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Carbon nanotube network structure induced strain sensitivity and shape memory behavior changes of thermoplastic polyurethane

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ABSTRACT

Thermoplastic polyurethane (TPU) composites containing different carbon nanotube (CNT) contents ranging from 0.5 to 5 wt% were prepared and the main attention was focused on investigating the relation between the network structure of CNTs and the macroscopic physical properties of the composites. The network structure of CNTs in the TPU/CNT composites was demonstrated through morphological characterization and rheological measurement. Tensile properties, electrical properties, strain sensitivity and shape memory properties were comparatively investigated. The results showed that CNTs at content above 2 wt% formed the percolated network structure in the TPU composites. High content of CNTs exhibited excellent reinforcement effect. Adding a few CNTs greatly reduced the electrical resistivity of the composites. The TPU/CNT composites exhibited good strain sensitivity, and the variation of electrical resistivity during the stretching-restoring process was dependent upon CNT content. At room temperature, CNTs delayed the shape recovery behavior of the composites, especially when the percolated CNT network structure was formed. However, with the aid of electrical actuation, largely accelerated shape recovery behavior was observed for the TPU/CNT sample containing 5 wt% CNTs.

1. Introduction

Polymer-based composites prepared by adding carbon nanotubes (CNTs) are the hottest issues in the past twenty years. Due to the high strength and high modulus of CNTs and their large aspect ratio, CNTs have been proved the most ideal reinforcement agent for polymers [1,2]. Due to the similar chain-like structure to polymer molecular chains and the large surface area, CNTs exhibit excellent nucleation effect on the crystallization of semicrystalline polymers [3]. Specifically, the high electrical and thermal conductivity characteristics of CNTs are very favorable for preparing conductive polymer composites [4–6]. The interfacial interaction between CNTs and polymer matrix and the dispersion state of CNTs are the main factors determining the properties of CNT-based composites.

When a certain concentration is achieved, CNTs tend to form a percolated network structure in the matrix, which not only influences the crystallization behavior of semicrystalline polymer but also influences the electrical and thermal conductivity of composites. For example, the percolated CNT network structure reduces the chain mobility of semicrystalline polymer, which results in the decrease of spherulite growth rate [7]. However, once the percolated network structure is formed, polymer composites usually exhibit largely enhanced electrical conductivity, and in this condition, the composites are changed from insulated material to conductive material [4,8,9]. The percolated CNT network structure can be detected indirectly by measuring the rheological properties [10–13]. Generally, with the increase of CNT content, the increase of storage modulus (G') is much higher than that of loss modulus (G''), and a plateau is present at low frequencies in the modulus curves. The transition from liquid-like to solid-like viscoelastic behavior at low frequency range is mainly related to the significantly restrained long-range molecular chain motion induced by the presence of CNT network structure [14].

The electrical response of the conductive polymer composites under load condition is interesting and it has been one of the main subjects of recent researches. Through recording the variation of electrical properties, the deformation or damage in the material can be diagnosed before the mechanical failure of the material. Due to the intrinsic coupling of electrical properties and mechanical deformation ability, CNTs have been believed ideal candidates for future multi-functional materials as sensors and actuators.

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Therefore, much work has been carried out to prepare the strain sensors with high sensitivity [15–20]. Among those factors that influence the strain-sensitivity of the conductive composites, the CNT network structure exhibits very important role and it has been used to monitor the damage evolution in the material [21–23].

Polyurethane (PU) attracts much attention since it has been synthesized. Due to the excellent physical properties and good biocompatibility, PU has found many applications in the fields ranging from automotives, rollers systems, and films to biomedical products [24]. Recently, the application of PU as smart materials has been a main subject of many researches due to its high tunable microstructure, high strain recovery, easy processing, light weight and low cost [25,26]. Different kinds of PU-based shape memory materials have been developed through adding another polymer [27–30] or nanofillers [31–33]. Because adding CNTs greatly improves the electrical conductivity of PU and the composites can be used to prepare the electrically actuated shape memory material, the PU/CNT composites with shape memory behavior have been widely researched [34–38]. However, it should be stressed that in the literatures, most of researches only prove that the PU/CNT composites have good shape memory behavior in a certain condition and few work investigates the relation between CNT microstructure and shape memory behavior of the composites. For example, in the work of Gu et al. [37], only 1 wt% CNTs were used to prepare PU/CNT composites. Jung et al. [39] investigated the electrical actuated shape memory behavior of different PU/CNT composites containing 4 wt% CNTs. Raja et al. [40] investigated the effect of CNT content on the mechanical properties, thermal and electrical conductivity of the PU/CNT composites. However, when they analyzed the variation of shape memory property of composites, only the sample containing 5 wt% CNTs was investigated. Although Mahapatra et al. [38] investigated the content of CNTs on the shape memory behavior of the PU/CNT composites and they found that more than 98% shape recovery and a rapid recovery time of 9 s in both thermal triggering and electrical actuating shape memory behavior could be achieved, it is worth noting that in their work, the thermal triggering shape memory behavior was investigated at ambient temperature of 50 °C, which was much higher than the glass transition temperature of PU. Similarly, enhanced shape recovery ability at 60 °C has been reported by Deka et al. [35]. Obviously, the effect of CNT network structure on the shape memory behavior of PU/CNT is still not clear. The PU/CNT shape memory materials have potential applications ranging from frozen food packaging to medical apparatus and instruments.

