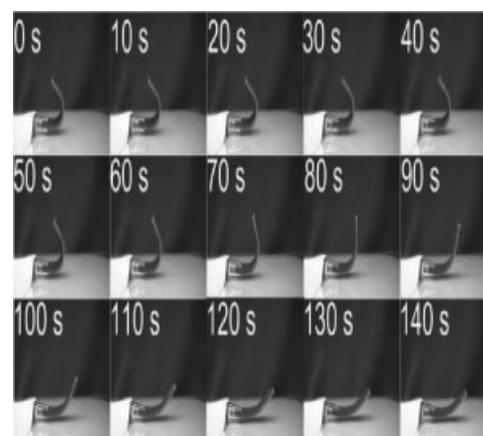


# Carbon Nanopaper Enabled Shape Memory Polymer Composites for Electrical Actuation and Multifunctionalization

Haibao Lu, Yanju Liu, Jinsong Leng\*

Shape memory polymers (SMPs) are fascinating materials, with promising potential in a range of applications as actively moving polymers, which can undergo significant macroscopic deformation in a predefined manner between/among shapes in the presence of an appropriate stimulus. This work aims to present a systematic and up-to-date account of a carbon nanopaper enabled SMP composite from electrical actuation to multifunctionalization. Studies exploring nanopaper enabled SMP composites in various design principles in manufacturing, characterization, improvement, and development were included, especially for those induced by electricity and rendered multifunctional; making the article a comprehensive account of and systemic progress in SMP composite incorporated with carbon nanopaper.



## 1. Introduction

Actively moving polymers are materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli.<sup>[1]</sup> There are a number of types of actively moving polymers, some of which are already common and being researched extensively, such as, shape memory polymers (SMPs), electro/magneto rheostatic, gels, chromic polymers, photomechanical polymers, dielectric elastomers, etc.<sup>[2]</sup> The classification of actively moving polymers has always been

presented on the basis of their major responsive behaviors. Each individual type of actively moving polymers has a different property which can be significantly altered. The property that can be altered influences what types of applications the active polymer can be used for. Some everyday items are already incorporating these materials from aerospace to biomedicine, and the number of viable applications is exponentially growing due to their promising potential.<sup>[3]</sup> SMPs are one of the most popular members of actively moving polymer, originated from their unusual properties, such as the shape-memory effect (SME), pseudoelasticity or large recoverable strain, and adaptive properties which are due to the (reversible) phase transitions in the materials.<sup>[4]</sup> SMPs are similar to other stimuli-responsive polymers, in which a change in macroscopic properties is resulted from an external stimulus, such as heat, light, electricity, and so on.<sup>[5–8]</sup> This also includes a combination of two or more responses at the same time. Therefore, SMPs have attracted keen attention as promising candidates for actively moving polymers, since

Prof. J. S. Leng, Dr. H. B. Lu

National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology (HIT), Harbin 150080, China

E-mail: lengjs@hit.edu.cn

Prof. Y. J. Liu

Department of Astronautical Science and Mechanics, Harbin Institute of Technology (HIT), Harbin 150001, China

they function in response to external stimuli by changing shape. This unique characteristic enables the SMP materials to be used in a myriad of fields, especially for aerospace engineering and bio-medicine.

With the potential applications of SMPs increasing, some major limitations still exist and impose major challenges to their broad utilization.<sup>[9]</sup> Some of the key limitations include low recovery force due to low recovery strength, and low recovery speed due to the low thermal conductivity and inertness to electromagnetic stimuli (in contrast to SMAs). Until now, polymeric materials have been preferentially used for their properties of electrical insulation, not conduction. Fortunately, many valuable research efforts have begun to address these challenges. With regard to the latter challenge, a variety of approaches for the electrical actuation of SMPs have been developed, and have led to the recovery of SMP composites being induced by electrically resistive Joule heating through incorporation with electrically conductive fillers, such as carbon nanotubes,<sup>[10]</sup> carbon particles, conductive fiber,<sup>[11]</sup> nickel zinc ferrite ferromagnetic particles, etc.<sup>[12]</sup> These conductive fillers generate heat according to Joule's law and eventually facilitate the heat transfer till to trigger shape recovery of SMP matrix. Many significant developments have been achieved for SMP composites, of which recovery actuation can be carried out by electrically resistive heating. However, for the fabrication of electro-induced SMP composites, almost all previous works were focused on conductive fillers blended into pure polymers. The resulting composites still could not achieve a high enough electrical conductivity to meet the requirements. A high loading level of filler is required to blend into the SMP resin. A high viscosity of the SMP resin will be therefore produced due to strong interactions between the resin and the conductive filler, thus preventing an efficient transfer of the properties of the filler to the matrix, and also making it difficult to achieve a uniform dispersion. This approach is not the best way to improve the conductive properties of polymers, as demonstrated in previous studies. Furthermore, the electrical conductivity of electro-active SMP composites is still relatively low, because of the limited efficiency of discrete fillers to form percolating conductive networks.

With this as motivation, an attractive technique of making conductive carbon nanotubes (CNTs) or carbon nanofibers (CNFs) into paper form has been scaled up for functional materials.<sup>[13]</sup> Consequently, the use of a CNF or CNT assembled paper integrated with an SMP matrix (in order to render the actuation by electricity) is described. The combination of outstanding electrical properties of carbon nanopaper and the SME of SMPs will help this type of composite to be multifunctional beyond its electrical actuation.<sup>[14]</sup> Despite this fact, a systemic review on carbon nanopaper enabled SMP composites is necessary and important for promoting the progress for electrically



**Dr. Lu** received his Ph.D from Harbin Institute of Technology (HIT) in 2010, and his project was focused on the electroactive and solvent responsive shape-memory polymer (SMP) blends and their constitutive equation. In 2009, he worked at the University of Central Florida (UCF), Orlando, and his project was on nanopaper enabled SMP composites. Thereafter, He joined the National Key Laboratory of Science and Technology on Advanced Composites in Special Environments in HIT. He has authored or co-authored over 60 articles, and has been honored with "excellent doctor in HIT" and "Top ten outstanding Graduate Student."

