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Shape memory-based tunable resistivity of polymer composites

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ABSTRACT

A conductive composite in bi-layer structure was fabricated by embedding hybrid nanofillers, namely carbon nanotubes (CNTs) and silver nanoparticles (AgNPs), into a shape memory polyurethane (SMPU). The CNT/AgNP-SMPU composites exhibited a novel tunable conductivity which could be facially tailored in wide range via the compositions or a specifically designed thermo-mechanical shape memory programming. The morphologies of the conductive fillers and the composites were investigated by scanning electron microscope (SEM). The mechanical and thermal measurements were performed by tensile tests and differential scanning calorimetry (DSC). By virtue of a specifically explored shape memory programming, the composites were stretched and fixed into different temporary states. The electrical resistivity (R_s) varied accordingly, which was able to be stabilized along with the shape fixing. Theoretical prediction based upon the tunneling model was performed. The R_s–strain curves of the composites with different compositions were well fitted. Furthermore, the relative resistivity and the Gauge factor along with the elongation were calculated. The influence of the compositions on the strain-dependent R_s was disclosed. The findings provided a new avenue to tailor the conductivity of the polymeric nano-composites by combining the composition method and a thermo-mechanical programming, which may greatly benefit the application of intelligent polymers in flexible electronics and sensors fields.

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1. Introduction

Shape memory polymers (SMPs), as one set of intelligent polymers which are capable of responding to external stimuli, have been catching intensive academic and industrial interests in the recent years [1–3]. The SMPs experience complex thermo-mechanical programming as applied into a typical shape memory cycle. Both the programming and the compositions of the polymers determined the shape memory effects. Thus, the shape memory performance of one certain type of SMPs could be tailored in wide range by chemical or physical approaches. For instance, T. Xie made perfluoro sulphonic acid ionomer (PFSA) exhibiting multi-shape memory effect by creatively designing an elaborate thermo-mechanical programming [4]. Similarly, R. Hoeher et al. disclosed that depending on the programming procedure, a lightly cross-linked polyethylene blend obtained a dual-, triple-, or quadruple-shape memory effect, with well-defined intermediate temporary shapes [5]. Besides the shape memory programming, incorporation of various types of nanofillers with the SMP matrix not only greatly reinforces the composites in mechanics, but also implants with novel functionalities being previously absent for the polymer matrix [6–8]. Y. Wu et al. explored a facile approach to fabricate a UV/heat dual-responsive triple shape memory polymer by simply mixing a metallosupramolecular unit into one part of epoxy resin [9]. Particularly, the incorporation of carbon/metal-based nanofillers with the SMPs implants the composites with electrical conductivity. Various types of conductive nanofillers, such as carbon nanoparticles/tubes/wires [10], graphene and silver nanoparticles (AgNPs)/nanowires (AgNWs) [11], have been reported to introduce into the polymer matrix. The carbon nanotubes (CNTs) have been considered as a promising candidate for the preparation of the conductive polymer composites due to the large aspect ratio and superior conductivity [12]. Compared to the composites consisting of sole type of nanofillers, the composites consisting of hybrid conductive nanofillers commonly exhibited advantages in terms of the conductivity and sensitivity. K. Takei et al. fabricated a highly sensitive whisker based on composite films of the CNTs and silver nanoparticles [13]. The CNTs formed a conductive network matrix with excellent bendability, and nanoparticles enhanced the conductivity and endowed

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the composite with high strain sensitivity. Similarly, micrometre-sized silver flakes and the CNTs were taken together by K.Y. Chun et al. who presented a highly conductive, printable and stretchable hybrid composite [14]. The CNTs, serving as one-dimensional, flexible and conductive scaffolds, constructed effective electrical networks among the silver flakes. L. Lin et al. compared the resistivity of the composites composed of the CNTs and carbon black (CB) under stretching. They found that the hybrid conductive nanofillers could reduce the entanglement in conductive network structure, thus increase the resistivity–strain sensitivity [15].

