

ORIGINAL ARTICLE

Electroactive shape-memory effects of hydro-epoxy/carbon black composites

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Electroactive shape-memory hydro-epoxy/carbon black composites are investigated in this study. The thermomechanical and the shape-memory properties of these composites are characterized using dynamic mechanical analysis and *U*-type shape-memory tests. These results indicate that the glass transition temperature (T_g) of the composites decreases first and then increases slightly as the carbon black content increases. The storage modulus at high temperatures increases as the carbon black content increases. The percolation threshold of the electroactive shape-memory hydro-epoxy composite is lower than that for many other composites. Because of the low percolation threshold, the electroactive shape-memory hydro-epoxy composite exhibits excellent shape-memory property. The sample filled with 1.9 wt% carbon black can recover nearly 100% of its original shape in only a few minutes under an applied voltage of 200 V.

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INTRODUCTION

A shape-memory polymer (SMP) is a type of smart material that has been widely investigated and used in aerospace deployable structures and in biomedical fields.^{1–7} An SMP is a polymer that can be fixed in one temporary shape and then recover its permanent shape upon application of an external stimulus. A thermally sensitive SMP, which uses a temperature change as its external stimulus, is the most common type. However, the application of a thermally sensitive SMP is often limited by external heat source restrictions. To overcome this problem, composites consisting of conductive ingredients and an SMP matrix have been developed.^{8–15} When a current passes through the conductive ingredient network within an SMP, the induced Joule heating could increase the internal temperature to one that is above the transition temperature, thus triggering deformation recovery. An electroactive SMP composite has a huge advantage over a thermally sensitive SMP in applications because electricity is more easily controlled and more conveniently applied than heat.

An SMP matrix has an important implication on the shape-memory property of composites. To date, an electroactive shape-memory polyurethane composite and an electroactive shape-memory styrene composite have been reported.^{15,16} However, the study of an electroactive shape-memory epoxy composite remains rather rare. In this work, to study the electroactive stimuli of a shape-memory epoxy composite, a composite consisting of carbon black and shape-memory hydro-epoxy is fabricated. The thermomechanical and the shape-memory properties of the electroactive shape-memory hydro-epoxy composite are systematically investigated in this paper.

EXPERIMENTAL PROCEDURE

Materials

The polymer matrix used in this study is a thermoset hydro-epoxy SMP, which is made in our laboratory. The T_g of the SMP is $\sim 80^\circ\text{C}$, which is defined by the peak in the loss tangent ($\tan \delta$) versus temperature curve. The carbon black (ketjenblack EC-600JD) is obtained from Akzo Nobel (Chicago, IL, USA). The carbon black is used as a conductive ingredient in the developed composite materials. The electroactive shape-memory hydro-epoxy composites with various weight fractions of carbon black are prepared using the following steps. First, a certain amount of carbon black is blended into the hydro-epoxy resin. Mechanical stirring is applied for 50 min, and then, equivalent amounts of curing agent are added into the blend. Mechanical stirring is applied again for 20 min, and the mixture is degassed in a vacuum oven at 60°C to obtain a bubble-free mixture. After that, the mixture is placed between two Teflon-covered glass plates with a 3.5-mm thick rubber spacer. A thermal curing program is performed at 80°C for 2 h, 150°C for 5 h and 180°C for 4 h. After the curing process, the SMP composites filled with carbon black are cut into rectangular shapes for testing. Electroactive shape-memory hydro-epoxy composites with carbon black weight fractions of 0.4 wt% (0.4), 0.9 wt% (0.9), 1.4 wt% (1.4), 1.9 wt% (1.9) and 2.4 wt% (2.4) are synthesized in this way.

Methods

Dynamic mechanical analysis. The thermomechanical properties of the electroactive shape-memory hydro-epoxy resin are investigated using a DMA (dynamic mechanical analysis) Q800 system (TA Instruments, New Castle, DE, USA) in multifrequency-strain mode from 25 to 200°C . A rectangular specimen for each carbon black content is measured to obtain the DMA curve of the composites. The specimen dimensions are $28 \times 13 \times 3.5 \text{ mm}^3$. The specimens are heated

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at a rate of 3 °C per minute, and an applied strain of 0.1% is oscillated at a constant frequency of 1 Hz.