In this work, we introduced different contents of CNTs into thermoplastic polyurethane (TPU) and investigated the formation of CNT network structure in the composites and the corresponding variations of mechanical properties, strain sensitivity and shape memory behaviors of the TPU/CNT composites. To the best of our knowledge, this is the first time to found direct relationship between CNT network structure and the shape memory behavior of TPU/CNT composites. We believe that through comparatively investigating the changes of the macroscopic physical properties, this work might provide a guide map for the design and preparation of the TPU/CNT smart materials.

2. Experimental details

2.1. Materials

Polyester-based TPU (tradename of WHT-1570) with a density of 1.19 g/cm^3 and a glass transition temperature of about −40 °C was purchased from Wanhua Polyurethane Co., Ltd. (Yantai, China). It should be stressed that TPU was completely amorphous. CNTs (tradename of Flo TubesTM 9000) were purchased from CNano Technology Co., Ltd. (Beijing, China). The purity of CNTs was more than 95%, and the average diameter and length of a single CNT were ca. 11 nm and 10 μm, respectively.

2.2. Sample preparation

TPU was dried in an oven at 60 °C for 10 h before it was used. The melt compounding of TPU/CNT was conducted on an internal mixer ZJL-300 (Changchun Zhineng Instrument, China) at a melt temperature of 190 °C. The screw speed was set at 100 rpm and the mixing duration was 10 min. In this work, the content of CNTs was varied from 0.5 wt% to 5 wt%. The sample notation was defined as TPU*x*C, where *x* represented the content of CNTs in the composites. After that, the composites were compression-molded at a melt temperature of 190 °C and a pressure of 5 MPa to obtain the plates with a thickness of 1 mm.

2.3. Scanning electron microscopy (SEM)

The dispersion of CNTs in the TPU/CNT composites was investigated using a scanning electron microscope (SEM) Fei Inspect (FEI, the Netherlands) with an accelerating voltage of 20 kV. The sample was first cryogenically fractured in liquid nitrogen. To characterize the dispersion of CNTs in the TPU matrix, the cryo-fractured surface of the representative TPU2C sample was coated with a thin layer of gold before crystallization. To characterize the network structure of CNTs, all the cryo-fractured surfaces were also characterized without coating gold.

2.4. Rheological measurement

The rheological measurement was carried out using a sample disk, which was cut from the compression-molded plate. The diameter of the sample disk was 20 mm. The measurements were conducted on a stress-controlled rheometer DHR-1 (TA Instrument, USA). During the measurement, the sample temperature was set at 190 °C and the measuring frequency was varied from 0.01 to 100 Hz. For all the measurements, the samples were measured within the linear viscoelastic strain range, which could be estimated by an initial survey through a dynamic strain sweep experiment at strains ranging from 0.01% to 100%. In addition, it was stressed that the measurement was carried out in nitrogen atmosphere.

2.5. Mechanical properties

Tensile properties of the TPU/CNT composite were measured on a dumb-bell specimen that was cut from the previously compression-molded plate. The width and the thickness of the specimen were 5.0 and 1 mm, respectively. The measurement was conducted on a universal tensile machine AGS-J (SHIMADZU, Japan) according to ASTM: D638 at room temperature (23 °C). A cross-head speed of 100 mm/min was used.

2.6. Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis (DMA) measurement was carried out using a DMA Q800 analyzer (TA Instrument, USA). A rectangular cross-sectional bar (with a length of 25 mm and a width of 5 mm) was cut from the previously compression-molded plate. During the DMA measurement, a tensile mode was selected. The temperature was heated from −80 to 10 °C at a heating rate of 3 °C/min and the frequency was set at 1 Hz.