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Fabrication and distribution characteristics of polyurethane/single-walled carbon nanotube composite with anisotropic structure

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Abstract

A polyurethane/single-walled carbon nanotube (SWCNT) composite with anisotropic structure is synthesized by two-step process. The effects of external force during the curing process of the composite as well as the tensile stress on the distribution of the SWCNTs in the matrix have been examined by using field-emission scanning electron microscope. The microstructure analysis results indicate that the different distributions of the SWCNTs in the matrix have appeared along two orthogonal directions for the composite samples.

Keywords: Anisotropic structure; Carbon nanotubes; Polymer composite materials

1. Introduction

Carbon nanotubes (CNTs) possess unique structure. With excellent mechanical and thermal properties [1–4], they are considered to be ideal reinforcement fibers for structural composites. Recently, efforts have been concentrated on introducing CNTs into polymer matrices to prepare polymer–carbon nanotube composites for high performance materials [5–7]. Many studies have shown that adding a few percent of CNTs by weight in polymer can significantly improve thermal, electrical and mechanical properties of composite materials [8–15].

The fabrication of high performance polymer/CNT composites is driven by the idea of creating an anisotropic structure at the nanoscale to obtain optimal mechanical properties. Aligned carbon nanotubes have many advantages over the randomly oriented ones. It is reported that the elastic modulus of polymer composite reinforced with aligned multi-walled carbon nanotube is considerably greater than that of polymer reinforced with randomly oriented carbon nanotube [16]. CNTs can be aligned via different methods [17,18]. However, the aligned CNTs usually lose their orientation and disperse randomly after being introduced into polymer matrices. For high performance polymer/CNT composite, it is crucial that CNTs are rearranged in polymer matrices [19–21].

In this paper, a polyurethane/single-walled carbon nanotube (SWCNT) composite with anisotropic structure is synthesized in two steps. The mixture of polypropylene glycol (PPG)-grafted SWCNTs and PPG reacts with TDI to obtain a pre-polymer composite, then the pre-polymer composite is cured in a metal mould with $150\times150\times2$ mm^3 concave (a confined environment) under the pressure of 10 tons. The distribution of CNTs along two different directions (parallel and perpendicular to external force) in the matrix under the high pressure condition as well as the confined environment is investigated by using field-emission scanning microscope (FESEM). The linkage of CNT with the polyurethane matrix is confirmed by Fourier Transform Infrared (FTIR) spectra.

2. Experimental section

2.1. Materials

The SWCNTs (purity 95 wt%, diameter ≤ 2 nm, purchased from Chengdu Organic Chemistry Co. Ltd, Chinese Academy of Science) synthesized by chemical vapor deposition was heated for 2 h at 400 °C to remove amorphous carbon before use. The polypropylene glycol (PPG, $\bar{M}_n = 1000$ provided by Gaoqiao Chemical Co.) was dehydrated in a vacuum oven at 100 °C for 12 h before use. Methylene-bis-*ortho*-chloroanilline (MOCA, made by Shanghai Chemical Co.) and toluene diisocyanate (TDI, purchased from Mitsui (East Asia) Co.

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Ltd, Japan) were used as received. Thionyl chloride ($SOCl_2$), concentrated nitric acid (HNO_3, 70%) and concentrated sulfuric acid (H_2SO_4, 98%) were obtained from Shanghai Reagents Co. and used as received.

2.2. Preparation of PPG-grafted SWCNTs

The purified SWCNTs were dispersed in a mixture of concentrated sulfuric and nitric acids (3:1 by volume) using an ultrasonicator with power of 100 W and nominal frequency of 50 kHz for 3 h at ambient temperature, then the system was heated to 70 °C and reacted for 2 h under a magnetic stirring condition. The acid-treated SWCNT powders were collected after being washed with sufficient distilled water, filtered with 0.22 μm millipore polypropylene membrane and desiccated in a vacuum oven. The carboxylic acid groups attached to the SWCNTs were converted into acid chloride intermediate by reaction with thionyl choride. The resulted material was subsequently treated with polypropylene glycol in the anhydrous tetrahydrofuran to produce PPG-grafted SWCNTs. The PPG-grafted SWCNT powders were collected after being washed with anhydrous tetrahydrofuran, filtered and desiccated.

2.3. Fabrication of SWCNT–PU composite

PPG-grafted SWCNTs (0.5 g) were dispersed in 65 g dried PPG via an ultrasonicator for 2 h at room temperature. Then TDI with a molar ratio of 1.8:1 to PPG was added to the suspension and reacted for 1.5 h under a violently stirring and vacuum condition at 80 °C, and the pre-polyurethane–SWCNT composite was obtained. The stoichiometric number of melt MOCA was mixed with the pre-polyurethane–SWCNT composite for 30–50 s under the violent stirring condition at 80 °C; following that, the mixture was cured for 2 h in a metal mold with $150\times150\times2$ mm^3 concave under 10 ton pressure at 90 °C.

