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Carbon-based reinforcement in shape-memory polymer composite for electrical actuation

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Abstract

Purpose – This article aims to present a systematic and up-to-date account of carbon-based reinforcements, including carbon nanotube (CNT), carbon nanofibre (CNF), carbon black (CB), carbon fibre (CF) and graphene, in SMP for electrical actuation.

Design/methodology/approach – Studies exploring carbon-based reinforcement in SMP composites for electrically conductive performance and Joule heating triggered shape recovery have been included, especially the principle design, characterisation and shape recovery behaviour, making the article a comprehensive account of the systemic progress in SMP composite incorporating conductive carbon reinforcement.

Findings – Shape-memory polymers (SMPs) are fascinating materials and have attracted great academic and industrial attention owing to their significant macroscopic shape deformation in the presence of an appropriate stimulus. The working mechanisms, the physico requirements and the theoretical origins of the different types of carbon-based

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reinforcement SMP composites have been discussed. Current research and development on the fabrication strategies of carbon-based reinforcement SMP composites have been summarised.

Practical implications – It was clear that SMPs with carbon-based reinforcements can be used as smart deployable space structure in the broad field of aerospace technologies.

Originality/value – Systematic review of the research and development of the utilisation of CNT, CNF, CB, CF and graphene to achieve shape recovery of SMP composites through electrically resistive heating, which will significantly benefit the research and development of smart materials and systems.

Keywords – Shape-memory polymers, Electrical actuation, Carbon nanotube, Carbon nanofibre, Graphene

Paper type Review paper

Introduction

Shape-memory polymers (SMPs) are polymers that "remember" their permanent shapes from deformed shapes. SMPs are useful for such things as actuators which are materials that have the capabilities of changing shape, stiffness, position, natural frequency, and other mechanical characteristics in response to temperature or other external stimuli (Behl and Lendlein, 2007; Mather *et al.*, 2009; Xie, 2011; Sun *et al.*, 2012). The potential uses for SMPs have broadened the spectrum of many scientific fields (Lendlein and Biodegradable, 2002; Maitland *et al.*, 2002). The study of the history and development of SMPs can provide an insight to a material involved in cutting-edge technology (Gall *et al.*, 2004; Paik *et al.*, 2006). Thermoplastic polyurethane (PU) SMPs have been found to be the most popular of all SMPs (Kim *et al.*, 1998; Tobushi *et al.*, 2008; Huang *et al.*, 2011). In the 1980's, polyurethane (PU) polymer was discovered to possess the unique property of having shape memory. It is found that such a shape memory behaviour is similar to that of shape memory alloys (SMAs). PU polymer has a special chemical makeup that gives it its shape memory properties (Kim *et al.*, 1998). Other SMPs include polystyrene, epoxy, polyethylene terephthalate (PET) and poly(ethylene oxide), which will be introduced in sequence (Mather and Rousseau, 2009; Xie, 2011). With so much research effort on the SMPs, the key factor of the shape memory effect is the driving force. Conventionally, the shape memory effect in SMPs requires two components at the molecular level namely, the cross-links, which determine the permanent shape and the so called "switching segments", which are used to maintain the temporary shape (Mather and Rousseau, 2009; Xie, 2011; Lendlein and Biodegradable, 2002).

SMPs are similar to other actively responsive polymers, of which a change in properties results from an external stimulus, such as heat, light, electricity and so on (Lendlein, 2010; Hu and Chen, 2010; Luo and Mather, 2010). This also includes a combination of two or more responses at the same time. Therefore, SMPs have attracted keen attention as promising candidates for smart materials, structures and systems, since they function in response to external stimulus by changing shape (Leng *et al.,* 2009). SMPs have only been around for a couple of decades so the concept of "shape memory" properties is fairly new (Kim *et al.,* 1998). However, SMPs can be useful in many exciting ways, since they are considered smart materials that respond to an external stimulus (Lendlein, 2010). Owing to the concept of SMP some applications that would be ideal are high performance textiles and as parts for automobiles (Hu and Chen, 2010; Luo and Mather, 2010; Leng, 2009). Other possibilities are medical device, deployable structures and morphing structures etc. (Leng, 2009). With the practical and potential applications of SMPs increasing, some major limitations impose many challenges to their broad utilisation, such as the low thermal conductivity and inertness to electromagnetic stimuli (Luo and Mather, 2010). By this motivation, 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 of electrically conductive fillers, such as carbon nanotubes, carbon particles, conductive fibre, nickel zinc ferrite ferromagnetic particles, etc. These conductive fillers render polymer electrical conductive and generate heat according to Joule's law and eventually facilitate the heat transfer to trigger shape recovery of SMP. Many significant developments have been achieved for SMP composites, of which recovery actuation can be carried out by electrically resistive heating. A systemic review on carbon-based reinforcement in SMP composites is necessary and important for promoting the progress for electrically conductive SMP composites. The purpose of this review is to provide details of all aspects of the SMP composites filled with a variety of conductive carbon-based reinforcement from fundamentals to applications on an intermediate level. It will show how reinforcement 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 SMP composites used will be reviewed. Moreover, this review focuses on recent advances in material designs, which are extremely necessary to develop more desirable and functional carbon-based reinforcement in SMP composites. Finally, a selection of examples is given and a brief outlook into future aspects is provided at the end of this article. Some properties of SMP composite, which have not been studied within previous works but show potential, will therefore also be discussed.

