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Selective localization of multi-walled carbon nanotubes in thermoplastic elastomer blends: An effective method for tunable resistivity–strain sensing behavior

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ABSTRACT

Conductive network morphology and interfacial interaction play important roles in determining resistivity–strain (ρ–ε) sensing behavior of conductive polymer composites (CPCs). In this work, thermoplastic elastomer blends consisting of poly(styrene–butadiene–styrene) block polymer (SBS) and thermoplastic polyurethane (TPU) were fabricated via different melt processing procedures, which could tune the above two issues simultaneously by selectively localizing multi-walled carbon nanotubes (MWCNTs) in SBS, TPU and both in SBS and TPU, respectively. It is observed that the composite fibers with selectively localized MWCNTs show distinct different ρ–ε sensing behavior. Work of adhesion calculation suggests stronger interfacial interaction between MWCNTs and SBS, however, wetting coefficient calculation indicates slightly better wetting of MWCNTs with TPU. Because of such stronger interaction and poorer dispersion, the composite fiber with MWCNTs distributed in SBS exhibits higher ρ–ε sensitivity than its counterpart with MWCNTs distributed in TPU, and with MWCNTs distributed in both phases, the ρ–ε sensitivity lies in between. Moreover, the ρ–ε sensing behavior was fitted with a model based on tunneling theory by Simmons. It is suggested that the change in tunneling distance and the number of conductive pathways could be accelerated significantly under strong interfacial interaction. This study could offer a new pathway and provide a guideline for the preparation of high-performance CPC resistivity–strain sensors with tunable sensitivity.

1. Introduction

Conductive polymer composites (CPCs) have been an active research topic for several decades due to their wide range of applications and ease of processing [1]. In recent years, CPCs have been extensively investigated as sensors to detect various external stimulis, such as strain [2,3], damage [4,5], temperature [6,7], liquids [8–10], vapors [11–13] and PH [14]. In terms of resistivity–strain sensors, CPCs are considered as promising candidates to detect resistivity change induced by strain. The practical use of carbon nanotube (CNT) structure demonstrates their application in the field of sensing technology as an active part of sensing structural composites [15,16]. Thermoplastic elastomer (TPE) with combined characteristics of rubber and plastic, has gained considerable amount of attention recently, which is critically important for the application of a good engineering thermoplastic material. Thus, CPCs containing TPE and CNT are valued as the prospective stretchable resistivity–strain sensors for detecting dangerous deformations and vibrations of mechanical parts in many fields of science and engineering.

A tunable resistivity–strain dependency (resistivity–strain sensitivity) is often required for different applications. Thus, the control of sensitivity is one of the most important issues for the preparation of resistivity–strain sensors. To modify the resistivity–strain sensitivities of these sensors, several methods have been proposed. Recently, our group has reported that mixed fillers containing CNTs and metallic particles in different volume ratios can be used to modify the resistivity–strain sensitivity of CPC fibers [17]. Dang et al. observed that CNTs with higher aspect ratio are preferred for higher sensitivity to pressure in CNT/silicone rubber composites [18]. Murugaraj et al. demonstrated that narrow distribution of tunnel gaps between overlapping nanochannels is responsible for the high electromechanical sensitivity of their CPCs [19]. And Hwang et al. reported that the concentration of poly(3-hexylthiophene) (P3HT) plays an important role in the piezoresistive sensitivity of P3HT-wrapped CNT/poly(dimethylsiloxane) composites [20].

In above investigations, different strategies have been considered for controlling resistivity–strain sensitivity in CPCs, however, they exhibit relative narrow range of tunable sensitivity.

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Systematic and efficient methods are still necessary for modifying sensitivity. Therefore, fundamental aspects of resistivity–strain sensing CPCs need to be reconsidered for the preparation of high performance sensors with tunable sensitivity. In CPCs, conductive networks are formed with conductive fillers in insulating polymer matrixes, which provide continuous conductive pathways for electrical current. In the case of entangled conductive networks, the response of electrical property to strain is governed by both conductive network morphology and interfacial interaction between filler and polymer matrix. As a result, these two issues should be regarded as the key factors in modifying resistivity–strain sensitivity. Nevertheless, these issues have barely been investigated simultaneously [21].

Polymer blending has been extensively studied as one of the most important methods to modify conductive network structure in CPCs [22–24]. As polymer blends offer more interface and phase structures in CPCs, different conductive network morphologies can be constructed from selective localization of conductive fillers in different phases, not to mention the abundant change of phase morphology in polymer blends during stretching [25]. Furthermore, different polymers tend to have different interfacial interactions with fillers due to their difference in chemical nature. Thus, using polymer blends can be considered as an effective method to tune both conductive network morphology and interfacial interaction in CPCs for the control of resistivity–strain sensitivity. However, such a method has yet to be reported for CPCs based on resistivity–strain sensors.