2.4. Characterization

Scanning electronic micrographs for fracture plane samples were obtained on a Hitachi S-5200 field-emission scanning electronic microscope. Besides the cross-section after tensile failure, other SEM cross-section samples were obtained by brittle fracture of the composite film in liquid nitrogen. Gold was sprayed on the surface of the samples. The gold-coated samples were mounted on aluminum stubs using electric adhesive tape paste. Then, the cross-section of the samples was examined with FESEM. Fourier transform infrared (FTIR) spectra of the samples were obtained using a Paragon 1000 spectrometer (Perkin–Elmer).

3. Results and discussion

The linkage of SWCNTs with PU chains was characterized by FTIR (Fig. 1). Fig. 1(a) showed the existence of two obvious absorption bands at 1723 and 3464 cm^{-1} for the infrared spectrum of acid-treated CNTs. The former can be assigned to characteristic of acid carbonyl (C=O) stretches and the latter is identified as O–H stretching mode in carboxylic acid groups. The results indicate that carboxylic acid groups have been attached to the CNTs. FTIR spectrum of the PPG-grafted SWCNTs was shown in Fig. 1(b). Compared with the infrared spectrum of acid-treated CNTs, three new peaks appeared around 2924, 2852 and 1078 cm^{-1}. The peaks at 2924 and 2852 cm^{-1} are associated with stretching vibrations of C–H in alkyl chain and the broad peak around 1078 cm^{-1} is identified as characteristic of ether link (C–O–C). Positions of the peaks are coincident with those of the characteristic peaks of corresponding groups in PPG FTIR spectrum shown in Fig. 1(c), indicating that PPG molecules have been attached to the SWCNTs. Hydroxyl peak appeared in Fig. 1(a)–(c) has disappeared in the infrared spectrum of PU–SWCNT composite (Fig. 1(d)), showing that the SWCNT has been successfully inserted in the polyurethane chains.

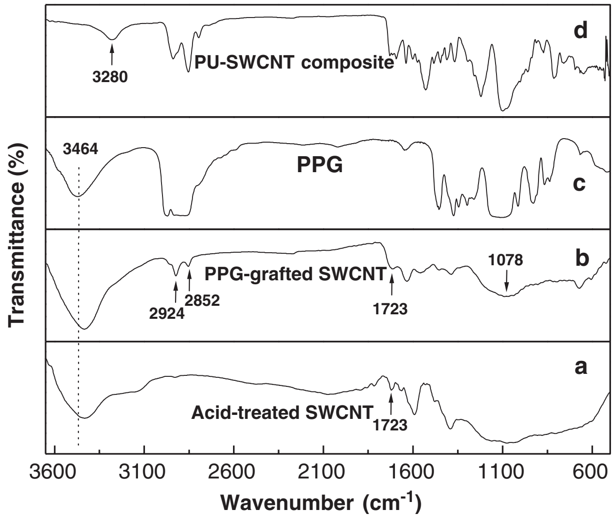
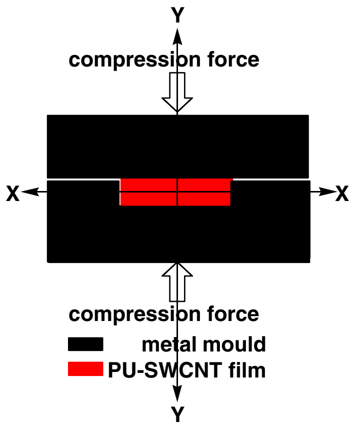


Fig. 1. FTIR spectra of acid-treated SWCNT, PPG-grafted SWCNT, PPG and PU–SWCNT composite.

Stress model of the composite during the curing process was shown in Scheme 1, where Y symbolized the plane parallel to direction of the compression force during the curing process and X symbolized the plane perpendicular to the compression



Scheme 1. Stress model of the composite under curing process.

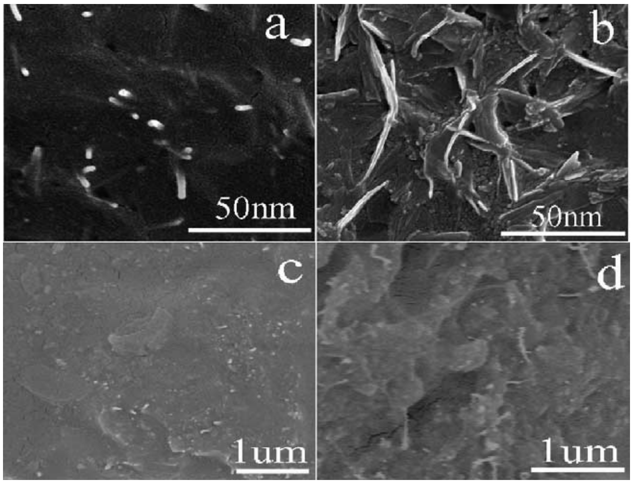


Fig. 2. Field-emission SEM images of PU–SWCNT composite: (a, c) fracture plane parallel to pressure direction (symbolized with Y in stress model) and (b, d) fracture plane perpendicular to pressure direction (symbolized with X in stress model).