SMP composite incorporated with carbon nanotubes

Electrically conductive polymers can be achieved via two approaches. One approach is to produce a polymer that is intrinsically conductive. The second is to dope or load conductive fillers into the insulating polymer. Carbon nanotube (CNT), carbon nanofibre (CNF), graphite and metallic particles are widely used as conductive filler. As one of the promising candidates, the CNT renders SMP composites electrically conductive. It has been reported that preliminary experimental results show that conductive SMPs can be achieved via a number of approaches. So far, five strategies have been developed to fabricate electrically conductive SMP composites containing CNTs. The first strategy is to mix CNTs directly with the polymer matrix. With the second strategy, surface-modified CNTs are blended with the polymer matrix to significantly improve the interfacial bonding. The third strategy involves converting the CNTs into paper or film form, which is then incorporated with the polymer matrix. The forth strategy is to align the CNTs in the polymer matrix in the presence of electric/magnetic field. The last strategy is to crosslink CNTs with the polymer matrix. On the other hand, it has been found that there are four challenges that almost all previous research works encountered, including dispersion of CNTs in polymer matrix, bonding between the polymer macromolecules and CNTs, the electrically conductive network in composites, and the electrical properties of composites.

In 2006, it was reported that electrically conducting PU SMP-CNT composite was prepared by *in-situ* manufacturing process (Yoo *et al.,* 2006). The investigation focused on the electrical conductivities and electrically triggering recovery behaviour. The shape recovery of SMP composites filled with CNTs was achieved with electrical current, not by applying heating. These achievements are expected to lead to the application of SMP composites as actuators, which will play an important role in many applications such as controlling micro-aerial vehicles.

Furthermore, multi-walled carbon nanotubes (MWCNTs) had been employed after being chemically surface-modified in a solvent mixture of nitric acid and sulphuric acid, to significantly improve the interfacial bonding among polymer macromolecules and MWCNTs (Cho *et al.*, 2005). Through preparing electro-activate SMP composites and investigating their characteristics, it was found that the shape-memory effect was dependent on the filler content and degree of surface-modification of the MWCNTs. The electrical resistivity of these surface-modified MWCNT composites was lower than that of the composites filled with untreated MWCNT at the same filler concentration.

In order to fully harness the impressive electrical properties of MWCNTs and to transfer their properties to polymer matrix, it is suggested, a stable suspension and dispersion of MWCNTs in an aqueous solution is critical (Lu and Gou, 2012). Our previous works have focused on the covalent stabilisation techniques to molecularly functionalise specific molecular species onto CNT surfaces for enhanced dispersion and functionality with the aid of dispersion by high-powered sonication. It was experimentally demonstrated that the CNTs reached their nano-size and homogenously dispersed into the polymer matrix. Finally, the dispersion used affects the quality of SMP composite significantly. Better distribution of the CNTs was achieved by *in-situ* polymerisation compared to direct mixing.

