversibility [1,2]. Due to these superior properties, CNTs are considered ideal filler for preparing polymer composites. Xiao et al. [3] found that Young's modulus and tensile strength of low density polyethylene increased by 89% and 56%, when the nanotube loading reached 10 wt%. Yang and co-workers [4] used PE-grafted multiwalled carbon nanotubes (MWNTs) as reinforcing agent for polyethylene (PE), and found that the storage modulus, Young's modulus, yield stress, tensile strength, ultimate strain, and toughness of PE were all improved. The PE-grafted MWNTs enabled a well dispersion of nanotubes in the PE matrix, and thus resulted in an improvement of MWNTs/PE interfacial adhesion. However, some studies also showed that CNTs, when incorporated into polymer matrix, did not necessarily warrant an enhancement of mechanical properties [5,6].

For polymer/CNT composites, the well dispersion of CNTs and the polymer/CNTs' interfacial adhesion are two main issues for warranting excellent mechanical properties [7]. Due to high aspect ratio of nanotubes, large interfacial areas are available for matrix-to-fillers' stress transfer, but an adequate interfacial adhesion is necessary in order to achieve a good load transfer [8]. The weak polymer/CNTs' interfacial adhesion prevents efficient stress transfer from polymer matrix to CNTs. In order to overcome these hurdles, it is desirable to modify the CNT surface to enhance the polymer/CNTs' interfacial interaction [9]. At present, the main approach for modifying CNTs is chemical covalent attachment of functional groups. The most commonplace modification approach in this category is acid oxidation. CNTs are opened at the end and the terminal carbons could be converted to carboxylic acids by oxidation in concentrated sulfuric or nitric or mixed acid [10–12]. Several other methods such as polymer wrapping [13], electrochemical [14], and mechanic-chemical [15] were also applied to functionalization of CNTs. A novel approach, so-called plasma treatment, became attractive for the researchers [16–18]. Li et al. [19–23] recently reported a polymer crystallization method to modify CNTs and nanofibers with semicrystalline polymers in a periodic manner, leading to a novel 'nanohybrid shish-–kebab' (NHSK) superstructure. In a NHSK, polymer crystalline blocks were periodically strung along the nanotube axis; CNTs formed shish while polymer lamellae formed kebabs. Periodicity could be

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controlled easily by tuning crystallization conditions. The reported method opened a gateway to periodically patterning polymers and different functional groups on individual CNTs in an ordered and controlled manner. Even more, shear enhanced interaction between polymer and CNTs during melt mixing was also reported by Moniruzzaman et al. [24] and Xiao and Zhang [25] after investigating high-shear mixing epoxy and single-walled carbon nanotubes (SWNTs). Rohatgi et al. [26] also showed an enhancement of strength and stiffness in liquid crystalline polymer/SWNT composites during high-shear mixing and extrusion.

In this article, the interfacial interaction between MWNTs and linear low density polyethylene (LLDPE) was improved by using dynamic packing injection molding (DPIM). The LLDPE/MWNT composites were first prepared via extrusion, then the composites were subjected to a repeated shear force imposed by DPIM, finally the molded samples were extracted by xylene, and the residual MWNTs were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, and soluble experiments. Our goals were mainly twofold: (1) explore a new way to improve the polymer/CNT interfacial adhesion; (2) explore the other possibility to obtain nanohybrid shish-–kebab, instead of in polymer solution. Our results indeed suggested an enhanced interaction between LLDPE and MWNTs by using DPIM, and for the first time, the nanohybrid shish-–kebab with MWNTs served as shish while LLDPE crystalline blocks as kebabs has been observed for the residual MWNTs. Obviously improved tensile property of LLDPE has been found by using such LLDPE-decorated MWNTs, compared with that by using raw MWNTs, as the reinforcing agent.