force direction. The microstructure characteristics of the composite were examined by FESEM. The SEM images of PU–SWCNT composite were shown in Fig. 2. The SEM samples of different cross-sections for the composite before tensile testing were obtained by brittle fracture of the composite film in liquid nitrogen. Distribution of the carbon nanotubes in the matrix along two different directions was unambiguously observed from the SEM images in Fig. 2(a) and (b). For the cross-section parallel to direction of the pressure during the curing process of the composite, the distribution of the CNTs in the matrix was shown in Fig. 2(a), where the white dots are CNT stubs exposed from the matrix. It is found that most of the CNTs prefer ordered orientation to random distribution. Whereas, on the cross-section perpendicular to the pressure during the curing process of the composite, many random white lines rather than white dots are clearly observed in Fig. 2(b), showing that the CNTs are prone to randomly horizontal distribution on the cross-section perpendicular to the pressure during the curing process of the composite. The dispersion of carbon nanotubes in the matrix was effectively evaluated from SEM images with low magnification, as shown in Fig. 2(c) and (d). It is clear that many white small dots are uniformly scattered at the fracture plane (Fig. 2(c)), indicating that CNTs in the matrix can be dispersed well. Fig. 2(d) shows that many horizontal CNTs are uniformly dispersed on the cross-section perpendicular to the pressure during the curing process of the composite.

To further examine the changes of the distribution of the CNTs in the composite after tensile testing, two cross-sections with orthogonal directions were observed by FESEM. Direction of the tensile force is perpendicular to the direction of the pressure during the curing process of the composite. One cross-section obtained by tensile failure of sample is parallel to the direction of the pressure during the curing process; the other obtained by brittle failure of sample in liquid nitrogen is perpendicular to the pressure direction. The distribution of CNTs in the composite after tensile testing was shown in Fig. 3.

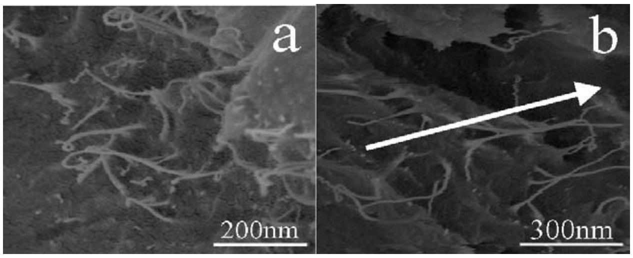


Fig. 3. FESEM images of PU–SWCNT composite after tensile test: (a) fracture plane after tensile failure, parallel to pressure direction and (b) fracture plane after brittle failure in liquid nitrogen, perpendicular to pressure direction.

The SEM image (Fig. 3(a)) provided the information on the cross-section parallel to the pressure direction. Most of the CNTs are axially arranged along the tensile force direction on the cross-section, indicating that compared with the sample before tensile testing, ordered orientation of CNTs have no obviously changed on the cross-section. After tensile failure, elastic recovery of CNTs causes curling at the end of CNTs. The form of the curl shows that the CNTs play the role of effective transfer load from the matrix to nanotubes when the composite is under the stress during tensile testing, and strong interactions are produced between nanotubes and the polymer matrix. For the cross-section perpendicular to the direction of the pressure during the curing process of the composite (Fig. 3(b)), the CNTs whose two ends are embedded in the polymer matrix are horizontally distributed on the cross-section and become straight along with the tensile direction, indicating that compared with the random CNTs in the sample before tension on the cross-section parallel to the pressure direction, the CNTs in the composite after tensile testing appeared an ordered orientation along with tensile direction on the cross-section, as shown by the white arrow.

4. Conclusion

PPG-grafted SWCNTs can be dispersed in the polymer matrix well. The results from FESEM show that CNTs in matrix take on different arrangement along two orthogonal directions. For the cross-section parallel to the direction of the pressure during the curing process of the composite, CNTs are apt to array erect to the plane. However, CNTs are inclined to be randomly dispersed on the cross-section perpendicular to the external force direction during the curing process. Compared with the distribution of the CNTs in the composite sample before tension, CNTs in the composite after tensile testing easily take on an ordered orientation along with the tensile direction on the cross-section perpendicular to the pressure direction, whereas the arrangement of the CNTs has not almost changed on the cross-section parallel to the pressure direction.

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