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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 preload 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

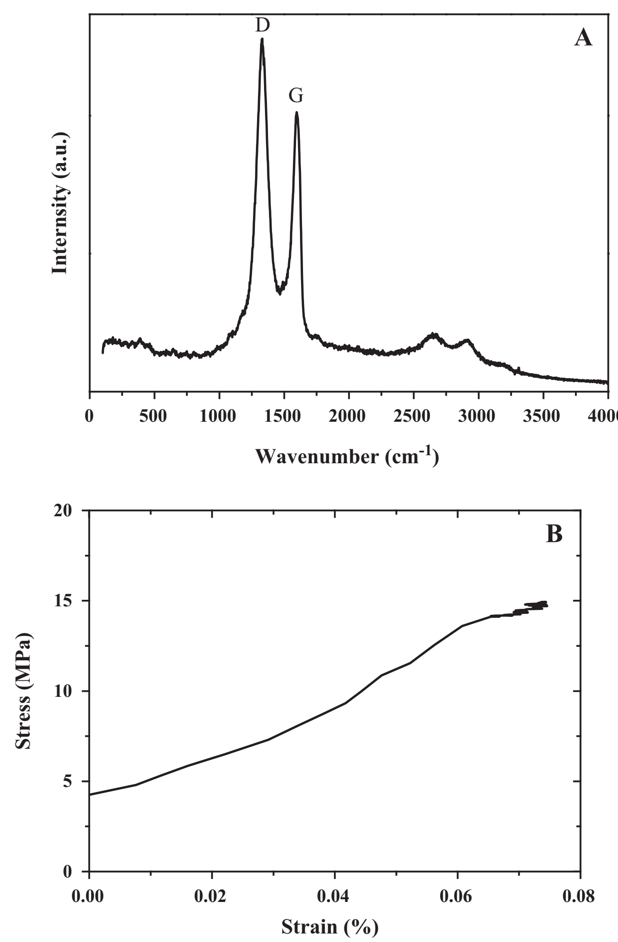

Fig. 1. (A) Raman spectra and (B) micro/nano-mechanical test curve of reduced graphene oxide paper (RGOP).

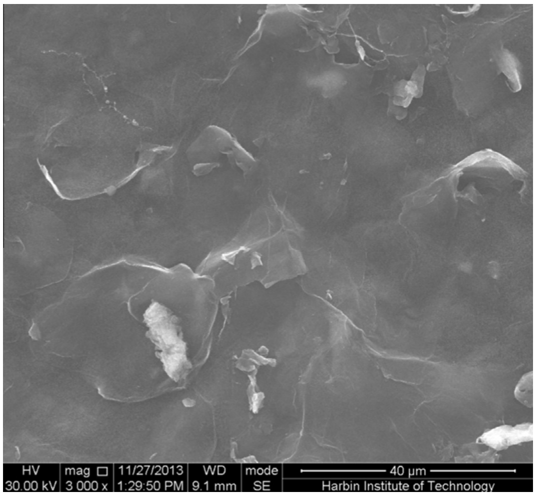

Fig. 2. SEM images of reduced graphene oxide paper (RGOP).

of the RGOP, it was used as a functional layer to fabricate the new composite.

3.2. Thermal properties of the composites

Fig. 3 presents the tangent delta, the storage modulus and the loss modulus as function of temperature, obtained from the DMA tests. Glassy modulus plateau at temperatures below its glass transition, a transition region in which modulus decreases with increasing temperature, and a rubbery plateau region in which modulus increases linearly with increasing temperature. The glass transition temperature (T_g) is one of the crucial characteristic parameters of thermo-mechanical deformation and shape recovery in SMP materials [19]. The T_g determined from the heating cycle is 93 °C for ER, as shown in Fig. 3.

Stress-controlled cyclic thermo-mechanical testing was used to characterize the cyclic shape memory behavior, as shown in Fig. 4. Five cycles were performed to examine the repeatability. Remarkably, ER exhibited good mechanical properties, which indicated that this kind of ER had cyclic fatigue resistance. Therefore, the ER possessing excellent shape memory effect and cyclic fatigue resistance was used as the matrix of the RGOP/ER composite.