Herein, we utilize polymer blends consisting of poly(styrene–butadiene–styrene) block polymer (SBS) and thermoplastic polyurethane (TPU) to fabricate CPC resistivity–strain sensors. Efforts are carried out to selectively distribute conductive fillers in one or two of the polymer phases. The effect of conductive filler location in polymer blends on the resistivity–strain sensing properties is systematically investigated. The conductive network morphology before and after stretching; the orientation of polymer matrix and conductive filler under strain is also studied to investigate the electrical property-strain sensing behavior of these CPCs. Finally, an analytical model is used to further understand the change of electrical property under strain.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs, Nanocyl 7000, Nanocyl S.A.) were used as conductive fillers in the composites. According to producer, these MWCNTs have an average diameter of 10 nm, length of 1.5 μm and a specific surface area of 250–300 m^2/g. SBS with S/B ratio of 40/60 and trademark of SBS-792 was kindly provided by Baling Company of Sinopec Co. Ltd., China. Polyester based TPU (IROGRAN 455-200) was provided by Huntsman Company.

2.2. Sample preparation

MWCNT composites were prepared in a Hakke internal mixer. All blends were mixed at 60 rpm under 160 °C. SBS/TPU/MWCNT composites were melt-blended via applying three different procedures: blending of premixed SBS-MWCNT or TPU-MWCNT composites with the respective unfilled polymer in a second step, direct blending of SBS-MWCNT and TPU-MWCNT in a second step. In order to minimize the possible transition of MWCNTs during the second step, these precompounds were melted in the mixer for 10 min while the mixing time of the second step was 5 min. Then, these composites were extruded as fibers with piston-mode Rosand RH70 (Malvern, Bohlin Instruments) capillary rheometer. The experimental procedures are summarized in Fig. 1.

In this paper, samples were denoted as *A*-*x*NT/*B*, where *A* and *B* represent the elastomer matrixes, *x* represents MWCNT content in *A* phase. *A*-*x*NT/*B* also represents that MWCNTs were premixed in *A* phase at first. For example, SBS-8NT/TPU represents that SBS-MWCNT containing 8 wt.% of MWCNTs was mixed with TPU in a second step.

2.3. Characterization

Contact angles were measured in a sessile drop mould with KRUSS DSA100. Pure elastomer samples for contact angle measurements were compression moulded at 180 °C under 10 MPa pressure for 10 min then cooled to 20 °C. Contact angles were measured on 3 ml of wetting solvent at 20 °C, and the results reported were the mean values of 3 replicates. The surface tensions, dispersion and polar components of these elastomers can be also obtained from contact angle measurements.

With gauge length of 50 mm, the melt-spun fibers were clamped between a pair of alumina electrodes in a SANS CMT4000 universal test machine. Electrical resistance was measured with a Keithley 6487 picoammeter under a constant voltage of 1 V to avoid strong electrical current within the sample. Both the resistance measurement set-up and tensile test machine were interfaced with a computer to record the resistance change during stretching. A constant rate of 10 mm/min was used for the simultaneous resistance–strain measurement. Cyclic stretching and recovery was also conducted to investigate the dynamic resistivity–strain behavior. It should be noted that the sample with a resistivity above 10^4 is considered as non-conductive due to the limitation of current set-up.

Morphological studies were carried out using a scanning electron microscope (SEM, JEOL JSM-5900LV) under an accelerating voltage of 20 kV. To investigate the conductive networks below the sample surface, un-coated specimens were used. The conductive networks in the polymer matrix are charged to emit enriched secondary electrons to make them visible [26]. In addition, these fiber specimens were cryogenically fractured in a direction perpendicular to flow direction in liquid nitrogen and the fracture surfaces were coated with a thin layer of gold to examine the blend morphology and MWCNT dispersion in the composites.

Polarized Raman spectra was recorded on a micro-Raman spectrometer (JY HR800) equipped with a microscope. Excitation was provided by He–Ne at 786 nm. A beam size of 1 μm was used. In order to determine the orientation level of MWCNTs, the dichroism Raman spectra were achieved by recording Raman spectroscopy along two directions normal between each other, which were parallel and perpendicular to the long-axis (length) direction of fiber, respectively. All spectra were baseline corrected and the peak position and intensity were fitted in the range from 1000 cm^{-1} to 2000 cm^{-1}.

3. Results and discussion

3.1. Resistivity–strain sensing behavior of SBS/TPU/MWCNT composite fibers

The resistivity–strain sensing behavior is examined by measuring the electrical resistance as a function of uniaxial strain to evaluate the potential of these fibers as resistivity–strain sensors. Fig. 2(a) shows the resistivity–strain dependence of SBS/TPU/MWCNT composite fibers. In spite of different starting points, all samples demonstrate a definitive trend where the resistivity increases logarithmically with increasing strain. As indicated by the slope coefficient of resistivity–strain (ρ–ε) curve, SBS-4NT/