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Electrical actuation properties of reduced graphene oxide paper/epoxy-based shape memory composites

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ABSTRACT

In order to explore the enabled design principles of electrically driven epoxy-based shape memory (ER) composites, reduced graphene oxide paper (RGOP) was used for manufacturing the material. Shape memory effect is induced by electrical resistive heating of RGOP possessing excellent heat conductive property and serving as a conductive layer to transmit heat to the polymer. The temperature distribution and shape recovery behavior of the composite have been recorded with infrared video. The investigation on shape recovery behavior of reduced graphene oxide paper/epoxy-based shape memory composites (RGOP/ER) reveals that the shape recovery speed increases with increased applied voltage. It is worth noting that the recoverability of the composite is approximately 100% taking only 5 s under 6 V, which is more energy saving than the previously reported data. The electrical actuation shape recovery rate of the composite can be controlled by programming the synergistic effect between the mass ratio and the applied voltage. This work provides a feasible route to construct efficient electrically actuated shape memory composites and to expand their potential applications.

1. Introduction

Shape memory polymers (SMPs) have made enormous advances in the past three decades [1,2], which can memorize temporary shapes and revert to their permanent shapes upon exposure to various external stimuli, such as heat [3,4], electricity [5–7], alternating magnetic field [8], light radiation [9], and chemicals [10–12]. Conventional SMPs are usually driven by an external heat source. The thermally induced SMPs can be actuated by increasing the ambient temperature above its thermal transition; however, it is difficult to control its actuation because of slow heat transfer and low thermal efficiency. In some applications, such as remote control of the actuator, electrical drive is a more convenient and efficient method than external heat-triggered actuation.

Electrically actuated shape memory composites have been generally synthesized by SMPs and conducting filler, such as carbon nanotubes (CNTs) [13], nanocarbon particles [7], carbon black [14] and Ni powder [6]. One of carbon materials, graphene with its unique two-dimensional structure has attracted significant interest due to its excellent electrical, thermal, and mechanical properties [15,16]. Bhattacharyya et al. have been successful in manufacturing well-designed sandwich composite films using poly-methyl methacrylate and graphene oxide films [17]. Liu et al. have prepared RGOP possessing high modulus and good conduction ability. Previously, we have reported epoxy-based SMPs possessing excellent shape memory effect and great potential applications in smart structures [4]. RGOP-enabled epoxy-based SMP has not been reported so far. Based on the electrical conductivity and high modulus of the RGOP, we have used it as a functional layer to fabricate a new composite.

The novel epoxy-based SMP composite fabricated for this study displayed good shape memory effect in response to applied voltage. The structural properties of the specimen were characterized by Raman spectra and scanning electron microscope (SEM), and the thermo-mechanical properties were analyzed by dynamic mechanical analysis (DMA). Under different applied voltages, the shape recovery process of the specimen was investigated. The temperature distribution and recovery behavior of sample were recorded with infrared video in a recovery test. Interestingly, RGOP/ER exhibited good electric-induced shape-memory effect and the results could enable the design principles of electrically driven SMP composites to be established. Electrically driven

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epoxy-based SMP composite is a promising example in a range of possible applications involving actively moving polymers that can undergo significant macroscopic deformation in a predefined manner in the presence of an appropriate stimulus. These composites can greatly enhance the performance of the SMPs and widen their potential applications.

2. Experimental details

2.1. Synthesis of materials

All the chemicals were of analytical grade and were used in 'as received' conditions without any further purification. The polymer matrix used in this research was an epoxy-based shape memory polymer, which was made in our laboratory following the procedure given in Ref. [4]. The SMP composites were fabricated by coating RGOP onto the surface of SMP sheets by resin transfer molding. In this process, shape memory resin was used as the matrix and mixed with the hardener at a proper ratio. The resulting mixture was degasified in a vacuum oven to completely remove air bubbles, and subsequently the resin transfer molding technique was introduced to make the SMP composite. The RGOP was placed on the bottom surface of the mold and the polymer mixture was then injected into the mold. After filling the mold, the resin was cured to obtain the SMP composite.