2. Experimental

2.1. Materials

A commercially available LLDPE with melt flow index (MFI) of 2.0 g/10 min (190 °C, 2.16 kg), weight-average molecular weight (Mw) of 2.1×10^5 g/mol and molecular weight distribution (MWD) of 3.9, was supplied by Jilin Petrochemical Corp. (Trade marked as 7042). It had a melting point of 123 °C and density of 0.92 g cm^{-3}. The raw MWNTs were kindly provided by Shenzhen Nanotechnology Co. Ltd. The main range of diameter of the raw MWNTs was about 10–20 nm and their length was about 5–15 μm, the purity was lager than 95%, ash (catalyst residue) is less than 0.2%. MWNTs were used without any pre-treatment.

2.2. Samples' preparation

Melt blending of LLDPE and MWNTs was conducted using a co-rotating twin-screw extruder (TSSJ-25) with a barrel temperature of 160 °C. After pelletized and dried, the blends were injected into a mold with aid of an SZ 100 g injection-molding machine with a barrel temperature of 180 °C and injection pressure of 900 kg cm^{-2}. In order to enhance the interaction between LLDPE and MWNTs, special molded equipment named as Dynamic Packing Injection Molding (DPIM) was attached on the injection machine. The processing parameters and the characteristics and detail experimental procedure of DPIM were described elsewhere [27–30]. The major feature of DPIM is that the melt was firstly injected into the mold then immediately forced to move repeatedly in a chamber by two pistons that moved reversibly with the same frequency (0.3 Hz); the solidification simultaneously occurs from the mold wall to the mold core part during the proceeding of shear process. Since the oscillatory shearing and the solidification (cooling) were proceeding simultaneously, the dynamic packing process could be regarded as a nonisothermal situation. The shear rate was about 10 s^{-1} calculated from the geometry of mold, and the duration time of dynamic packing process was about 3 min. We also carried out injection molding under static packing by using the same processing parameters but without shearing for comparison purpose. After that, the molded samples were extracted by boiling xylene for 48 h to remove LLDPE matrix, and the remained MWNTs were collected and used for characterization. For a clarity purpose, the MWNTs obtained by DPIM under the effect of shear are named as S*x*, *x* represents the weight percentage of MWNTs in the composites, while the MWNTs obtained by static packing injection molding (SPIM) without shear named as *un*-S*x*. For example, S3 represents MWNTs collected from the composite containing 3 wt% MWNTs after DPIM processing.

2.3. Characterizations and measurements

Fourier transform infrared (FTIR) spectra for the collected MWNTs were measured on a Nicolet560 spectrophotometer in the range of 4000–400 cm^{-1} under a transmittance mode. Scanning electron microscopic (SEM) experiments were carried out on an X-650 Hitachi SEM with an accelerated voltage of 20 kV. An Instron Universal Testing Machine was used to evaluate the tensile properties under a crosshead speed of 50 mm/min according to GB/T1040-92 standard, and the measured temperature was around 20 °C. For each sample, the best and worst results among the measured data have been deleted. The rests were averaged. The typical stress–strain curves closed to the averaged values were chosen and are shown in Fig. 4.

3. Results and discussion

3.1. Dispersion of MWNTs in composite

Dispersion of MWNTs in composite was inspected via SEM after fracturing the injection-molded bars in liquid nitrogen. As shown in Fig. 1, for the composites containing 3 wt% MWNTs, since MWNTs were not modified by any pre-treatment before melt blending, some aggregates are observed for the sample obtained by SPIM; whereas for the composite prepared via DPIM, the dispersion of MWNTs is homogeneous and no aggregates of MWNTs are observed in a large area. With increasing MWNTs' content up to 10 wt%, the aggregation of MWNTs becomes serious. Although the aggregations emerge for the composite containing 10 wt% of MWNTs obtained via DPIM, the aggregates' size is still smaller than that obtained by SPIM. So it can be concluded that shear force during dynamic packing injection molding has successfully facilitated well dispersion of MWNTs in LLDPE.