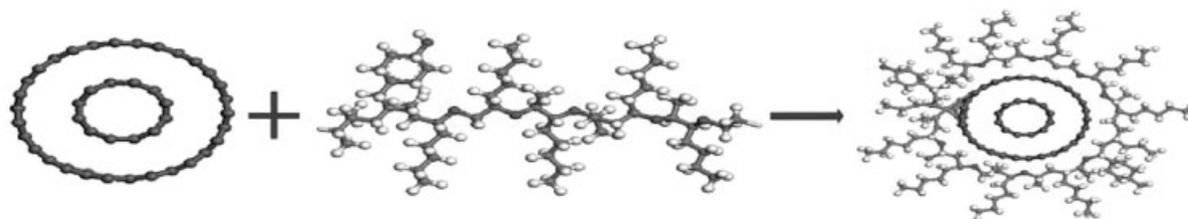


**Professor Liu**, the faculty member of the Department of Aerospace Engineering and Mechanics at Harbin Institute of Technology. She obtained her PhD in the field of Materials from Centre for Composite Materials and Structures of HIT, China in 1999. From 1999 to 2005, she was a research fellow at Nanyang Technological University, Newcastle University and Intelligent Sensor Systems Ltd., successively. Until now, she has authored or co-authored 4 books chapters, 13 issued patents, and over 150 scientific papers in different journals and conference proceedings, including Progress in Material Science, Applied Physics Letters, and Smart Materials & Structures.



**Professor Jinsong Leng** is a Cheung Kong Chair professor and the Director of the Center for Smart Materials and Structures (CSMS) at Harbin Institute of Technology, China. He served as the Editor in Chief of International Journal of Smart and Nano Materials (Taylor & Francis, UK), Associate Editor of Smart Materials and Structures (IOP, UK) and Associate Editor of Journal of Intelligent Materials Systems and Structures (SAGE, UK) etc. He has been elected as an Executive Council Member of the International Committee on Composite Materials (ICCM), Fellows of SPIE, IOP, IMMM and Associate Fellow of AIAA.

conductive SMP composites. The purpose of this review is to provide details of all aspects of the nanopaper enabled SMP composites from fundamentals to applications on an intermediate level. It will show how nanopaper can be used in a smart fashion potentially leading to electrical responses at the desired point of action. A description of the physical basis behind these effects will be provided and the most important types of nanopaper used will be reviewed. Moreover, this review focuses on recent advances in material designs which are extremely necessary to develop more desirable and functional nanopaper enabled SMP composites. Finally, a selection of examples is given and a brief outlook into future aspects is added at the end of



■ Figure 1. Representative configuration of CNT and surfactant.

this article. Some properties of nanopaper enabled composite, which have not been studied within previous works but show potential, will therefore be also discussed as well.

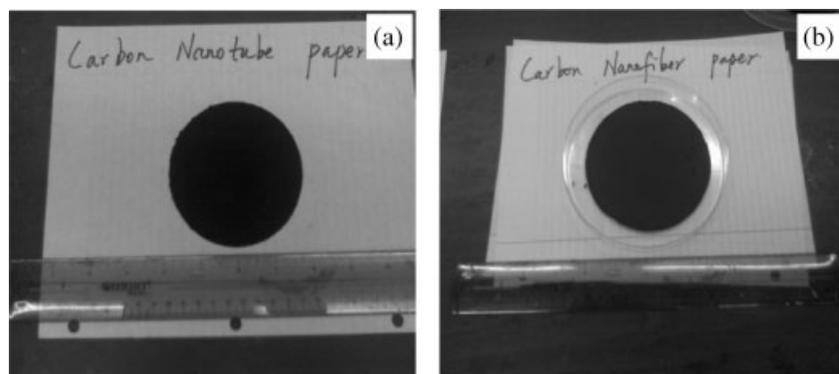
## 2. SMP Composite Coated with Nanopaper

Conductive CNT and CNF nanopapers are primarily introduced for the actuation of shape recovery of an SMP by electrically resistive Joule heating.<sup>[15,16]</sup> The carbon nanopaper was manufactured using a traditional pressure vacuum deposition process. The generally accepted method of making carbon nanopaper involves the use of non-ionic surfactants, which aids the CNTs or CNFs dispersion into the aqueous or organic solvent. The interaction between the CNT and the non-ionic surfactant is presented in Figure 1. The suspension needed to be sonicated for a sufficient amount of time at room temperature, and then suspension was filtered through a hydrophilic or hydrophobic membrane filter with the aid of pressure to form nanopaper. The suspensions were membrane filtered under positive pressure to yield uniform films. The carbon individual was bonded by Van der Waals forces. After filtration, the remaining water and surfactants in the nanopaper was dried in an oven at 120 °C for 2 h. Figure 2a and b, respectively, show the CNT and CNF nanopaper specimens. The nanopapers were found to be porous, with the pore size determined by the weight concentration of the carbon individual. The nanopaper has a porous structure with the individuals entangled with each other. No large aggregates

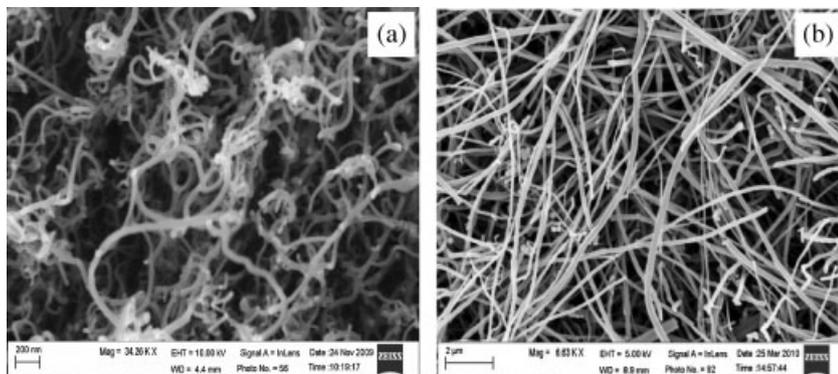
were found, indicating a uniform distribution and close packing in the nanopaper. A network structure was formed by the molecular interactions and mechanical interlocking between nanotubes or nanofibers, as shown in Figure 3a and b. Such a continuous network made of individual nanotubes or nanofibers acts as a conductive path for electrons, making the nanopapers electrically conductive. Since CNTs and CNFs are two of the most electrically conductive materials known, nanopaper is considered one of the best candidates for a conductive material that would allow an insulating polymer to behave like a conductor. This, in turn, could lead to even greater advances in enabling these continuous networks to act as conductive paths for electrons.