This is evident as shown in the scanning electronic micrographs in Figure 1 (Lu and Gou, 2012). The CNT nanopaper prepared was placed on the bottom of the mould. The SMP resin was then injected into the mould. After the mould-filling, the resin was cured to obtain the SMP composite. Subsequently, the CNTs were electrically aligned into chains in the SMP composite and served as long-distance conductive channels for electronic current. Figure 2 presents the electrically induced shape recovery of styrene-based SMP upon application of 7.1V electric voltage (Lu and Gou, 2012). These experimental results support that the CNT is one of the more effective fillers to render the SMPs electrically conductive. Compared to the SMP composites filled with random CNTs, the electrical resistivity in those with chained CNTs was reduced for more than 100 times (Yu, 2011).

Recently, another approach to make conductive SMP composite was presented. Thus, single-walled CNTs (SWCNTs) were doped into PU polymer matrix and react with the hydrogen bonds of PU to successively construct a new hydrogen-bonded plane. And it was found that the optimum condition for the formation of conductive networks of PU-SWCNT hybrid materials was the incorporation of 3% SWCNTs into PU. The composite containing 4% SWCNTs showed a good electroactive shape recovery property under electric voltage (Lee and Yu, 2011).

Finally, Table I summarises the electrical properties of all of the above-mentioned SMP composites containing CNTs for purpose of comparison. Generally, the electrical conductivity decreased with the increase of the CNT content. And the electrical properties of the SMP composite result in the electric power and the shape recovery behaviour.

SMP composite incorporated with carbon nanofibre

Similar with CNT, carbon nanofibre (CNF) also possess excellent thermal and electrical conductivities. In addition, the mechanical properties (tensile strength and tensile modulus) of CNF are better than carbon fibre. Therefore, CNF have also received considerable attentions in the fabrication of functional polymeric composites due to their ready availability and much lower price in comparison with CNT. For the CNF, four strategies have been utilised to fabricate electrically conductive SMP composites, of which shape recovery can be induced by applying an external electric current. The first strategy involves mixing the CNFs directly with the polymer matrix. With the second strategy, the oxidised CNFs are blended with the polymer matrix to improve the interfacial bonding. The third strategy involves converting CNFs into paper or film form, which are then incorporated with the polymer matrix. The last strategy involves the use of hybrid filler of CNF.

In 2009, Gunes *et al.* (2009) incorporated CNF into PU SMP to improve the mechanical performance of the resulting composite. The composites were prepared by melt mixing of the PU matrix and the CNFs. The electrical percolation of CNF containing resulting SMP composites was demonstrated to be lower than that of those containing carbon black. Consequently, the vapour grown CNF was also incorporated into the SMP matrix by *in-situ* manufacturing method. Their investigation focused on the electrical conductivities and electrically triggering recovery behaviour. The shape recovery of SMP composites filled with CNFs was achieved by electrical current, not by applying heating (Tang *et al.*, 2013; Dong *et al.*, 2013). Furthermore, oxidised CNFs were then employed for significantly improving the interfacial bonding among polar polymer macromolecules and CNFs (Gunes *et al.*, 2009). Through preparing electro-activate SMP composites and investigating their characteristics, the shape-memory effect could be shown to be dependent on the filler content and degree of reaction between polymer macromolecules and CNFs. In order to fully harness the electrical properties of CNFs and to transfer their such properties to the polymer matrix, it is critical to ensure that a stable suspension and dispersion of CNFs in an aqueous solution is achieved. Our previous works have focused on the covalent stabilisation techniques to molecularly functionalise specific molecular species onto CNF surfaces for enhanced dispersion and functionality with the aid of dispersion by high-power sonication. It was experimentally demonstrated that, via this approach, the CNFs reached their nano-size and homogenously dispersed into the polymer matrix. Finally, the dispersion used affected the quality of SMP composite significantly. Better distribution of the CNFs was achieved by *in-situ* polymerisation compared to direct mixing. This is evident from the scanning electronic micrographs shown in Figure 3 (Lu *et al.*, 2010). The suspensions were then membrane filtered under positive pressure to yield suitable compositions for the fabrication of uniform films. The SMP composites were fabricated by laminating the CNF papers prepared onto the surface of SMP sheets via hot-pressing. Figure 4 presents the electrically induced shape recovery of styrene-based SMP upon application of 8.6V electric voltage (Lu *et al.*, 2010). The CNF was also incorporated with nickel nanostrands to synergistically blend with the polymer matrix (Lv *et al.*, 2011). The hybrid filler could synergistically form a continuously conductive network for the electrical current and therefore render the composite electrically conductive.