Scanning electron microscope. The FEI Quanta 200 scanning electron microscope (FEI Company, Eindhoven, Netherlands) is used to observe the distribution changes of the carbon black. The optical microscope images of the composites are captured in the high vacuum mode.

Electrical resistivity test. Rectangular specimens ($80 \times 15 \times 3.5 \text{ mm}^3$) are used to determine the electrical resistivity of the electroactive shape-memory hydro-epoxy composites. Before testing, both ends of the specimens are clamped with two copper electrodes along their lengths. The resistance R is monitored by a digital multimeter (UT61E, UNI-T). The volume electrical resistivity ρ is calculated using the equation $\rho = RS/L$, where R is the electrical resistance, S is the cross-sectional area of the specimens and L is the length of the specimens.

U-type shape-memory test. Rectangular specimens ($80 \times 15 \times 3.5 \text{ mm}^3$) are used to evaluate the shape-memory property of the electroactive shape-memory hydro-epoxy composites. A shape-memory test is performed according to the following steps. (1) The specimens are heated up to a certain temperature in an oven and held for 10 min to fully heat them. The temperatures used are $T_g + 10^\circ\text{C}$, $T_g + 20^\circ\text{C}$ and $T_g + 30^\circ\text{C}$. (2) The specimens are bent into U shapes, circling a center axis with a 10-mm diameter at a 30° per second bending rate. The U-shaped specimens are then quickly removed from the oven and dipped into a cold water bath (20 °C) with a constant applied external force. (3) To quantify the shape-memory property, the U-shaped specimens are placed into an oven set to the temperature at which they are deformed, and the shape recovery process is observed. The recovery time is recorded as the time at which the specimens stop changing shape. Five specimens are measured for each carbon black content at the designated temperatures to obtain the average recovery time; this recovery time is designated as the shape recovery time for that temperature.

Electroactive shape recovery property test. To determine the electroactive shape recovery property of the composites, the electroactive shape recovery of the shape-memory hydro-epoxy composites with a carbon black weight fraction of 1.9 wt% is triggered under the voltages of 150, 175, 200, 225 and 250 V. Electroactive shape recovery property tests are performed as described above, the only difference between electroactive shape recovery property test and U-type shape-memory test is that the shape recovery is triggered by an electric current.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

The glass/rubber modulus ratio is defined as the elastic ratio, and higher elastic ratios are beneficial for SMP shape retention. Figure 1a shows that the storage modulus (E') below T_g is approximately two orders of magnitude larger than the modulus above T_g , which means

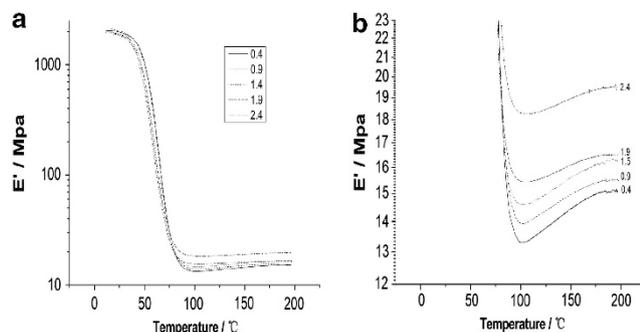


Figure 1 Storage modulus of the electroactive shape-memory hydro-epoxy composites as a function of temperature (a) and a partially enlarged view of the storage modulus curves at high temperatures (b).

that the electroactive shape-memory hydro-epoxy composite is an effective type of SMP composite. The partially enlarged view of the storage modulus curves at high temperatures is shown in Figure 1b, revealing that the rubber modulus of the shape-memory hydro-epoxy composites increases as the carbon black content increases. According to the rubber elasticity theory, the rubber modulus is related to the cross-link density such that the rubber modulus would increase as the cross-link density increases. The carbon black acts as physical cross-links in the structure of the electroactive shape-memory hydro-epoxy composites; thus, the rubber modulus increases with the increase in carbon black content.