The SMP composites were fabricated by coating nanopapers onto the surface of SMP sheets by resin transfer modeling. 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. Subsequently, the resin transfer molding technique was introduced to make the SMP composite. The nanopaper containing one of the various weight fractions was placed on the bottom of the mold. The polymer mixture was then injected into the mold. After filling the mold, the resin was cured to obtain the SMP composite.

The electrical resistivity of the nanopaper enabled SMP composite was measured with the four-point probe method. The electrical resistivity of the SMP composites coated with different weight fractions of nanopapers was different from each other. For example, the SMP composites were coated with one layer of carbon nanopaper containing (either) 0.6, 1.2, 1.8, or 2.4 g of CNTs (or CNFs). As the weight of each nanopaper increased, the average electrical resistivity of the composite sample regularly decreased from 4.877 to 0.937  $\Omega \cdot \text{cm}$  (while 5.268 decreased to 1.544  $\Omega \cdot \text{cm}$  for those coated with CNF nanopaper). The more carbon individuals present, the more conductive paths were formed in the nanopaper. Given more conductive paths in one bulk,



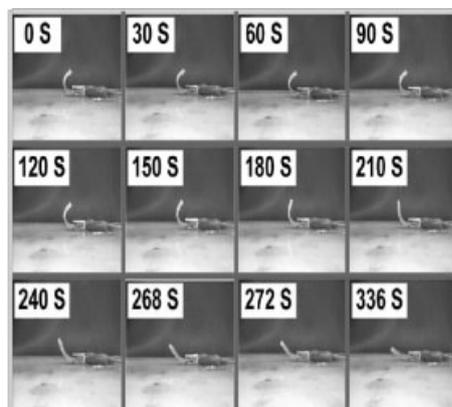
■ Figure 2. Nanopaper sample, for the (a) CNT nanopaper, and (b) CNF nanopaper.



**Figure 3.** Scanning electron microscopy (SEM) images for the (a) CNT nanopaper,<sup>[15]</sup> Reprinted with permission from Reference 15, Copyright 2008, Wiley-Vch Verlag GmbH & Co. (b) CNF nanopaper,<sup>[16]</sup> respectively, Copyright 2009, Institute of Physics and IOP Publishing.

more electrons are involved in an electrical circuit. Therefore, the electrical current amplitude and current-carrying capability increase because more electrons are forced to pass through the cross section of the bulk.

The thicknesses of the four composite samples with various weight concentrations of nanopaper were kept constant. And the function and effectiveness of the nanopaper in the actuation of SMP composites by electrically resistive Joule heating were experimentally demonstrated. Figure 4 shows the recovery of the SMP composite coated with 1.2 g CNT nanopaper as a proper electric current was applied. The shape recovery process of the flat (permanent shape) composite specimen with a dimension of  $100 \times 6 \times 3 \text{ mm}^3$  was demonstrated. Meanwhile, Figure 5 records the recovery of SMP composite coated with 1.8 g CNF nanopaper induced by the electricity.



**Figure 4.** Series of photographs showing the macroscopic shape-memory effect of an SMP composite integrated with 1.2 g of CNT nanopaper. The permanent shape is a flat strip of composite material, and the temporary shape is deformed as a right-angled shape,<sup>[15]</sup> Copyright 2008, Wiley-Vch Verlag GmbH & Co.

While the dimensions of SMP composite coated with 1.8 g CNF nanopaper is  $120 \times 20 \times 6 \text{ mm}^3$ .

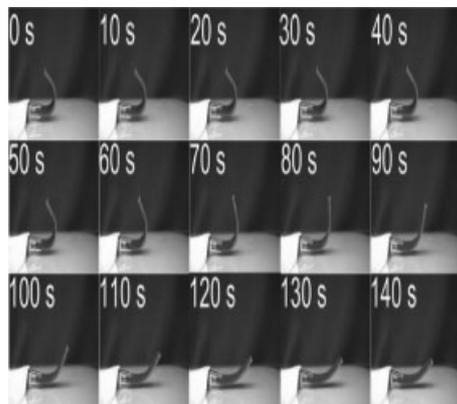
In these experiments, the SMP composite specimen did not show a 100% recovery ratio as it did not completely return to its initially flat shape. This small absence of complete shape recovery could be attributed to the interfacial friction between the nanopaper and the underlying SMP. The SMP component may lack enough mechanical strength to pull the nanopaper back to its original shape. On the other hand, due to the extreme difference in thermo-electric properties between the nanopaper and the underlying SMPs, their bonding is always thermally degraded after a rela-

tive high electric current is applied. Consequently, the efficiency of heat transfer from the nanopaper to the underlying SMP composite is herein limited. This was exemplified by the smoke emitted during the process of recovery actuation.

### 3. SMP Composite Incorporated with Nanopaper and Blended CNFs

To significantly improve the electro-induced performance and behavior of an SMP composite coated with carbon nanopaper. The synergistic effect of carbon nanopaper and CNF was exploited for the electrical actuation of SMP composite. The combination of carbon nanopaper and CNF was initially used to improve both the thermal and electrical conductivities of the SMP. The carbon nanopaper was coated on the surface of the SMP composite in order to achieve the actuation by electrical resistive heating. On the other hand, CNFs were blended with the SMP resin to improve the thermal conductivity to facilitate the heat transfer from the nanopaper to the underlying SMP composite to accelerate the electroactive response.