Although the combination of “electrical conductivity” and “shape memory” makes novel functions achievable, the studies have been emphasizing on the electro-triggered shape memory behaviors. Joule heat is commonly regenerated as external voltages are applied to the composite systems, leading to the various thermal transitions of the polymer matrix [16]. G.X. Fei et al. reported an electro-triggered spatial and temporal control of the shape memory process towards multiple shapes [17]. They also creatively fabricated an electro-activated surface micropattern tuning system using microinjection molding whose surface was able to recover to the original micropatterns with high accuracy [18]. As for the electrically conductive shape memory composites, the percolating conductive network of the nanofillers is deformed along with the composites under stretching. Given that the electrical conductivity of the composites entirely derives from the percolating conductive network, the morphological and structural evolutions of the nanofillers network determine the variation of the conductivities. Thanks to the shape fixing capability of the shape memory matrix, the variation of the conductivity could also be temporarily fixed in the shape memory cycle. By virtue of the shape-dependent conductivity, we once explored one set of novel shape memory-based sensory materials. A silver nanowire-containing shape memory composite was capable of recovering to the original shape from the temporary shapes along with simultaneous changes in the electrical resistivity as exposed upon temperature stimulus [6]. There are two strategies to tailor the conductivity of the shape memory composites. The first is changing the compositions, i.e. the type and volume ratio of the conductive nanofillers; the second is experiencing specifically designed thermo-mechanical shape memory programming. Herein, we presented how to tailor the conductivity of a conductive shape memory polymer composites by combining the composition design and thermo-mechanical programming. Hybrid conductive nanofillers comprising of AgNWs and AgNPs were fabricated into a shape memory polymer matrix via transfer process. Afterwards, the morphological, thermal and shape memory properties of the composites were investigated. The composites exhibited tunable electrical resistivity as exposed to a typical shape memory thermo-mechanical programming. Furthermore, the sensitivity of the resistance variation was greatly influenced by the compositions. The strain-dependent resistivity and the sensitivity were modeled and numerically simulated based upon tunneling theory. The findings provide a new avenue to tailor the electrical properties of the composites by combining internal compositions with external thermo-mechanical factors, which may greatly benefit the development of intelligent polymers in the fields of multi-functional polymers and electronics.

2. Experimental

Multi-wall carbon nanotubes (CNTs, 97%, Aladdin) in the size of average 10 nm (diameter) × 1.5 μm (length) were pretreated prior to usage [19,20]. The CNTs were suspended in the mixture solution of H_2SO_4 and HNO_3 in the volume ratio of 3:1. After stirring for 3 h at 75 °C, the suspension was cooled down to the room temperature before centrifuging at the speed of 10,000 rpm for 15 min. The pretreated CNTs were obtained by washing three times with water and ethanol. Silver nanoparticles (AgNPs, Aldrich) were in spherical size with the diameter of 30–60 nm. The shape memory polyurethane (SMPU) MS4510, provided by Mitsubishi Heavy Industries Ltd, was chosen in the study. The SMPU has been well known as a non-crystalline shape memory polyurethane [21]. The SMPU solution in dimethylacetamide (DMAc) at the concentration of 80 mg/ml was prepared for the next composites fabrication. The CNT/AgNP-SMPU composites were fabricated by transfer process according to previous literature [22], which were briefly described as following: Weighted amounts of the CNTs and the AgNPs were suspended in methanol at the aid of ultrasonic vibration. The suspension at the solid concentration of 8 mg/ml was dip-coated on a pre-cleaned glass substrate before moderately evaporating the solvent at the ambient temperature, which led to the conductive CNTs/AgNPs films. Finally, the films were put in the vacuum at 60 °C for 2 h in order to remove the trace solvent completely. The dip-coating was carried out twice for each sample with 2–3 ml total amount of the CNTs/AgNPs suspension. The rectangle release substrate in the size of 25 mm × 80 mm(width × length) was homogeneously covered by the conductive nanofillers. Subsequently, the SMPU solution in DMAc was dip-coated onto the conductive films. A single-side conductive film in bi-layer structure was peeled off after solidifying at 80 °C for 12 h in vacuum. Three composite samples were fabricated containing the conductive layer of 23% in weight percentage. The samples were labeled as SMCAg-0, SMCAg-10 and SMCAg-30 whose numbers represented for the weight ratio of the AgNPs to the CNTs in the conductive layers.

The morphological, thermal and mechanical properties were investigated by scanning electron microscope (SEM, Hitachi, S-4800), Differential Scanning Calorimetry (DSC, Perkin-Elmer Diamond) and tensile tests (SUST, China) with a temperature chamber. The SEM measurements were carried out under an accelerating voltage of 20 kV. The composites had the average thickness of 50 μm. They were cut into rectangular shape with the width of 3 mm before clamping between a pair of clamps to create a gage length of 20 mm. The composites were stretched at 80 °C at a constant rate of 15 mm/min and cooled down to fix the temporary shapes. The resistivity of the composites in different temporary shapes was recorded with electrochemical workstation (CHI660D, ChenHua, PR China) under a constant voltage of 1 V. The resistivity and tensile test measurements were both interfaced with a computer for data collection.

3. Results and discussion

3.1. Fabrication and morphologies of the CNT/AgNP SMPU composites

CNT-containing polymer composites are commonly fabricated via dispersing the CNTs in the polymer bulk [12,23]. However, it is always challenging to well disperse the CNTs in solvents and polymer matrix. On the contrast, the transfer process, which was applied in this study, took advantages of well dispersion of the CNTs and convenient construction of the conductive network without complex surface modification [22]. It was found that the hybrid nanofillers consisting of the acid treated CNTs and the AgNPs were well dispersed in the methanol at the aid of the ultrasonic shake. The hybrid suspension was deposited onto the glass substrates, forming a conductive film after evaporating the solvent. The transfer process enabled the conductive film to transfer into the SMPU matrix from the substrate completely. The compositions and the thickness of the hybrid conductive films were facially controlled by changing the AgNPs contents and the dip-coating parameters, such as volumes and concentrations of the CNTs/AgNPs suspension. The hybrid conductive network almost maintained its

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