T_g is a key characteristic parameter of the thermomechanical behavior and the shape recovery of an SMP composite. Here, the peak in the $\tan \delta$ versus temperature curve is defined as T_g . T_g values obtained from the $\tan \delta$ versus temperature curves have been provided in Figure 2. The figure reveals that the T_g of the shape-memory hydro-epoxy composites is much lower than that of the pure shape-memory hydro-epoxy resin. Figure 2 also reveals that T_g decreases as the carbon black content increases but increases slightly when the content of carbon black is increased to 2.4 wt%. In fact, regardless of which dispersion method is used, the carbon black cannot be dispersed completely in the polymer matrix. Therefore, an aggregation of carbon black exists in the polymer matrix. The aggregations would adsorb the hydro-epoxy resin, and an interfacial layer would be formed on the surface of the aggregations.¹⁷ Hence, it is difficult for the hardeners to access the internal areas of the aggregates, and thus, the hydro-epoxy resin would not be fully cured. The degree of curing decreases as the carbon black content increases, which would lead to a decrease in the number of chemical cross-links. Hence, T_g decreases as the carbon black content increases. However, the number of physical cross-links increases with an increase in the carbon black content, which would raise the glass temperature. Consequently, T_g increases slightly when the carbon black content is increased to 2.4 wt%.

Electrical property analysis

Figure 3 shows that a sharp transition of the volume resistivity occurs when the carbon black content increases from 0.4 wt% to 1.9 wt%. This finding indicates that the conductive ingredient network is

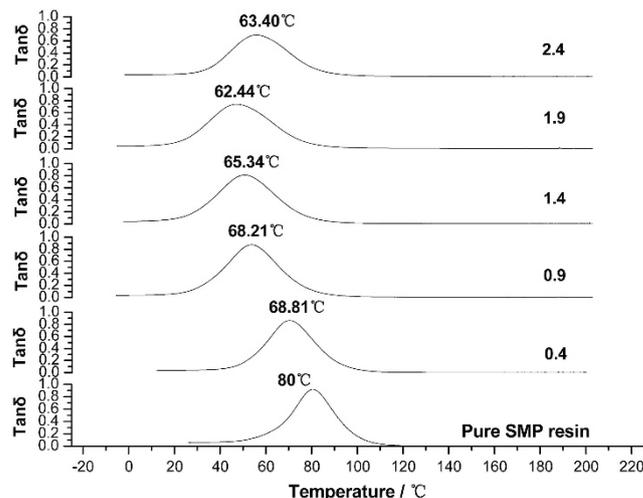


Figure 2 Loss tangent ($\tan \delta$) of the electroactive shape-memory hydro-epoxy composites as a function of temperature.

gradually formed when the carbon black content increases from 0.4 wt% to 1.9 wt%. Hence, the percolation threshold would be observed between 0.4 wt% and 1.9 wt%. This result demonstrates that the percolation threshold of the electroactive shape-memory hydro-epoxy composites with carbon black is lower than for that many other conductive composites.^{18–22} A low percolation threshold is beneficial for electroactive SMP composites because by only adding a small

amount of conductive filler, these composites would possess excellent conductive properties. Moreover, the shape-memory property of the composites would not be strongly damaged. Figure 3 also shows that the volume resistivity decreases to a low and stable level when the carbon black content increases from 1.9 wt% to 2.4 wt%. This finding indicates that the complete conductive ingredient network has been formed when the content of carbon black is > 1.9 wt%.

Figure 4 shows the microstructures of the electroactive shape-memory hydro-epoxy composites with various contents of carbon black. The aggregations of carbon black are clearly displayed in Figures 4c, d and e. As shown in Figure 4, when the carbon black content is lower, the carbon black distributes separately from each other in the shape-memory hydro-epoxy matrix. However, with an increase in the carbon black content, the carbon black connects with each other, and complete carbon networks are gradually formed.

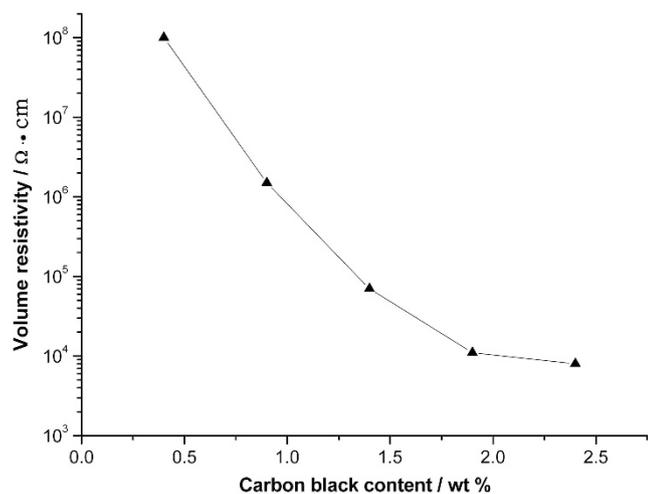


Figure 3 Relationship between the volume resistivity and the carbon black content at room temperature.