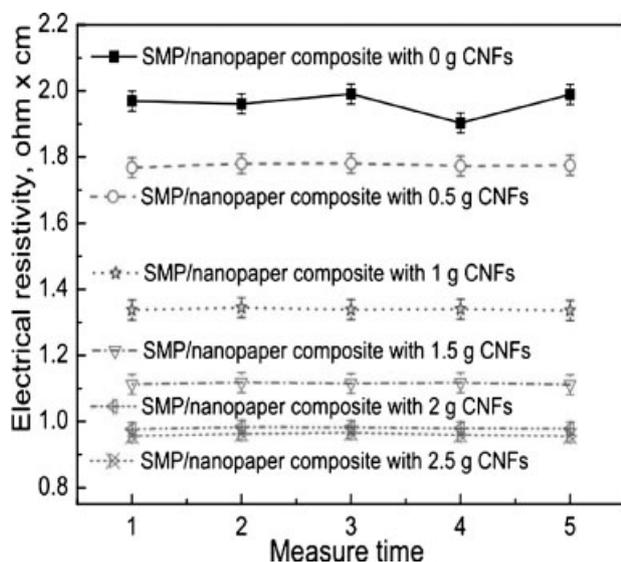
In the manufacturing process of an SMP composite, the CNFs were blended into the SMP resin with different weight fractions. Due to the nanosized effect, the viscosity of the mixture was increased and the resulting mixture was degasified in a vacuum oven to completely eliminate any air bubbles. Afterward, the resin transfer molding was used to fabricate the SMP composite. As an example, the nanopaper containing 1.8 g of CNFs was placed on the bottom of the mold. The SMP matrix incorporated with CNFs was then injected into the mold. After filling the mold, the resin was cured in the heating oven to fabricate the SMP composite. The electrical properties of the SMP composites were also measured with the four-point probe method. The



**Figure 5.** Series of photographs showing the macroscopic shape-memory effect of an SMP composite integrated with 1.8 g of CNF nanopaper. The permanent shape is a flat strip of composite material, and the temporary shape is deformed as a right-angled shape.<sup>[16]</sup> Copyright 2009, Institute of Physics and IOP Publishing.

electrical resistivities of the SMP composites blended with different weight fractions of CNFs in the SMP resin were plotted against different locations, as shown in Figure 6. As the content of the blended CNFs increased from 0 to 2.5 g, the average electrical resistivity of SMP composite regularly decreased from 1.951 to 0.960  $\Omega \cdot \text{cm}$ . Experimental results indicated that when more CNFs were blended into the SMP resin, the electrical resistivity of the SMP composite decreased. Meanwhile, it was also expected that the improved electrical conductivity would help the SMP part have a better thermal conductivity.<sup>[17]</sup>

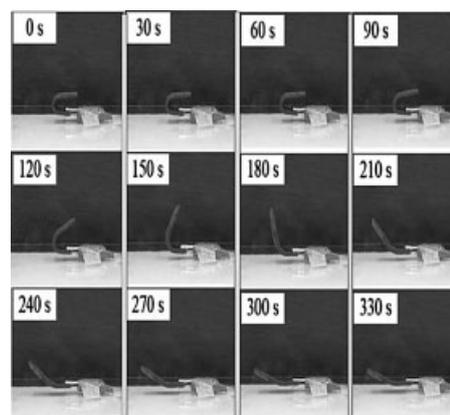
The electrical actuation of SMP composites was evaluated by recovery ratio as a function of recovery time. The



**Figure 6.** Electrical resistivity of an SMP composite coated with CNF nanopaper and incorporated with various weight contents of CNFs.<sup>[17]</sup> Copyright 2010, American Institute of Physics.

recovery ratio refers to the degree for the composite specimen to return to its permanent shape from the temporary shape. The recovery time indicates the speed of the SMP composite in response to external stimuli. The flat composite specimen with a dimension of  $180 \times 12 \times 7.5 \text{ mm}^3$  was bent into an “n”-like shape at a relatively high temperature and remained in this shape while cooling down to room temperature. The actuation of the SMP composite was driven by an electrical current under a constant electric power of 0.8 W. As shown in Figure 7, the composite specimen blended with 2.5 g of CNFs in the SMP resin had the fastest response to the electrical stimulus. However, it had the lowest shape recovery ratio of approximately 83%. On the other hand, the SMP composite blended with 0.5 g of CNFs had the slowest response, as it returned to its permanent shape within 361 s, with a the recovery ratio of approximately 98%. Therefore, the blended CNFs had a positive effect on the recovery time of the tested SMP samples, but negative effect on the recovery ratio, as seen in Figure 8.

As is known, the relative motion of macromolecular segments or chains is the primary mechanism of the SME. During the process of recovery, the packed macromolecular segments needed to return to the permanent shape to achieve the SME. On the other hand, the blended CNFs do not have SME and therefore they cannot return to the original configuration by themselves. Here, the opposing motion between the CNF individuals and the SMP segments produces interfacial friction, resulting in a decreased recovery ratio in comparison to the pure SMP. Furthermore, the weight content of the blended CNFs increased, the recovery ratio gradually decreased. In contrast, these conductive CNFs could improve the conductivities of the SMP to facilitate the heat transfer from the nanopaper to the SMP composite, increasing the recovery time of the tested samples as the contents of blended CNFs increased.



**Figure 7.** Series of photographs demonstrating the macroscopic SME of the SMP composite. The permanent shape is a flat strip, and the temporary shape is a right-angle shape.<sup>[17]</sup> Copyright 2010, American Institute of Physics.