In addition, dynamic mechanical properties were determined using DMA/SDTA861^e in tensile mode at a frequency of 5 Hz. One notable attribute of the storage modulus data in Fig. 5 are the variations of storage modulus, which at 25 °C are 1947 MPa and 2319 MPa for ER and RGOP/ER, respectively. The results show that the storage modulus of the composite increases for RGOP, which is consistent with the results obtained by micro/nano-mechanical tests of RGOP, discussed earlier. In other words, RGOP improves the tensile strength of the RGOP/ER composite, which is beneficial for enhancing the fatigue resistance, too.

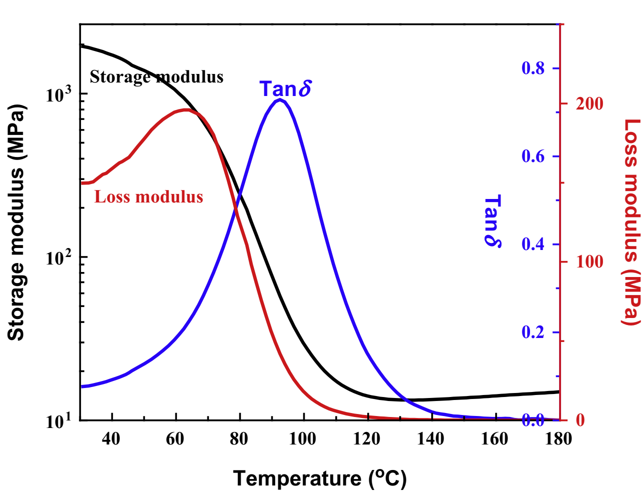

Fig. 3. DMA thermogram of epoxy-based shape memory polymer (ER).

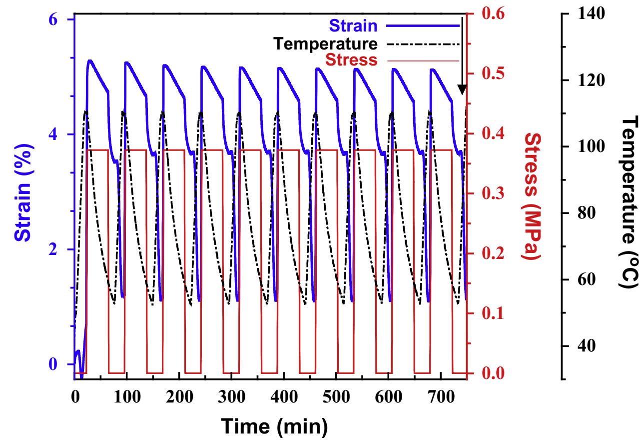

Fig. 4. Five shape memory cycles of epoxy-based shape memory polymer (ER).

3.3. Electrical actuation shape memory effects of the composites

The shape memory characterization data provided in Fig. 6 demonstrate that the shape memory composite synthesized in this study exhibit good shape memory behavior. As reported by Lu et al. [13], the electrical actuation shape memory behavior can be properly quantified by the recovery angle in view of the low elongation of RGOP. However, RGOP, with the excellent heat conduction property and high modulus, plays a key role as a functional layer in fabricating the novel electrically driven shape memory composite. For shape memory behavior tests the specimens were heated up to 113 °C (T_g + about 20 °C) in an oven and held for 15 min for full heating. Then, specimens became soft and were bent into "U"-like shape around a mandrel with a radius of 5 mm at a bending rate of 10 °/s. The bent specimens fixed on the mandrel were subsequently cooled to 25 °C. No apparent recovery

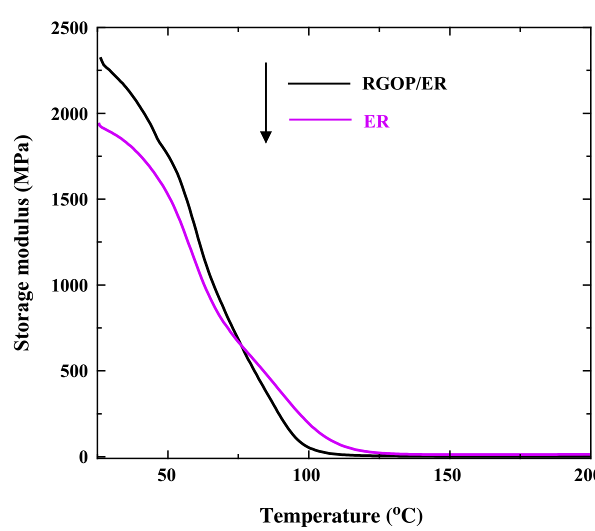

Fig. 5. The storage modulus vs temperature curves for reduced graphene oxide paper/epoxy-based shape memory composite product (RGOP/ER) and ER.