Table II summarises the electrical properties of all of the above-mentioned SMP composites incorporated with CNFs for purpose of comparison. Similar to CNT, CNF also plays the same role in determining the electrical properties of composites. And the experimental results have proven that CNF is also an effective conductive filler to render the SMP electrically conductive.

SMP composite incorporated with carbon black/fibre

Carbon black (CB) is a very commonly used conductive filler in polymer composite. PU SMP has been shown to gain a significantly improved thermal conductivity and mechanical performance by added CB. The effect of CB on the structure, electric conductivity, strain recovery behaviour, and their relationships on the PU SMP was initially studied in comparison with other types of conductive fillers, such as CNT, CNF and graphene (Li *et al.*, 2000). It was proven that the CB was an effective filler for the reinforcement of the PU matrix and the maintenance of the stable physical crosslinking structure of the polymer to store the elastic energy in the recovery process. Furthermore, the electrical percolation threshold was characterised for the CB enabled SMP composites. A number of subsequent researches followed this work, ranging from mechanical characterisation to recovery test.

In 2009, Leng *et al.* (2009) used CB to improve the thermal conductivity of SMP to trigger the shape recovery by infrared light. Generally, the CB is incorporated with other conductive filler to synergistically improve the electrical properties of the SMP. Two strategies have been utilised in manufacturing electrically conductive SMP composites. The first strategy is to directly add the CB into the polymer matrix. The second strategy is to use hybrid filler of CB to synergistically lower the electrical resistivity of the resulting SMP. Thus, CB was incorporated into ethylene-1-octene copolymer SMP to improve the mechanical strength, modulus, electrical property of the resulting composites (Le *et al.*, 2011). In this work, different types and concentration of CB were mixed into the copolymer matrix which was cured under a compression pressure. The formation of CB network and its temperature dependent rigidity were expected to affect the shape memory performance. And the relationship between the shape memory behaviour and the CB properties was discussed. The electrical resistivity of the two types of SMP composites prepared was 150 and 8 ohm·cm, respectively. The lower electrical resistivity is strong related to the larger specific surface area of the CB. Furthermore, the effect of specific surface area of CB on the mechanical strength and modulus of SMP was also investigated. And it was found that the CB could significantly improve these properties of the SMP composites. However, the recovery ratio was severely depressed with the increase in the filler content of CB.

Carbon fibre as a traditional fibre reinforcement has also been incorporated into styrene-based SMP. This type of SMP composite was consequently used in a smart hinge for deployable structure (Lan *et al.*, 2009). The composite was fabricated in the same approach as other CF reinforced thermosetting polymer. Instead of significantly improving the mechanical performance, the CF fibre networks also sever as the continuous paths to render the composite electrically conductive. Based on the experimental results, it was found that the storage modulus of the resulting SMP composite was improved in comparison with the pure SMP. And the shape recovery ratio became stable (above 90%) after more than 50 thermomechanical cycles. The mechanism behind the bending deformation of SMP composite was identified as microbuckling. Finally, the deployable hinge could be triggered to actuate a solar array by a 20V electric voltage. The recovery time was 80s. This work was expected to extend the application range of SMPs and SMP composites in aerospace, such as for the solar-based power generation (Hollaway, 2011). However, CF is usually used to improve the mechanical properties of the SMP matrix due to that the largely reversible strain of SMP will be severely depressed. Therefore, there have been many studies on the hybrid filler of short CF and conductive nano-sized particles to synergistically improve the mechanical performance and functional properties of SMP composites (Lu *et al.*, 2010). This hybrid filler could enhance the mechanical strength of polymer, but also the continuously conductive network was formed to significantly improve the electrical property. Thus, CB were dispersed homogeneously within the polymer matrix and served as interconnections between the fibres, while the short CF acted as long distance charge transporter by forming local conductive paths. The experimental results showed that the electrical conductivity was 2.32 $S\cdot cm^{-1}$ for the SMP composite doped with 5 wt% CB and 2 wt% short CF (Leng *et al.*, 2007). Therefore, the shape recovery of SMP composite can be induced by a 24V electric voltage, as shown in Figure 5 (Leng *et al.*, 2008). This work pioneered the studies on achieving synergistic effect of two types of conductive dopants for electrically conductive SMP composites. Many excellent works are based on this principal design (Lu *et al.*, 2010; Lv *et al.*, 2011; Lu *et al.*, 2011; Lu and Liang, 2011). Figure 6 presents a synergistic effect of MWCNT nanopaper and nickel nanostrand on the electrical properties and electro-activated shape recovery behaviour of SMP nanocomposite (Lu and Liang, 2011; Lu *et al.*, 2013). The combination of MWCNT nanopaper and nickel nanostrand has been used to improve the electrical and thermal conductivities of the SMP nanocomposite, respectively. The electrical MWCNT nanopaper that served as a continuously path for electric current was laminated on the surface of SMP to provide the SMP nanocomposite with a low electrical resistivity to achieve shape recovery induced by electricity. Magnetic nickel nanostrands had been blended with and, vertically aligned into the SMP resin in a magnetic field, to improve the thermal conductivity and facilitate the heat transfer from the nanopaper to the SMP composite part. It was also demonstrated that the electrically responsive time and recovery ratio of SMP nanocomposite were significantly improved in comparison with that doped with randomly dispersed nickel nanostrand.