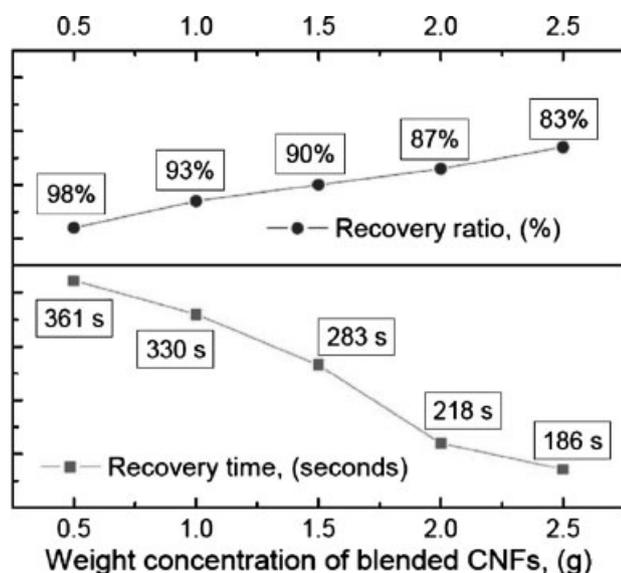


Figure 8. Shape recovery behavior of the SMP composites coated with 1.8 g of CNF nanopaper and blended with various weight contents of CNFs.<sup>[17]</sup> Copyright 2010, American Institute of Physics.

#### 4. SMP Composite Incorporated with Nanopaper and Magnetic Alignment

The synergistic effect of self-assembled carbon nanopaper and vertical alignments on the SMP composite was further studied to mitigate the negative effect of randomly dispersed CNFs on the recovery ratio. The combination of nanopaper and magnetic alignment was thus employed to improve both electrical and thermal conductivities of the SMP. The conductive nanopaper was used to improve the electrical property by coating on the surface of the SMP composite, to enable the shape recovery induced by electricity. Electromagnetic fillers were then blended with, and vertically aligned into the SMP resin in a magnetic field, to facilitate the heat transfer from the nanopaper to the underlying SMP part and effectively accelerate the electro-active recovery performance.<sup>[18,19]</sup> The vertical alignments directs the electric current to pass through the insulating polymer, and transfer the electric power into resistive heating power. The schematic illustration is presented in Figure 9.

In the previous experiment, it has been demonstrated that the electrical and thermal conductivities of the SMP have been significantly improved by the blended conductive CNFs. However, the recovery ratio of the tested SMP composites was slightly decreased by the randomly dispersed conductive fillers in

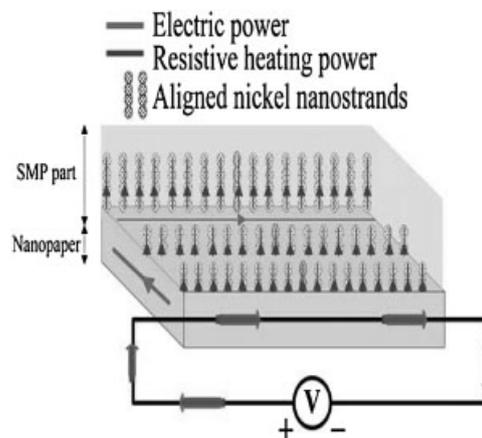


Figure 9. The schematic illustration of the nickel nanostrands being vertically aligned to help resistive heating power to transfer from the nanopaper to the underlying SMP.<sup>[18]</sup> Copyright 2011, RSC Publishing.

the recovery process. Here, electromagnetic nickel nanostrand and CNTs were, respectively, blended with, and vertically aligned within the SMP resin on a magnetic field, in order to facilitate heat transfer. Figure 10a and b reveal magnetic nickel nanostrands and CNTs aligned in the presence of a magnetic field. The morphology and structure of the aligned nickel nanostrands and CNTs were observed at an accelerating voltage of 10.00 and 20.00 keV, respectively.

The SMP composite blended with 8 wt.-% vertically aligned nickel nanostrands was further utilized to demonstrate the electrically triggered actuation. Experimentally, the recovery process was characterized using a modified bending test method. The flat SMP composite was initially bent in a “U”-like shape at a proper temperature. This temporary shape was retained until the specimen was cooled back down to room temperature. No apparent recovery was found after being kept in the air for 2 h.

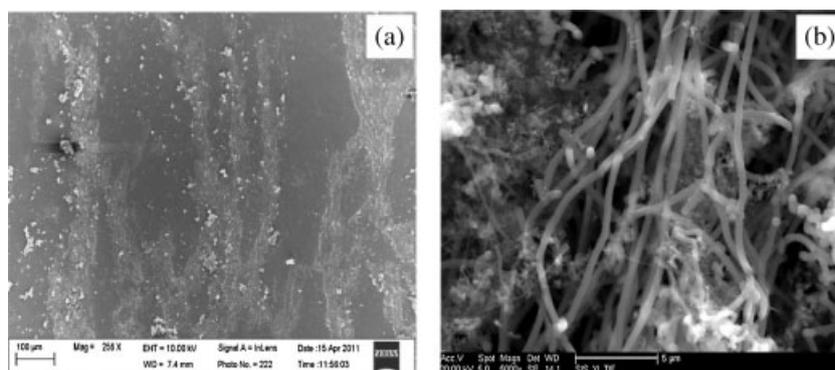


Figure 10. (a) SEM image of the orientation of the nickel nanostrands observed via the thickness of the composite.<sup>[18]</sup> Copyright 2011, RSC Publishing. (b) Observation of the magnetic CNT alignment.<sup>[19]</sup> Copyright 2011, American Institute of Physics.

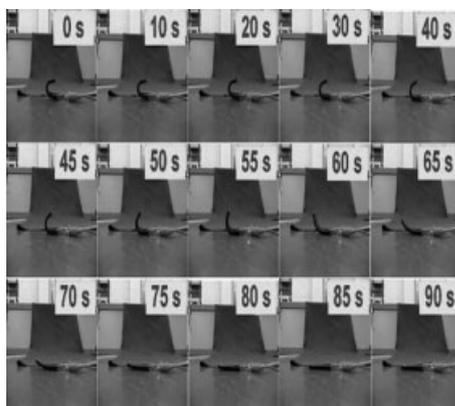


Figure 11. Electrically resistive heating-induced SME of SMP/nanopaper nanocomposites with 8 wt.-% vertically aligned nickel nanostrands.<sup>[18]</sup> Copyright 2011, RSC Publishing.