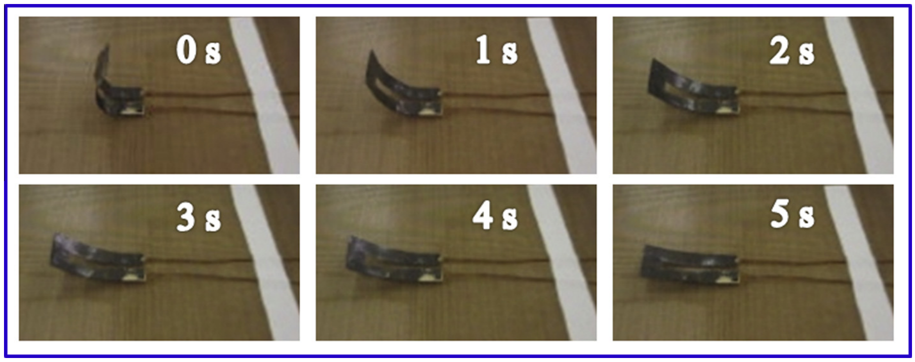

Fig. 6. Shape recovery process photo of reduced graphene oxide paper/epoxy-based shape memory composite product (RGOP/ER) under applied 6 V Dc.

was observed even after the deformed SMP sheet was left in air for 12 h. To study the shape recovery behavior, bent specimens were subjected to applied voltages of 1 V, 2 V, 3 V, 4 V, 5 V and 6 V for the composite to restore the original shape.

To distinguish from the original state S_p with initial angle A_p, the state in shape recovery process was referred to as recovered shape S_r with recovered angle A_r, and with the recovered time t_r. To quantify the shape memory effect, the shape recovery ratio (R_r) is quantified as follows:

$$R_r(\%) = \frac{A_r}{A_p} \times 100 \tag{1}$$

Shape memory behavior of different specimens was compared under varying applied voltages. The shape recovery demonstrations of the SMP specimens were recorded by a video recorder and the infrared thermal camera, Figs. 6 and 7. Moreover, Table 1 shows the data of RGOP/ER basic properties and shape memory recovery process. The shape recovery of SDS-ER was obvious at the beginning, and then it became more significant. A change in shape from temporary shape to permanent shape of RGOP/ER was completed within 5 s under 6 V. The traditional thermo-active shape memory composite wastes much energy to keep the ambient temperature above its thermal transition besides heating the sample. On the other hand, the electrically driven shape memory performance that can be expected from this new SMP system is more convenient and energy-efficient than the heat-triggered actuation.

In order to discuss the temperature field distribution, surface temperature distribution was carried out on the sample. The temperature rises to 102.39 °C with an increased temperature of 74.81 °C compared to the initial temperature at 1s, as shown in Fig. 7A. In subsequent snapshots, the actuator becomes brighter globally. The temperature increase is above T_g and thus activates the actuator. The surface temperature distribution is described in Fig. 7B. Obviously, most of the colors are red, which means that the temperature on the overall surface has a relatively uniform distribution. The uniform temperature distribution indicates that these resistors have a similar resistance. Thus, the surface temperature distribution indicates that the composite has a uniform electric heating performance.

Table 1
The data of reduced graphene oxide paper/epoxy-based shape memory composite (RGOP/ER) basic properties and shape memory recovery process.

Specimen	S (cm^2)	d_{RGOP} (cm)	d_{com} (cm)	R (Ω)	U_a (V)	t_r (s)	T_h (°C)
RGOP/ER	6.5	0.004	0.1	9.0	6	5	240.11

S- surface area, d_{RGOP}- thickness of RGOP, d_{com}- thickness of RGOP/ER, R- resistance, U_a- applied voltage, t_r- shape recovery time, T_h- highest temperature.