SMP composite incorporated with graphene

SMP composites reinforced by carbon-based nanomaterials such as CNT and CNF have frequently been reported and studied. However, their trend to form aggregates in polymer matrices limits their uses in the composites. To improve the dispersion of carbon-based nanomaterials, surface modification or the use of surfactants is essential. In this respect, graphene is an effective nanomaterial for obtaining desired SMP composites. Graphene has analogous chemical properties with nanotubes and also has a similar structure with layered nanoclay. Therefore, it has a significant potential to develop various desired mechanical, electrical and thermal properties of the composites. The development of graphene-enabled electrically conductive SMP composites has attracted a great deal of attention.

Three strategies have been utilised in manufacturing graphene-based SMP composites. The first strategy is to mix graphene with the polymer matrix directly. The second one is to blend functionalised (or oxidised) graphene with polymer matrix to improve the interfacial bonding. And the last strategy is to convert graphene into paper or film form, which is then incorporated with the polymer matrix. In previous researches, both graphene and functionalised graphene were employed to improve the mechanical, recovery performances and self-healing abilities of SMP composites (Xiao *et al.*, 2010; Dong *et al.*, 2013). Furthermore, it was found that the modulus increase for SMP composites containing functionalised graphene was 25 to 30% higher than those containing raw graphene (Yoonessi *et al.*, 2012). In addition, the toughness and flexibility were both found to have been improved (Thakur and Karak, 2013). Such observations supported that graphene and functionalised graphene had a strong influence on the mechanical performance of SMPs. Graphene was also proven to effectively enhance the electrical conductivity. Experimental results reported have shown the electrical conductivity of PU SMP doped with 1.0 wt% graphene to be 10^{-2} S·cm^{-1} and that the electrical actuation via resistive heating needed a 100V electric voltage (Choi *et al.*, 2012).

Another strategy to achieve the electrical actuation of graphene-enabled SMP composites is to form the graphene-based paper (Lu and Gou, 2012). Thus, graphene and CNF were both used to form electrically conductive paper. Graphene was employed to improve the electrical conductivity in the basal plane due to its layer structure. On the other hand, CNF was used to bridge the gaps between layers and improve the inter-layer electrical conductivity of graphene. Therefore, a continuous network of graphene and CNF synergistically enhanced electrical property of the paper. The experimental results showed that the electrical conductivity of SMP composite incorporated with 1.8g conductive paper (0.6g graphene and 1.2g CNF) was approximately 1.5 $S \cdot cm^{-1}$. Figure 7 presents the electrical actuation of graphene-enabled SMP composite by a 25V electric voltage. Furthermore, the optimisation of temperature distribution of SMP composite was also improved in the electrically driven recovery process.

Concluding remarks

In this article, we review the progress and advance in the SMP composite incorporated with conductive carbon-based fillers for electrical actuation. A number of examples and experimental results have been presented and discussed to cover recent research and development on the utilisation of CNT, CNF, CB, CF and graphene to achieve the shape recovery of SMP composites through Joule resistive heating. As can be seen, together with synergistic effect of two types of conductive fillers, the feature of carbon-based fillers enabled SMP composite is able to effectively reshape the design of electrical actuation in many ways. With great efforts in the last few years, the electrical actuation in SMP composites is expected to be a solution for exploring many more practical and potential applications for this kind of smart materials. Furthermore, researches on the SMP composites driven by electrically resistive heating are also expected to significantly improve the development of SMPs.