3.2. Dissolution experiment

In order to reveal the effect of shear force on the interaction between MWNTs and LLDPE, the LLDPE/MWNT composites prepared by two injection molding methods were extracted by boiling xylene for 48 h to remove LLDPE. The residual MWNTs were collected and dissolved in xylene again. After ultrasonic treatment, the photographs of these suspensions are shown in Fig. 2(a)–(c) for the sheared MWNTs, un-sheared MWNTs and raw MWNTs, respectively. The CNTs' concentration is 0.2 mg/mL for all samples. After ultrasonication for 10 min, black suspensions are obtained, 5 min later, the raw MWNTs' deposited and solution became demixed and clear. After 15 min and 25 min, the un-sheared and sheared MWNTs start to be deposited and demixed, respectively. It is believed that the difference of mixing time in xylene comes from the difference of interaction between MWNTs and LLDPE. After being shear melt mixed, the surface of MWNTs could be wrapped

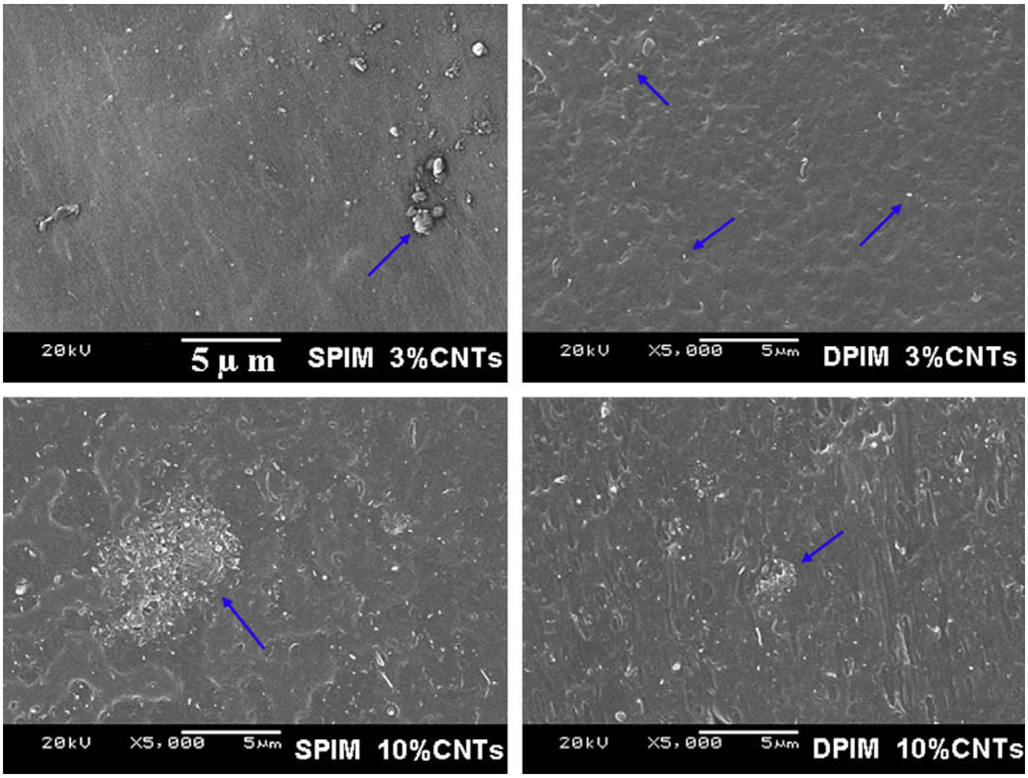

Fig. 1. SEM images of dispersion of MWNTs for as-prepared composites.

by LLDPE, which would accelerate the dispersion of MWNTs and prevent the agglomeration in xylene. It is strongly suggested that the shear force has strengthened the interaction between MWNTs and LLDPE, and lead to an improved solubility of MWNTs in xylene. Xylene is not a good solvent for PE at room temperature, and the solution was unstable. Thus MWNTs deposited quickly contrasting to Zhang's results [31], in which the mixing time of PS/MWNTs is longer.