Shape-memory property analysis

To investigate the shape-memory property of the electroactive shape-memory hydro-epoxy composites, the rectangular specimens are tested at $T_g + 10^\circ\text{C}$, $T_g + 20^\circ\text{C}$ and $T_g + 30^\circ\text{C}$ using the U-type shape-memory test. According to the results, full recovery can be observed after only a few minutes at different temperatures. Hence, the shape recovery ratio (R_r) of the electroactive shape-memory hydro-epoxy composite is almost 100%. This finding indicates good shape-memory performance and further indicates that adding a small amount of carbon black does not damage the shape-memory property of the hydro-epoxy composites.

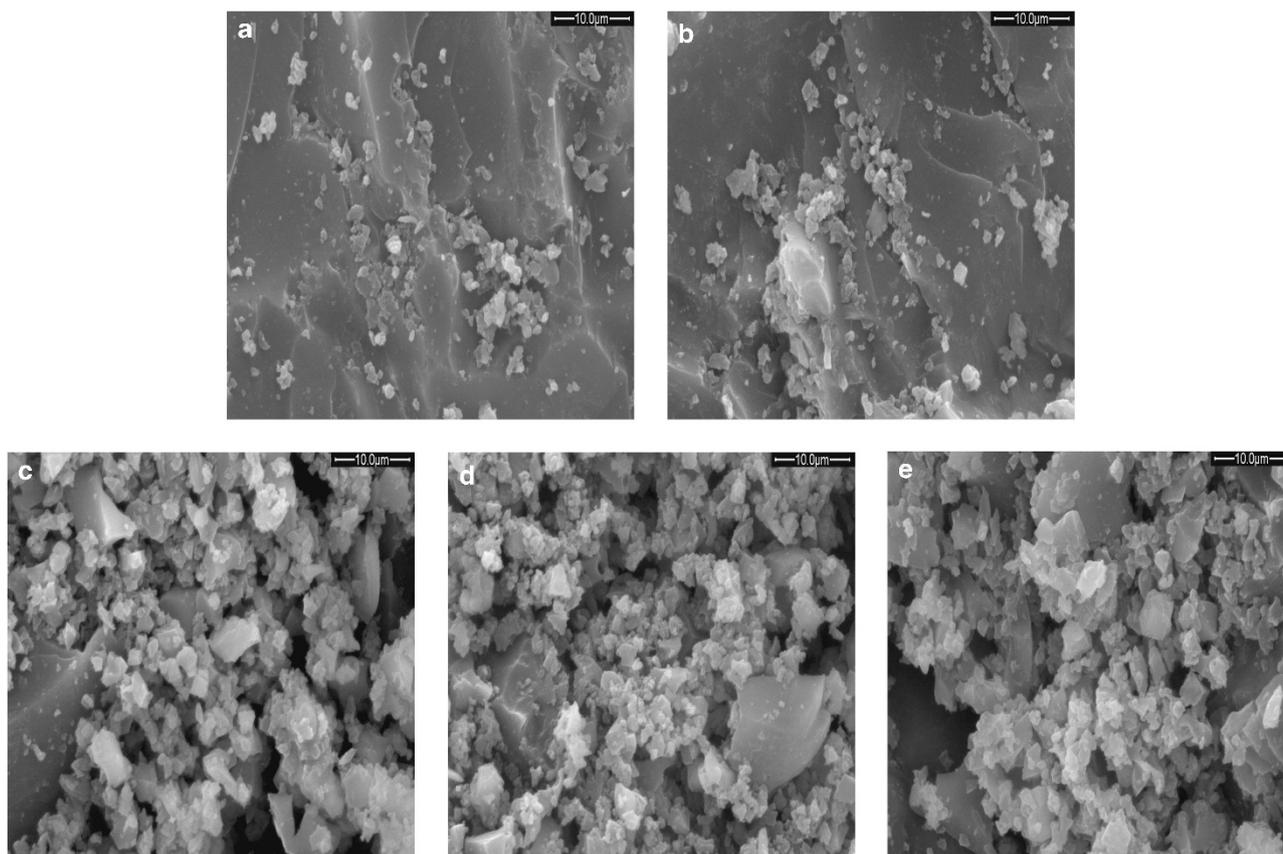


Figure 4 Scanning electron microscope images of the electroactive shape-memory hydro-epoxy composites with 0.4 wt% (a), 0.9 wt% (b), 1.4 wt% (c), 1.9 wt% (d) and 2.4 wt% carbon black (e).