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Table I Electrical properties of SMP composite with CNTs

Filler type	Matrix type	Filler content	Electrical conductivity ($S \cdot cm^{-1}$)	Voltage (V)	Ref.
Raw MWCNT	PU	3.0wt%	0.28	50	Yoo *et al.,* 2006
Surface-modified MWCNT	PU	5.0wt%	10^{-3}	40	Cho *et al.,* 2005
MWCNT paper	Styrene	7.02 wt%	≈.	7.1	Lu and Gou, 2012
MWCNT alignment	Styrene	1.0 wt%	≈.0	25	Yu *et al.,* 2011
Crosslinked SWCNT	PU	4.0wt%	≈.0wt	30	Lee and Yu, 2011

Table II Electrical properties of SMP composite with CNFs

Filler type	Matrix type	Filler content	Electrical conductivity ($S\cdot cm^{-1}$)	Voltage (V)	Ref.
Raw CNF	PU, Polyester, epoxy	7.0wt%	10^{-11}	NA	Gunes *et al.,* 2009; Tang *et al.,* 2013; Dong *et al.,* 2013
Oxidised CNF	PU	5.0wt%	10^{-5}	NA	Gunes *et al.,* 2009
CNF paper	Styrene	7.02wt%	≈t%7	8.6	Lu *et al.,* 2010
Hybrid filler of CNF	Epoxy	2.5wt% CNF and 7.5wt% nickel nanostrand	≈.5w	36	Lv *et al.,* 2011

Figure 1 Morphological studies and network structure of MWCNT in nanopaper, SEM image of a MWCNT nanopaper at the size of 200 nm, *reproduced from* Lu *et al.* (2012) *with permission*.

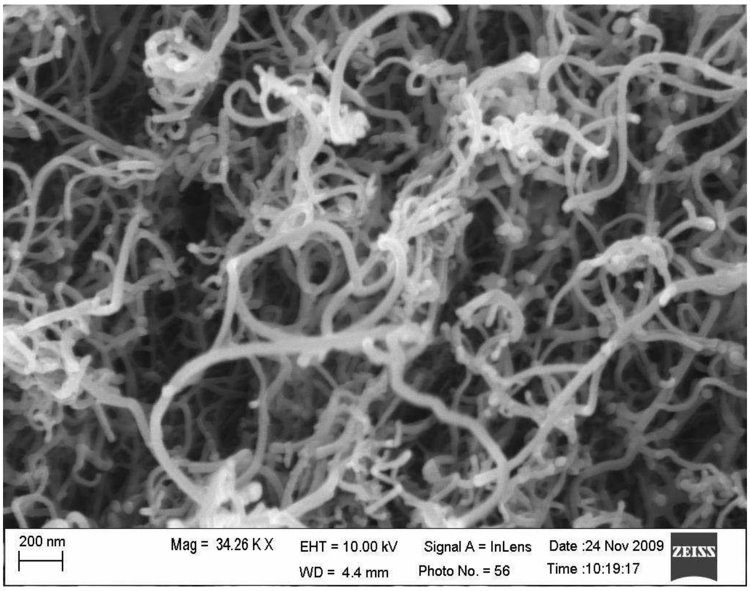

Figure 2 Series of photographs showing the macroscopic shape-memory effect of SMP composite integrated with 1.2 g MWCNT nanopaper. The permanent shape is a flat strip of composite material, and the temporary shape is deformed as right-angled shape, *reproduced from* Lu *et al.* (2012) *with permission*.