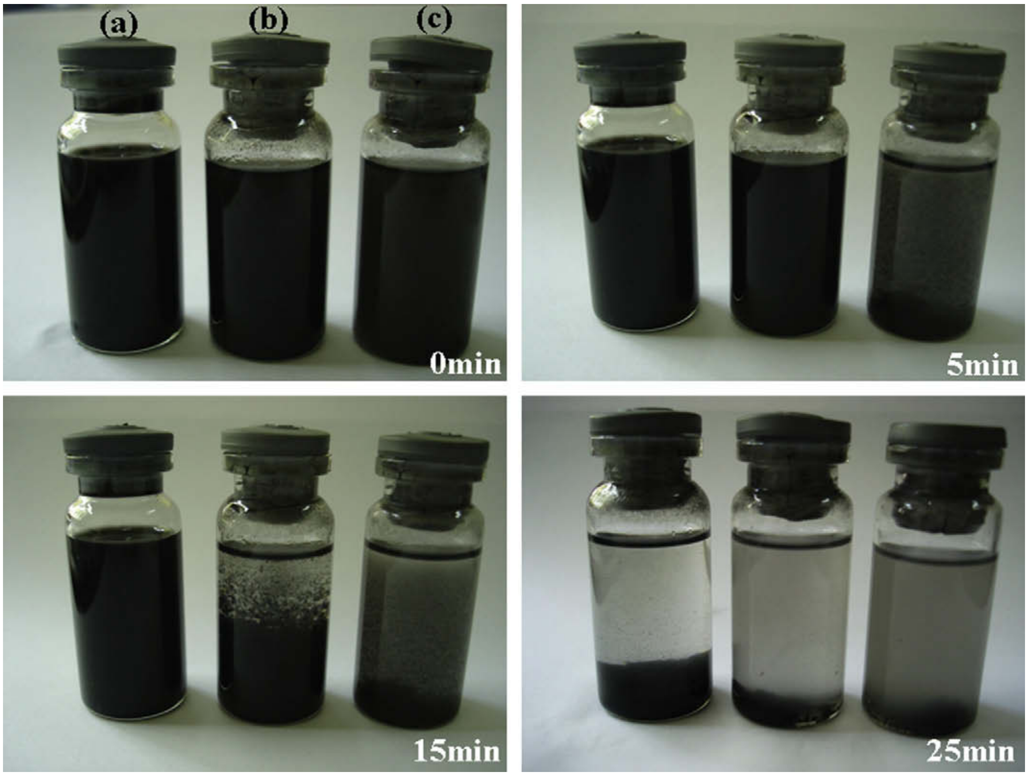

Fig. 2. The photo of different MWNTs dissolved in xylene at different times: (a) S10, (b) un-S10, (c) raw MWNTs.

3.3. Formation of nanohybrid shish–kebab

The morphologies of the extracted MWNTs, together with the raw MWNTs, are shown in Fig. 3(left). It can be seen that the raw MWNTs' surface is smooth. However, the MWNTs extracted from the composites are wrapped by LLDPE. Especially for S10, it is evident that MWNTs form the central stems and LLDPE crystalline lamellae are decorated on the MWNT surface (blue arrows). (For interpretation of the references to color in this text, the reader is referred to the web version of this article.) This morphology is similar to the classical polymer shish–kebab superstructure formed in elongation/shear flow field. The unique superstructure in S10 is named as nanohybrid shish–kebab (NHSK), as in the case reported by Li et al. [19–23] for solution crystallization. The lateral dimension of kebab is about 50–100 nm, and LLDPE lamellae aligned compactly between each other. The NHSK structure can be also observed in S3. Compared with the composites prepared under shear, the LLDPE crystal lamellae are almost invisible in un-S3. When the amount of MWNTs is up to 10 wt%, a small quantity of LLDPE kebab is emerged in un-S10. Furthermore, the periodicity and thickness of kebab in un-S*x* are smaller than those of S*x*. The difference of MWNTs' surface structure between S*x* and un-S*x* is probably due to shear enhanced interfacial adhesion between MWNTs and LLDPE matrix. The extracted MWNTs were then characterized by FTIR measurement and the results are also shown in Fig. 2(right). The absorbance at 2916 cm^{-1}, 2848 cm^{-1}, 1470 $\text{cm}^{-1}$and 717 cm^{-1} is the characteristic peak of LLDPE. Agreed with the SEM image, the intensities of these characteristic bands increased significantly for S10, which indicates that large amount of LLDPE lamellae wrapped on the surface of MWNTs are caused by oscillatory shearing during DPIM processing.