Figure 5 shows the shape recovery times at $T_g + 10^\circ\text{C}$, $T_g + 20^\circ\text{C}$ and $T_g + 30^\circ\text{C}$. As shown in Figure 5, the shape recovery time increases with increasing carbon black content at $T_g + 10^\circ\text{C}$, $T_g + 20^\circ\text{C}$ and $T_g + 30^\circ\text{C}$. In the U -type shape-memory test, specimens are bent to U shapes at a high temperature, and then, the shape is fixed in a cold water bath. The strain energy is stored in the form of internal stress in the temporary shape. Upon subsequent heating, the stored strain energy is released in the form of a recovery force, which would

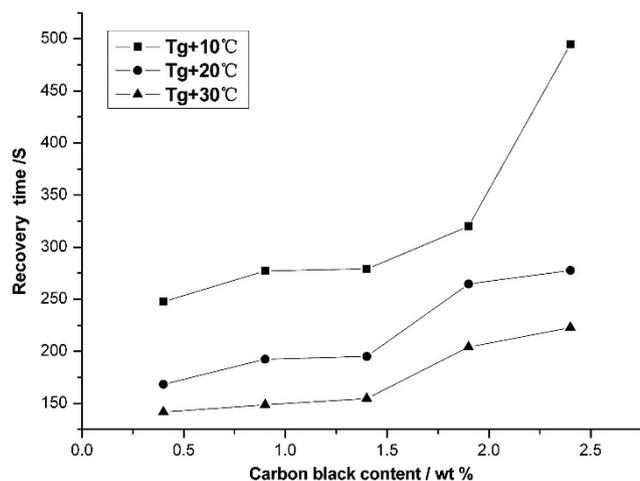


Figure 5 Relationship of the shape recovery time on the carbon black content at different temperatures.

drive the samples towards their original shapes. The shape recovery time is mainly determined by segment flexibility. The number of chemical cross-links decreases as the carbon black content increases, resulting in improvement in segment movement. However, the number of physical cross-links increases with an increase in the carbon black content, which would hinder segment movement. Ultimately, the impact from the decrease in the number of chemical cross-links is more than compensated for by the increase in the number of physical cross-links, resulting in a net reduction in segment movement. Hence, the shape recovery time increases as the carbon black content increases. Figure 5 also reveals that a smaller change in the shape recovery time is observed as the temperature increases. This is a result of the segment movement being less hindered as the temperature increases; thus, a smaller change in the shape recovery time is observed.

To investigate the electroactive shape-memory property of the hydro-epoxy composites, a sample with 1.9 wt% carbon black powder is investigated. Figure 6 shows that the recovery of the original shape occurred after only a few minutes. Moreover, the shape recovery ratio (R_r) of the electroactive shape-memory hydro-epoxy composite is almost 100%. This finding indicates good electroactive shape-memory performance. The voltage is an important factor for the electroactive shape recovery process. In this study, the relationship between the shape recovery time and the voltage at room temperature is investigated. According to the results, full recovery can be observed under the applied voltages of 150, 175, 200, 225 and 250 V. The relationship of the shape recovery time on the voltage at room temperature is shown in Figure 7, revealing that the shape recovery