2.2. Characterization of materials

Micro/nano-mechanical tests were carried out on a universal testing machine (Agilent Technologies T 150 UTM, USA). The specimens were tested on XploRA™ Raman microscope (HORIBA Jobin Yvon) and the scanning electron microscope (SEM) analyses were performed with an environmental microscope (FEI-Quanta 200F). The thermo-mechanical properties of the specimens were investigated using dynamic mechanical analysis (DMA) performed on DMA/SDTA861^e (Mettler-Toledo AG Analytical, Switzerland) in a tension mold, using rectangular specimens with dimensions of 20 mm × 3 mm × 2 mm. The dynamic mechanical properties were measured within a temperature range of 25–150 °C at a heating rate of 5 °C/min with a constant frequency of 5 Hz. The stress-controlled thermo-mechanical properties of shape memory cycles were characterized on a DMA Q800/RSA3 (TA Instruments, America) using a tensile fixture at force control mode. The rectangular sample was first heated to 110 °C at a rate of 4 °C/min and kept in an isothermal condition for 5 min. The sample was then stretched at 110 °C at a force ramping rate of 2 N/min from its "permanent" shape at the beginning of the Nth testing cycle to the elongated shape under a final tensile force of 3 N. It was then cooled to 30 °C (2 °C/min) with the force kept constant. After being held at 30 °C for 5 min, the applied force was released to the pre-load force 1 mN. Finally, the temperature was ramped from 30 to 110 °C at a heating rate of 4 °C/min and kept isothermal for 5 min. Five cycles were performed to examine the repeatability. The temperature distribution was recorded with infrared video (InfraTec GmbH, Germany).

3. Results and discussion

3.1. Characterization of RGOP

Raman spectroscopy is commonly used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. Therefore, it provides a fingerprint by which the molecule can be identified. Raman spectroscopy can evaluate amorphous components or the number of defects based on the ratio of the D-band to the G-band. The crystalline ordering of RGOP was investigated by Raman spectroscopy. Among distinct peaks for graphene materials, the two major D and G peaks are normally used for identification. As shown in Fig. 1A, the absorption peaks at 1330 cm^{-1} and 1592 cm^{-1} are assigned to D-band and G-band, respectively. Generally, the D-band corresponds to the presence of disordered sp^2 carbon. The G-band represents the originated graphitic structure of carbon material. The D/G intensity ratio can be used to evaluate the defect concentration and crystal purity of the sample. The results in Fig. 1A show that the larger D/G intensity ratio of RGOP is likely due to the absence of a significant number of defects. This implies a decrease in the average size of the carbon sp^2 due to the reduction of graphene oxide [18].

Micro/nano-mechanical tests of RGOP indicate the modulus of RGOP reaching up to 25 GPa and the maximum stress of it reaching approximately 15 MPa. However, the elongation at break of RGOP is only 0.08% as shown in Fig. 1B. So it may be said that RGOP will enhance the modulus and improve the tensile strength of the composite as long as the elongation can be kept very small. For observing the sheet structure and morphology of RGOP, SEM measurement was performed. The existence of reduced graphene oxide sheets is confirmed by SEM image in Fig. 2. The RGOP image presents the unique sheet-like structure with smooth surface in which the size and shape of reduced graphene oxide are not uniform. The average diameter of reduced graphene oxide sheet structure is about 20 μm. The results from SEM images are in good agreement with Raman spectroscopy analysis. The RGOP resistivity was only 7.5 mΩ cm. Based on the electrical conductivity and high modulus

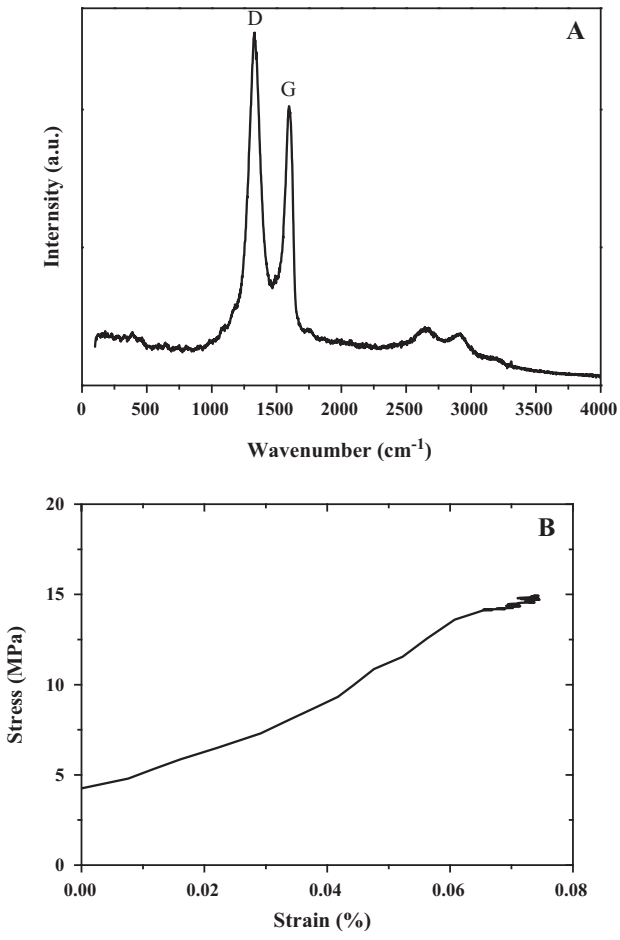

Fig. 1. (A) Raman spectra and (B) micro/nano-mechanical test curve of reduced graphene oxide paper (RGOP).