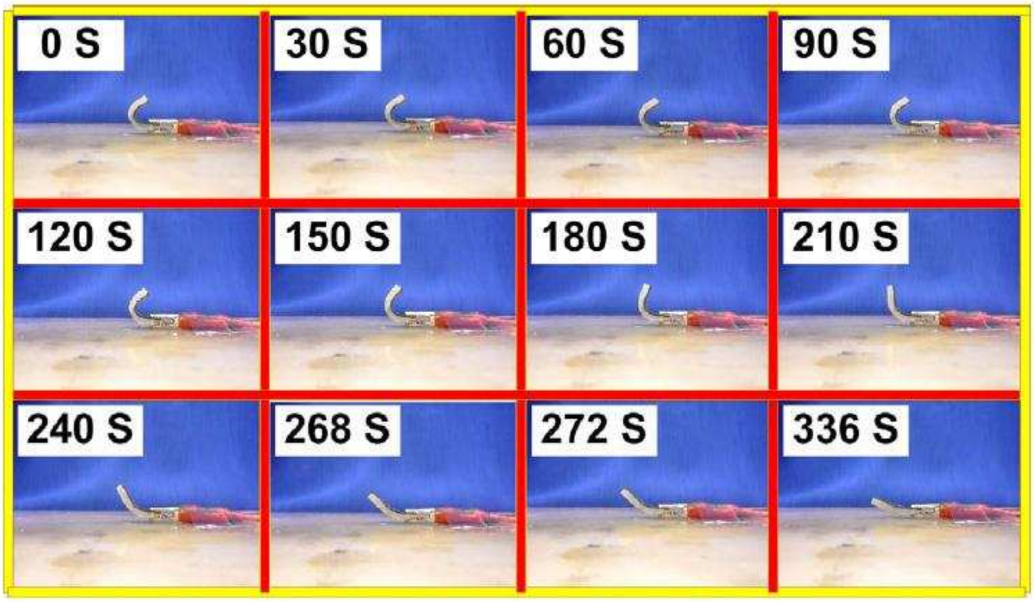

Figure 3 Morphology and network structure of CNFs was prepared based on non-ionic surfactants and high-power ultrasonic technology, *reproduced from* Lu *et al.* (2010) *with permission*.

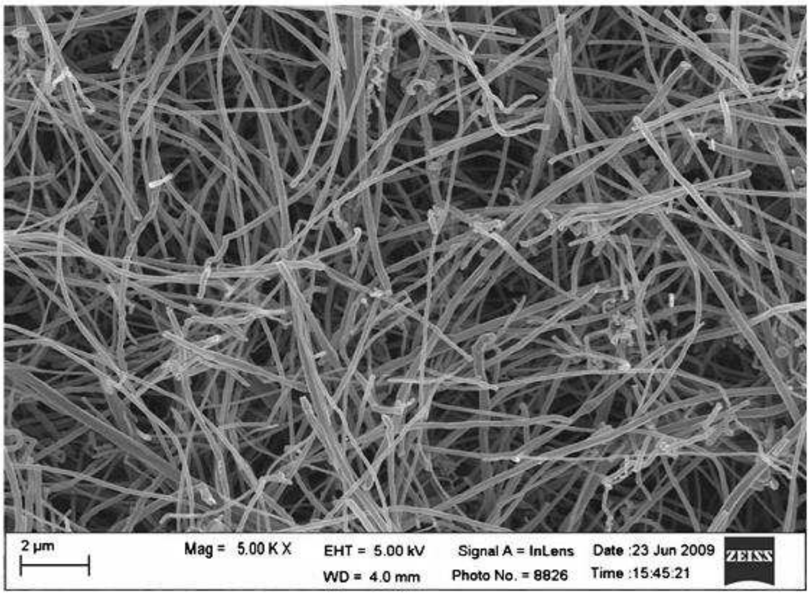

Figure 4 Series of photographs showing the macroscopic shape-memory effect of SMP composite integrated with 1.8 g CNF nanopaper. The permanent shape is a flat strip of composite material, and the temporary shape is deformed as a right-angled shape, *reproduced from* Lu *et al.* (2010) *with permission*.