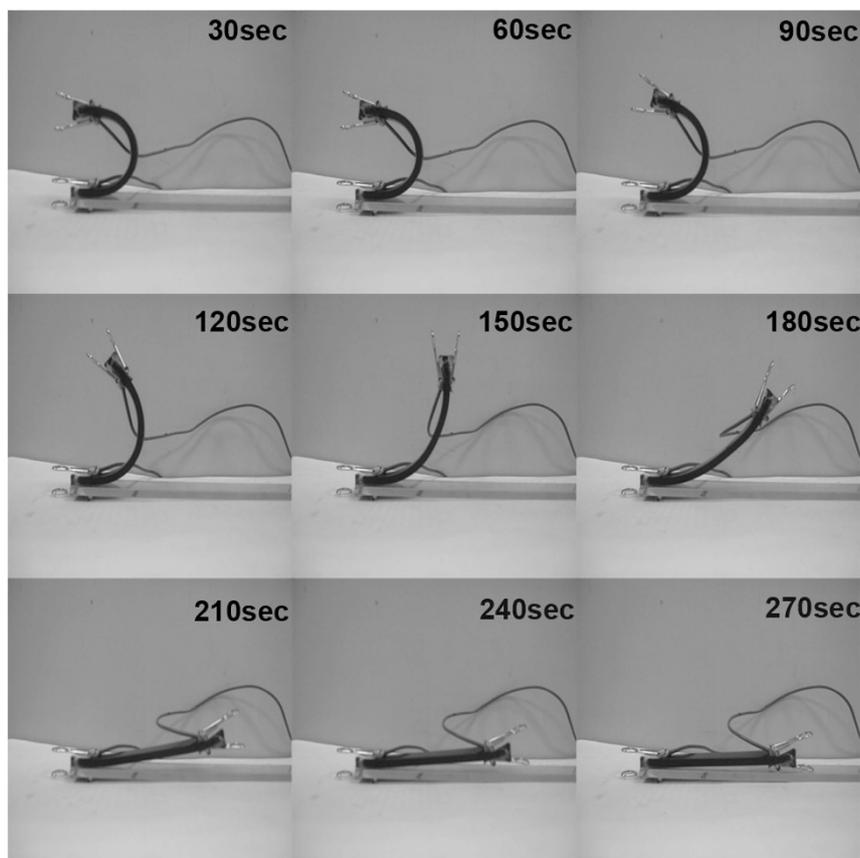


Figure 6 Sequences of the shape recovery of a sample with 1.9 wt% carbon black by passing an electrical current through the sample at a voltage of 200 V. A full color version of this figure is available at *Polymer Journal* online.

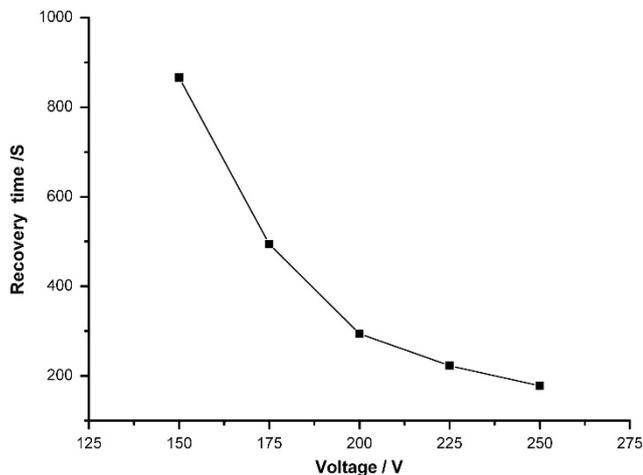


Figure 7 Relationship between the shape recovery time and the voltage at room temperature.

time decreases as the voltage increases. According to Joule's law, the Joule heating is related to the voltage such that increased Joule heating would be induced with an increase in the voltage. Consequently, as the voltage increases, the temperature of the sample simultaneously increases, leading to a higher recovery rate.

CONCLUSION

A series of novel electroactive shape-memory hydro-epoxy composites with different amounts of carbon black incorporated is fabricated. The elastic modulus of the electroactive shape-memory hydro-epoxy composites increases as the carbon black content increases. Due to the presence of powder aggregation, the hydro-epoxy resin does not fully cure. The number of chemical cross-links decreases and the number of physical cross-links increases as the carbon black content increases. T_g first decreases as the carbon black content increases but then increases slightly when the content of the carbon black is increased to 2.4 wt%. The percolation threshold of the electroactive shape-memory hydro-epoxy composites is lower than that in many other conductive composites. During the shape recovery demonstration, the electroactive shape-memory hydro-epoxy composite with 1.9 wt% carbon black can recover nearly 100% of its original shape in only a few minutes under an applied voltage of 200 V.

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