Figure 11 presents the recovery of the SMP composite from a fixed bent shape to its originally straight shape under a constant voltage. The deformed composite specimen began to return to its original shape after the electrical current had been applied for 10 s. The specimen showed a very low recovery ratio during the first 20 s. It then exhibited a faster recovery performance until 60 s. During the last 15 s, a slight change in shape recovery was observed. Finally, the SMP composite showed a nearly 100% recovery ratio, as presented in Figure 11. This experimental result helps demonstrate the contribution of the magnetic alignment in comparison to randomly dispersed conductive filler. In summary, these aligned nickel nanostrands uniformly transferred the electrically resistive heating from nanopaper to the underlying SMP part in the vertical significantly improved heat transfer and dispersion. At the same time,

they had no negative effect on the recovery ratio of the SMP composite. Therefore, the recovery performance (like recovery speed and recovery ratio) of the SMP composite with carbon nanopaper and magnetic alignment is significantly improved.

Furthermore, the recovery experiments were conducted under two different voltages for each of the SMP composites with either the vertically aligned or randomly dispersed CNTs. The resulting recovery profiles were shown in Figure 12a, revealing that the recovery time of the SMP composite with vertically aligned CNTs was shorter than that of the randomly dispersed CNTs for both voltages. This experimental result further testify that the vertically aligned CNTs facilitate the heat transfer from the nanopaper to the SMP part, and give the SMP high speed electrical actuation. Moreover, to demonstrate the excellent recovery performance and reveal more detailed kinetics information, the recovery ratio as a function of recovery time were further analyzed by introducing a standard Boltzmann function. At the beginning, the parameters in the function were calculated by the corresponding recovery ratio and recovery time. Then the function had been mathematically treated to get the second derivatives of the function. Finally, the data of recovery ratio and recovery time were used again to plot the fit curves for the Boltzmann function. The induction time was defined as the time between “0” and the first positive peak on the second derivative plot. This corresponds to an induction period of the recovery profile, during which the SMP composites were heated from the environmental temperature to their switching temperature. Figure 12b shows that the induction time of the SMP composite with vertically aligned CNTs was 15.9 s shorter than that with randomly dispersed CNTs under the 36 V triggering voltage.

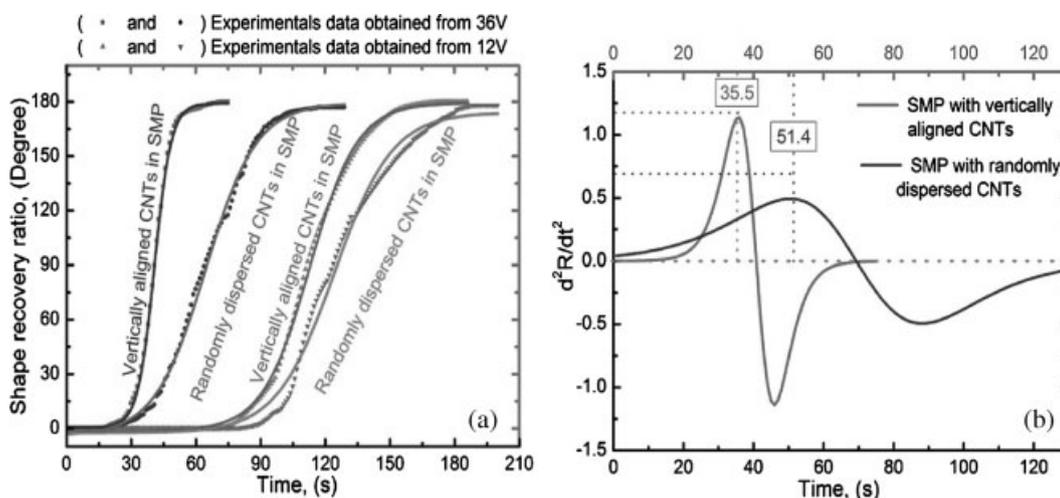


Figure 12. (a) Recovery profiles of the SMP composites with aligned and randomly dispersed 8 wt.-% magnetic CNTs under 12 and 36 V voltages, respectively. (b) Induction and recovery times of the SMP composites for the two voltages studied.<sup>[18]</sup> Copyright 2011, American Institute of Physics.

## 5. SMP Composite Incorporated with Nanopaper for Multifunctionalization

Almost all recent studies focus on the intrinsic function of the SME in SMPs, including efficient fixing of a temporary shape, recovery to an equilibrium shape, and the exploitation of different stimuli as triggers. However, we herein describe a carbon nanopaper enabled SMP composite in which a conductive capability provides additional functionality besides electrical actuation. In a combination of electrically conductive carbon nanopaper and the SME in SMP, the developed composites are integrated with both sensing and actuating capabilities. Carbon nanopaper has been utilized for detecting variation in temperature and water content, in addition to it also being used to achieve the actuation of an SMP by applying an electric current. In conjunction with the sensing capabilities of nanopaper, the developed composites also have an actuating capability by integrating them with the recovery strength in the recovery process of SMP.<sup>[14]</sup>

