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Shape memory-enhanced water sensing of conductive polymer composites

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ABSTRACT

Electrically conductive polymer composites have been widely utilized as the sensory materials being capable of response to various types of stimuli. A shape memory-enhanced water sensing was unprecedentedly reported for polymer composites comprising of carbon nanotubes (CNTs) and shape memory polyurethane (SMPU). The morphological, thermal, mechanical and micro-structural properties of the CNT–SMPU composites were investigated. Two swelling processes were specifically designed to measure the water sensing of the composites. It was found that the shape memory thermo-mechanical programming enlarged magnitudes of the resistivity variation, which may be attributed to the combination of the swelling effect and the re-orientation/local movements of the CNTs along with stress/strain energy release. The findings may greatly benefit the applications of the smart polymers in the fields of sensory materials and flexible electronics.

1. Introduction

Polymeric composites containing various types of nanofillers have been widely explored towards implanting with the reinforced mechanics as well as novel functions [1,2]. The carbon nanotubes (CNTs) are one set of the most prominent candidates to construct functional polymer composites. The CNT-containing polymer composites commonly possess superior electrical conductivity, which have been applied as the sensory materials, such as gas [3], pressure [4] and strain [5] sensing. The combination of the shape memory polymers (SMPs) and nanofillers lead to shape memory polymer composites. The previous studies of the conductive shape memory polymer composites emphasized on the mechanical reinforcement and electro-responsiveness. However, there has been little literature concerning the stimuli sensing of the polymer composites by far. The electrical conductivity of the composites varies along with the shape changes in a typical shape memory thermo-mechanical programming. By virtue of the shape-dependent conductivity, we once exploited a novel temperature sensing silver nanowire-shape memory composites [1]. Herein, a shape memory-enhanced water sensing was unprecedentedly reported for CNT-containing polymer composites. Compared to the direct immersion into water, the composites experiencing shape memory programming exhibited enlarged magnitudes of the variation in resistivity. The findings may greatly benefit the development of the conductive shape memory polymer composites in the fields of the sensory materials and flexible electronics.

2. Experimental

The CNT–SMPU composites were fabricated via transfer process according to our previous study [2], which was briefly described as below: multi-wall CNTs suspension in methanol was dip-coated onto a glass substrate before adding the SMPU solution in dimethylacetamide; the composite films were peeled off after solidification in vacuum. The composite films, cut into the size of 15 mm*3 mm*60 μm (length*width*thickness), were labeled as PUC-01, PUC-02 and PUC-03, representing for the CNTs contents of 5, 12 and 20 wt% respectively. The investigations with Scanning Electron Microscope (SEM, Hitachi, S-4800), tensile tests (SUST, China), micro-Raman spectrometer (JY HR800, excited by He – Ne at 786 nm and a beam size of 1 μm) and Integrated Thermal Analyzer (STA 409 PC, NETZSCH) were performed. The composites in dry state were extended by different percentages at 90 °C at the rate of 10 mm/min. The variation of the electrical resistivity (R_s) during the immersion was recorded with an electrochemical workstation (CHI660D, ChenHua, PR China) under a constant

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voltage of 1 V.

3. Results and discussion

3.1. The morphological, mechanical and structural investigations

The CNT–SMPU composites were in bi-layer structure, consisting of the conductive layer constructed by the CNTs and the SMPU matrix (are shown in Fig. 1a and b). It was clearly found that the fibril-like CNTs network whose one part was embedded into the matrix meanwhile the other part was left on the surface, making the composites single-side electrically conductive [2]. Acid treatment endowed the CNTs with an abundant of polar groups. The thickness of the CNTs layer could be well controlled by adjusting the dip-coating process, which was determined in the range of 5–30 μm.

The composites maintained the stretchability originating from the SMPU matrix. The elongation in break was 27%, 33% and 34% in turn for the composites of PUC01, PUC02 and PUC03 (is shown in Fig. 1c). Meanwhile, the strength of the composites was greatly improved, which was consistent with the results of the previously reported CNT-containing polymer systems [6,7]. The maximum stress increased from 44 MPa to 70 MPa with the increase of the CNTs content. Fig. 1d shows the Raman spectra of the composites. Three dominant peaks locating at 1329, 1591 and 2109 cm^{-1} were found. The former two peaks were indicative of the D and G bands of the CNTs while the latter peak was assigned to the –NH–CO groups of the PU matrix [8].