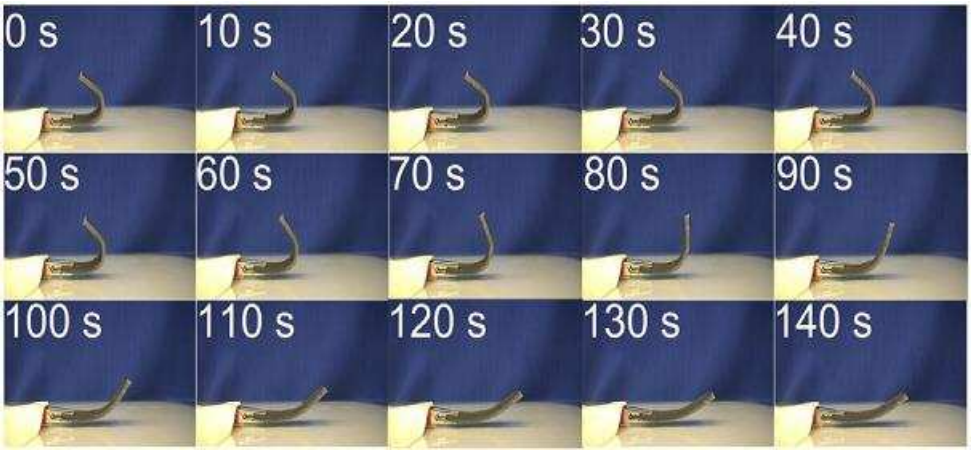

Figure 5 Series of photographs showing the macroscopic SME of SMP composite filled with 5wt% CB and 2wt% short CF composite. The permanent shape is a plane stripe of composite material, and the temporary shape is deformed as right-angled shape, *reproduced from* Leng *et al.* (2008) *with permission*.

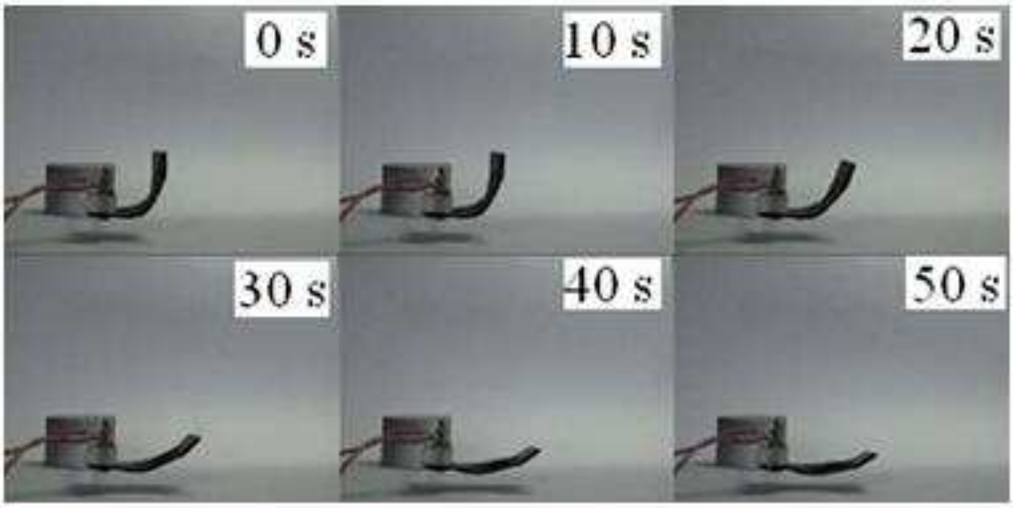

Figure 6 Schematic illustration of the nickel nanostrands being vertically aligned to help resistive heating power to transfer from the nanopaper to the underlying SMP, *reproduced from* Lu *et al.* (2011) *with permission*.

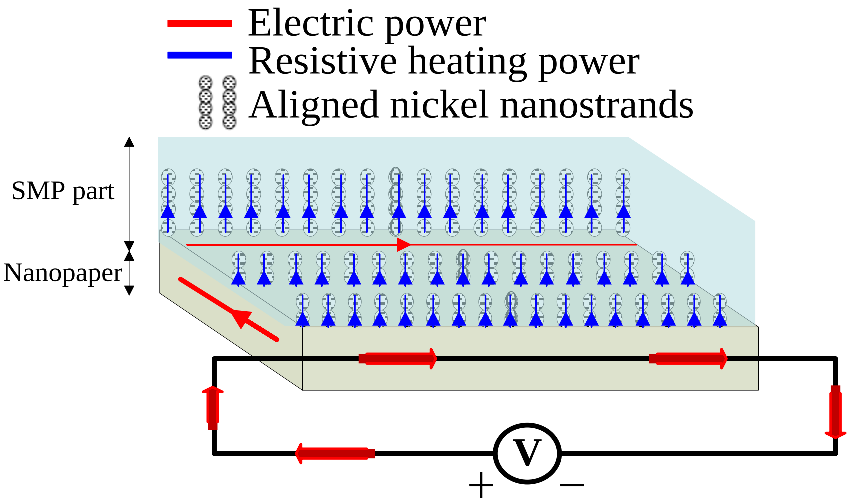

Figure 7 Electrically responsive behaviour of SMP composite with pure CNF buckypaper under a constant electric voltage of 25 V, *reproduced from* Lu *et al.* (2012) *with permission*.