In this section, the thermal sensing capability of carbon nanopaper was initially characterized by the electrical resistivity dependent temperature experiment. Nanopapers with various weight concentrations were used. Figure 13 shows the change in electrical resistivity of nanopapers as a function of temperature, increased from room temperature to 120 °C. Experimental results revealed that the electrical resistivity of all of the carbon nanopapers gradually decreased with an increase in temperature. Taking the nanopaper with 2.4 g of CNTs, for example, the initial and final values of electrical resistivity were 0.9354  $\Omega \cdot \text{cm}$  (at room temperature) and 0.4989  $\Omega \cdot \text{cm}$  (at 120 °C), respectively. The reason for this was that when the temperature increased, the electrons in the nanopaper had picked up energy. This consequently resulted in an

accelerated electron flow within the nanopaper. The velocity of the cyclic electron flow in this electrical circuit was thus accelerated, lowering the electrical resistivity of the bulk material. Therefore, the electrical resistivity of the tested nanopaper samples was lowered. Furthermore, it was found that the electrical resistivity of the nanopaper with 0.6 g of CNTs showed the most reduction as the temperature increased. As detailed, the electrical resistivity decreased from 4.8904 to 3.6671  $\Omega \cdot \text{cm}$  (1.2233  $\Omega \cdot \text{cm}$ ) as the temperature increased from room temperature to 120 °C for the 0.6 g weighted nanopaper, while the decrease in electrical resistivity of the 2.4 g MWCNT nanopaper was 0.4365  $\Omega \cdot \text{cm}$ . This result can also be attributed to electron movement in the electrical circuit. That is the micro-Brownian motion of the individual will become more significant with temperature increased. Therefore, in the nanopaper with more weight concentration, there are many more carbon individuals involved to prevent or postpone the beamed electrons motion in the electrical circuit. Thus, the beamed electron motion is influenced by the Brownian motion. It is summarized that the velocity of cyclic electron flow and Brownian motion in the electrical circuit are two factors that have a determinable effect of temperature on the electrical property of nanopaper.

At the same time, the dependence of electrical resistivity of water content on the nanopaper was investigated to explore another sensing capability in SMP composite. Being a porous structure, the ability to detect water content inside a water-permeable nanopaper is important. Studies on the synergistic effects of electrical properties and water content nanopaper will become prominent for practical applications. At the beginning of testing, the nanopapers absorbed 300% of their respective weights of distilled water. After which, the nanopaper samples were dried in a vacuum oven at 120 °C for varying durations, from 0 to 30 min at a regular of 2.5 min. The weight and electrical resistivity for each nanopaper were then measured. The quality of evaporated moisture and the weight ratio of the water to nanopaper based on the change in weight of the nanopaper, were calculated. Figure 14a shows the weight ratios of water to nanopaper as a function of drying time, in 2.5 min increments. Figure 14b shows the change in electrical resistivity of the nanopapers as the water content in the samples decreased from 300% to approximately 0%. These experimental results revealed that the changes in electrical resistivities were 1.873  $\Omega \cdot \text{cm}$  for the 0.6 g CNT nanopaper, 3.517  $\Omega \cdot \text{cm}$  for the 1.2 g CNT nanopaper, 6.918  $\Omega \cdot \text{cm}$  for the 1.8 g CNT nanopaper, and 9.663  $\Omega \cdot \text{cm}$  for the 2.4 g CNT nanopaper. Furthermore, the resistivities for all the nanopaper samples significantly dropped as water content decreased. From this point, the nanopapers showed a slight increase in electrical resistivity and began to level off. As is known, the dielectric constant of water is always higher than that of the CNTs. Thus, with high water content, the

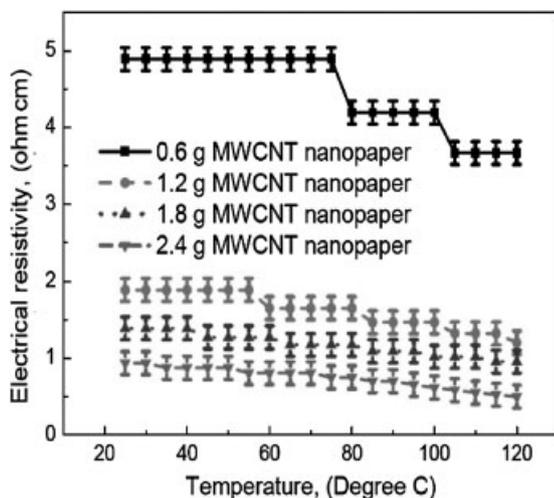


Figure 13. Values of electrical resistivity versus temperature for the CNT nanopaper,<sup>[14]</sup> Copyright 2011, Elsevier.

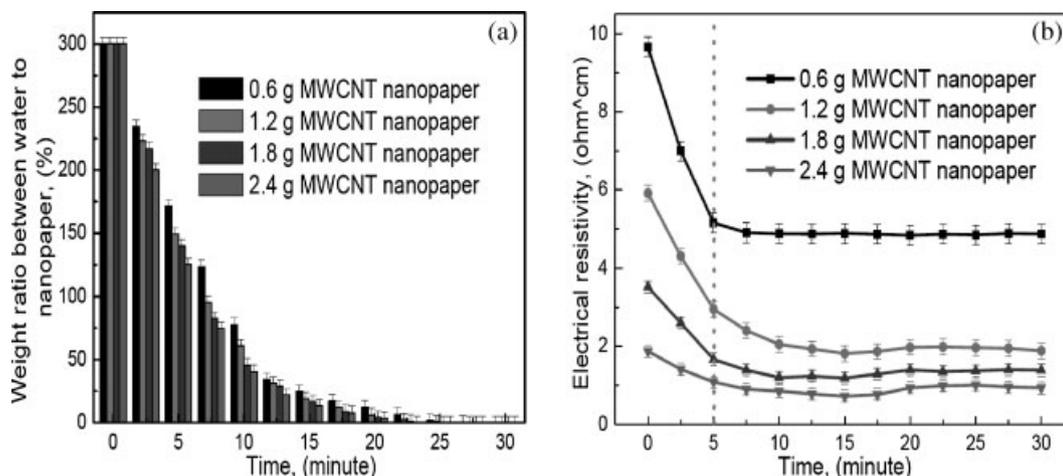


Figure 14. (a) Values of weight ratio between water and nanopaper versus drying time and (b) values of electrical resistivity versus drying time for the MWCNT nanopaper,<sup>[14]</sup> Copyright 2011, Elsevier.

dielectric constant of a nanopaper sample is proportionally high, resulting in altered electrical properties of system.