3.2. Water sensing process design and thermal gravity analysis

Unlike the traditional strategy, the SMPC in this study responded to the water stimuli via changes in the resistivity. In order to disclose the influence of the shape memory programming on water sensing, two processes were designed, which are schematically illustrated in Fig. 2a. Compared to the direct immersion into the water (Process A), the composites experienced a two-step thermo-mechanical programming, namely extension from the original shape to the temporary shapes at a high temperature and cooling down to fix. Afterwards, the extended composites were immersed into water (Process B).

The variation of the R_s through the two processes should be quantitatively measured and discussed in the next section. Fig. 2b and c presents the TGA and differentiation thermal gravity (DTG) curves of the composites swollen with water, respectively. The composites were subjected to dramatic weight loss at nearly 100 °C, resulting from the evaporation of the absorbed water. The PUC-03 had the largest weight loss of nearly 20% compared to the other composites, suggesting that the composites with more CNTs contents were able to absorb much amount of water. Furthermore, the peaks locating at 355–365 °C were assigned as the thermal decomposition of the composites. The decomposition temperatures slightly shifted upwards as the CNTs contents increased, reflecting the interaction of the CNTs with the SMPU matrix via hydrogen bonding [7].

3.3. Resistivity variation under water stimulation

The dry-state composites had different R_s of 0.048, 0.036 and 0.022 Ω m for PUC-01, PUC-02 and PUC-03 respectively. The R_s rapidly increased within the initial 500 s, which followed a nearly linear increase as the composites experienced process A (are shown in Fig. 3a and b).

The resistivity variation may result from the disconnection of the CNTs network due to the swelling effect during solvent absorption [6,9]. The variation magnitude of the R_s was determined to be 31.4%, 25.0% and 27.2% in turn. By contrast, a shape memory-enhanced water sensing was found in process B. PUC-03 and PUC-01 were chosen and arbitrarily extended by different percentages. The corresponding R_s–time curves are presented in Fig. 2c and d. The PUC-03 had the R_s of 0.026 and 0.036 Ω m as extended by 5%

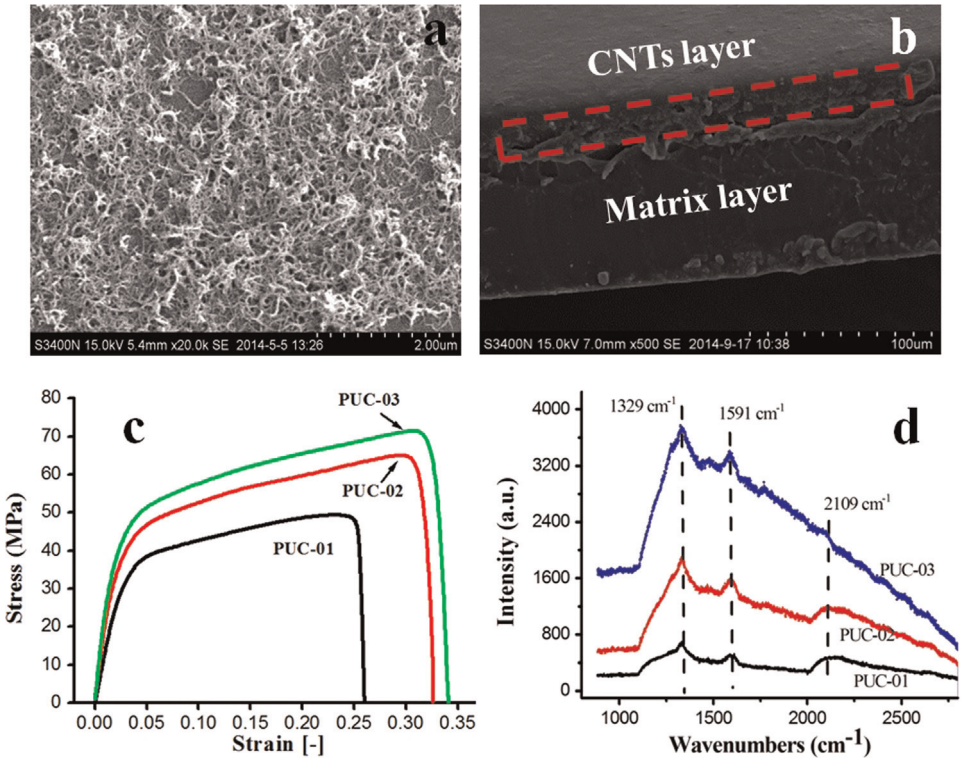

Fig. 1. SEM images of the surface (a) and cross section (b) of the composite PUC03; Stress–strain curves (c) and Raman spectra (d) of the composites.