In order to find out the origin for the formation of the observed nanohybrid shish–kebab, the samples were extracted by xylene for 24 h, 48 h, 72 h and 96 h. The results of 72 h and 96 h were similar to that of 48 h, which indicates that some LLDPE chains could be chemically bonded on the surface of MWNTs during dynamic packing injecting molding and cannot be completely removed by xylene. Since the boiling temperature of xylene is about 140 °C, during extraction experiments at such a temperature for quite long time (e.g., 48 h), the LLDPE must be melted. Thus the observed nanohybrid shish–kebabs are most likely due to the crystallization of LLDPE after taking out from the Soxhlet extractor. To really prove that the so-called nanohybrid shish–kebabs could be also formed during the dynamic packing injection molding, transmission electron microscopic (TEM) observations should be carried out to examine the micro-morphology of the samples via ultra-thin cutting of specimens from the injection molded bars.

3.4. Mechanical enhancement of LLDPE by using LLDPE-decorated MWNTs

The polymer lamellae-decorated MWNTs are considered ideal reinforcement materials for preparing polymer/CNT nanocomposites with excellent mechanical properties. Fig. 4 shows the stress–strain curves of pure LLDPE and LLDPE composites with 0.5 wt% MWNTs. The composites were prepared as follows: sheared and un-sheared MWNTs were blended with LLDPE in extruder, respectively, and then subjected to a conventional injection-molding machine for sample preparation. The yield strength and broken strength of pure LLDPE are about 8.5 MPa and 16.5 MPa, respectively. The yield strength and broken strength are increased up to 10.5 MPa and 18.5 MPa, respectively, by adding 0.5 wt% of