To evaluate the energy consumption of RGOP/ER, the energy efficiency per SMP volume (η) may be quantified as follows:

$$\eta(\mathrm{W/cm^3}) = \frac{P}{V} = \frac{UI}{S(d_{com} - d_{RGOP})} \tag{2}$$

η- energy efficiency per SMP volume, P- power output, V- ER volume of the composite, U- applied voltage, I- current, S- surface area, d_{com}- thickness of RGOP/ER, d_{RGOP}- thickness of RGOP.

Furthermore, it must be noted that the shape recovery rate strongly depended on the applied voltage. Table 2 presents the shape recovery data of RGOP/ER at different applied voltages. It is plain to see that the shape recovery time of the specimen under 4 V is about 5 times more than that for the specimen under 6 V for

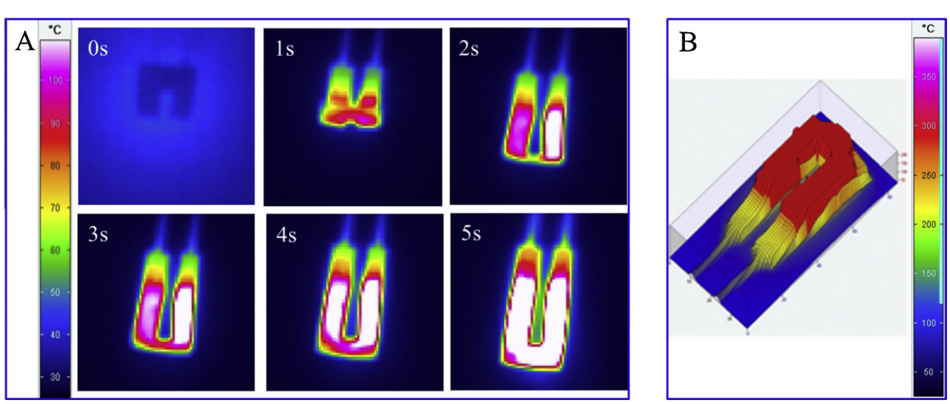

Fig. 7. Shape recovery process infrared thermal images of reduced graphene oxide paper/epoxy-based shape memory composite product (RGOP/ER) under applied 6 V Dc: (A) 2D surface temperature distribution of shape recovery process photos and (B) 3D surface temperature distribution photo at 5 s.

Table 2
Shape recovery data of reduced graphene oxide paper/epoxy-based shape memory composite (RGOP/ER) at different applied voltage.

U (V)	T_h (°C)	t_s (s)	t_c (s)	R_r (%)	I (A)	η (W/cm^3)
1	35.27	–	–	–	–	–
2	62.87	60	300	5	0.22	0.71
3	105.17	8	90	90	0.33	1.59
4	160.71	3	25	90	0.41	2.63
5	220.84	0	12	95	0.52	4.17
6	240.11	0	5	98	0.60	5.77

U- applied voltage, T_h- highest temperature, t_s- time of starting shape recovery, t_c- time of completing shape recovery, R_r- shape recovery ratio, I- current, η- energy efficiency per SMP volume.

complete recovery. Interestingly, the RGOP/ER composite presented good recovery properties and the energy efficiency [20] in low voltage. Upon shape recovery test, the low entropy state drove the individual chains toward their initial states. According to the laws of thermodynamics, when temperature increases, entropy typically increases [21]. As a consequence, the recovery time of the SMP is shortened with increasing voltage. Shape memory effect was carried out by electrical resistive heating generated by RGOP. Furthermore, RGOP possessing excellent heat conductive property can serve as a conductive layer to transmit heat to the polymer.

4. Conclusions

In this work, RGOP has been used for successfully constructing a composite product. As expected, it could be used to construct an electrically driven epoxy-based SMP composite. Shape memory effect was carried out by electrical resistive heating generated by RGOP. The investigation on shape recovery behavior of reduced graphene oxide paper/epoxy-based shape memory composites (RGOP/ER) has revealed that the shape recovery speed increases with increased applied voltage and the recoverability of the composites is approximately 100% taking only 5 s at 6 V. The present results indicate that the electrical actuation shape memory composite is more energy saving than the thermo-active actuation which is the most common responsive method of SMPs but also requires to keep the ambient temperature above thermal transition besides heating the sample. This work provides a feasible route to covert the plain shape memory composites to efficient electrically actuated shape memory composites.

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