Consequently, the actuating properties of the conducting SMP composite are studied by introducing a parameter called recovery strength. To determine the recovery strength, dynamic mechanical analyzer (DMA) tests were conducted to determine the storage modulus and loss modulus of the composite as a function of temperature. And then, the elastic modulus (here was used as the recovery strength) was calculated based on the values of storage modulus and loss modulus.<sup>[20]</sup> After that, the SMP composites were presumed to show their shape recovery performance within the temperature range of 20–100 °C. In combining excellent electrical properties with the SME, the electrical actuation of the SMP composite (cut from 2.4 g CNT nanopaper enabled SMP composite) has been demonstrated and used to actuate the motion of a 0.5 g weight. As a proper electric current was applied, the recovery of the SMP composite was observed to be completed in 88 s. As displayed in Figure 15, the SMP composite initially showed a low recovery ratio during the first 7 s. It then began to exhibit a faster recovery behavior until 80 s. The final shape is close to the original flat shape. And the 0.5 g weight was lifted from 0 to 30 mm in height. Therefore, this demonstration revealed that the developed SMP composite possessed an actuating capability by integrating the recovery strength of the recovery process in the SMP, with sensing capabilities of the nanopaper.

## 6. Conclusion

In this review, we introduced the basic design and mechanisms behind the carbon nanopaper enabled SMP composite for electrical actuation. After which, a number of

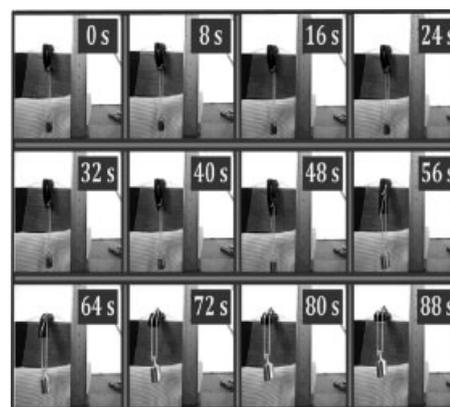


Figure 15. Series of photographs showing the electro-activated SME of an SMP composite and actuating the motion of a 5 g mass. The permanent shape is a plane strip of composite and the temporary shape is deformed as a right-angle,<sup>[14]</sup> Copyright 2011, Elsevier.

examples were presented to reveal the research and development of utilizing the nanopaper's electrically induced actuation for SMPs. As we can see, together with synthesis control of aligned nickel nanostrands and CNTs (or to their extension, other electromagnetic conductive particles), the feature of nanopaper enabled SMP composite was able to effectively reshape the design of electrical actuation in many ways. With our efforts in the last 5 years, the nanopaper enabled SMP composite was expected to be a solution for exploring electrical actuation in many more applications.

Acknowledgements: This work has been financially supported by National Natural Science Foundation of China (NSFC) 51103032, China Postdoctoral Science Foundation funded major project,

20110490104 and Special funding of China Postdoctoral Science Foundation (2012T50350). We would also like to thank Dr. Jihua Gou for conducting some of the experiments reported here. Figure 9, 10(a), and 11 are Reproduced by permission of The Royal Society of Chemistry.

Received: June 21, 2012; Revised: August 31, 2012; Published online: November 1, 2012; DOI: 10.1002/mame.201200235

Keywords: composites; functionalization of polymers; high performance polymers; stimuli-sensitive polymers

- [1] M. Behl, A. Lendlein, *Soft Matter* **2007**, *3*, 58.  
[2] A. Lendlein, *J. Mater. Chem.* **2010**, *20*, 3332.  
[3] J. L. Hu, S. Chen, *J. Mater. Chem.* **2010**, *20*, 3346.  
[4] J. S. Leng, H. B. Lu, Y. J. Liu, W. M. Huang, S. Y. Du, *MRS Bull.* **2009**, *34*, 848.  
[5] A. Lendlein, S. Kelch, *Angew. Chem. Int. Ed.* **2002**, *41*, 2034.  
[6] L. Sun, W. M. Huang, Z. Ding, Y. Zhao, C. C. Wang, H. Purnawali, C. Tang, *Mater. Des.* **2012**, *33*, 577.  
[7] P. T. Mather, X. F. Luo, I. A. Rousseau, *Annu. Rev. Mater. Res.* **2009**, *39*, 445.  
[8] A. Lendlein, R. Langer, *Science* **2002**, *296*, 1673.  
[9] X. F. Luo, P. T. Mather, *Soft Matter* **2010**, *6*, 2146.  
[10] K. Yu, Z. C. Zhang, Y. J. Liu, J. S. Leng, *Appl. Phys. Lett.* **2011**, *98*, 074102.  
[11] J. S. Leng, H. B. Lv, Y. J. Liu, S. Y. Du, *Appl. Phys. Lett.* **2007**, *91*, 144105.  
[12] Y. J. Liu, H. B. Lv, X. Lan, J. S. Leng, S. Y. Du, *Compos. Sci. Technol.* **2009**, *69*, 2064.  
[13] R. L. D. Whitby, T. Fukuda, T. Maekawa, S. L. James, S. V. Mikhailovsky, *Carbon* **2008**, *46*, 949.  
[14] H. B. Lu, Y. J. Liu, J. H. Gou, J. S. Leng, S. Y. Du, *Compos. Sci. Technol.* **2011**, *71*, 1427.  
[15] H. B. Lu, Y. J. Liu, J. H. Gou, J. S. Leng, S. Y. Du, *Int. J. Smart Nano Mater.* **2011**, *1*, 2.  
[16] H. B. Lu, Y. J. Liu, J. H. Gou, J. S. Leng, S. Y. Du, *Smart Mater. Struct.* **2010**, *19*, 075021.  
[17] H. B. Lu, Y. J. Liu, J. H. Gou, J. S. Leng, S. Y. Du, *Appl. Phys. Lett.* **2010**, *96*, 084102.  
[18] H. B. Lu, F. Liang, J. H. Gou, *Soft Matter* **2011**, *7*, 7416.  
[19] H. B. Lu, J. H. Gou, J. S. Leng, S. Y. Du, *Appl. Phys. Lett.* **2011**, *98*, 174105.  
[20] H. B. Lu, K. Yu, Y. J. Liu, J. S. Leng, *Smart Mater. Struct.* **2010**, *19*, 065014.