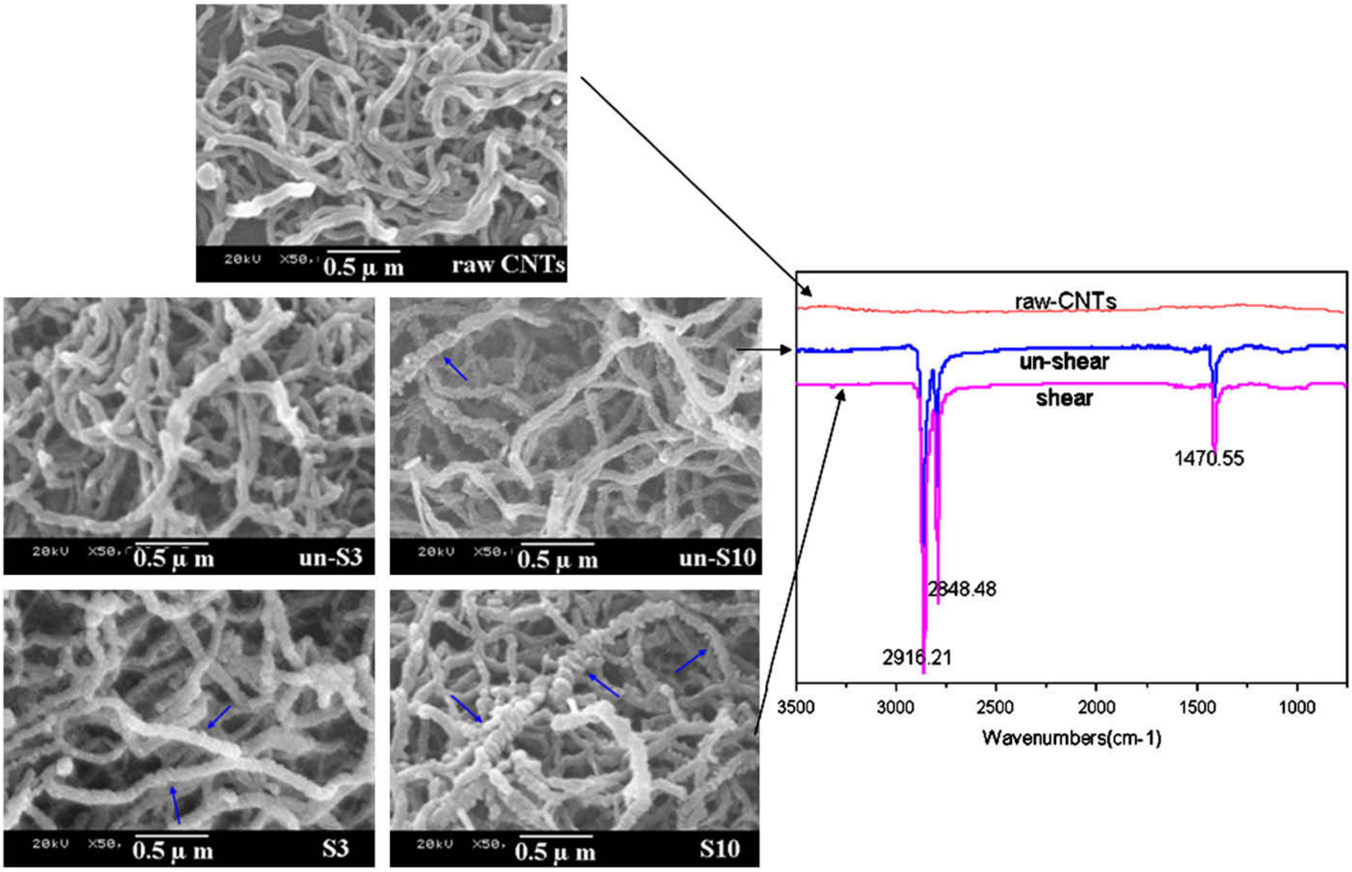

Fig. 3. SEM images (left) and FTIR (right) of raw MWNTs and the as-prepared MWNTs for un-S*x* and S*x*. The MWNTs were obtained by extracting in xylene for 48 h to remove the LLDPE matrix.

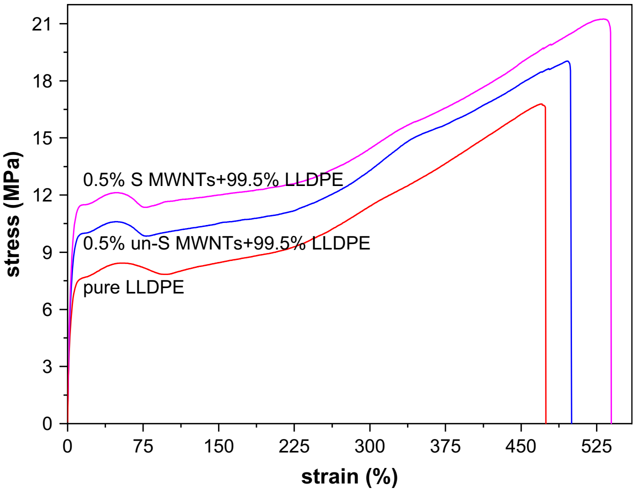

Fig. 4. The stress–strain curves of pure LLDPE and as-prepared composites by using the LLDPE-decorated MWNTs.

un-sheared MWNTs. A further increase of yield strength (12.5 MPa, 50% increase compared with pure LLDPE) is achieved by adding sheared MWNTs. More importantly, the ductility of composites is not compromised when the tensile strength is improved at the same time. It is well known that the ductility and strength of a polymer are usually reduced upon incorporation of CNTs [32,33]. But in our present work, the ultimate elongation of composites is even higher than pure LLDPE. The ductility and strength of LLDPE are simultaneously improved by the use of the LLDPE lamellae-decorated MWNTs.

4. Conclusion

In summary, shear enhanced interfacial adhesion between MWNTs and LLDPE is achieved, which has been confirmed by dissolution experiment and FTIR. The sheared MWNTs have a longer mixing time in xylene compared to the un-sheared and raw MWNTs. SEM micrographs confirmed the formation of MWNTs/LLDPE nanohybrid shish–kebab superstructure. The thickness and amount of LLDPE kebab for the sheared MWNTs are larger than the un-sheared ones. A simultaneously improved tensile strength and elongation of LLDPE have been achieved by adding LLDPE-decorated MWNTs. Our work provides a new way for the modification of MWNTs and worth to be further investigated.

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