Composites Science and Technology 69 (2009) 2064–2068

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Review of electro-active shape-memory polymer composite

Yanju Liu [a], Haibao Lv [b], Xin Lan [b], Jinsong Leng [b,*], Shanyi Du [b]

[a] Department of Aerospace Science and Mechanics, Harbin Institute of Technology (HIT), Harbin 150001, People's Republic of China
[b] Centre for Composite Materials, Harbin Institute of Technology (HIT), Harbin 150080, People's Republic of China

ARTICLE INFO

Article history:
Received 5 June 2008
Accepted 17 August 2008
Available online 29 August 2008

Keywords:
A. Polymer–matrix composite (PMCs)
A. Polymers
A. Smart materials
B. Electrical properties
B. Fibre/matrix bond

ABSTRACT

Shape-memory polymers (SMPs) have been one of the most popular subjects under intensive investigation in recent years, due to their many novel properties and great potential. These so-called SMPs by far surpass shape-memory alloys and shape-memory ceramics in many properties, e.g., easy manufacture, programming, high shape recovery ratio and low cost, and so on. However, they have not fully reached their technological potential, largely due to that the actuation of shape recovery in thermal-responsive SMPs is normally only driven by external heat. Thus, electro-activate SMP has been figured out and its significance is increasing in years to come. This review focuses on the progress of electro-activate SMP composites. Special emphases are given on the filler types that affect the conductive properties of these composites. Then, the mechanisms of electric conduction are addressed.

1. Introduction

Shape-memory polymers (SMPs) have the shape-memory effect as if they can be deformed and fixed into a temporary shape, and then recover their permanent shape by external stimulus [1,2]. SMPs were first introduced in the mid 1980s, and interest in these "smart" polymers continues to grow today [2]. The development in SMPs have grown rapidly in recent years, owing to their excellent structural versatility, low manufacturing cost, easy in processing, high elastic deformation (strain up to more than 200%, and low recovery temperature [3,4]. These unique characteristics lend them to be used in a myriad of fields, including clothing manufacturing, deployable space structures, morphing aircraft, medical treatment, and many other applications.

Same as other shape-memory materials, SMPs have the typical shape-memory effect (SME). However, their recovery can be triggered by various external stimuli, not only heat [5–9] such as SMAs, but also light [10,11], electricity [12–19], magnetic field [20–22] or solution [23–26], etc. Although so many efforts, focusing on stimuli-responsive SMPs and their composites, have been paid to date, still no convergent results were obtained. The demand to get rid of external heaters has led to conductive SMPs filled with fillers such as carbon nanotubes [12–14], carbon particles [15,18], conductive fiber [16] and nickel zinc ferrite ferromagnetic particles, etc. [17–19]. The researches of electro-activated polymeric composites have already been reported [12,13,16,27–30]. For example, an electrical conductivity of shape-memory polyurethane filled with 30% carbon black is about 1–10^{-1} S cm^{-1} [12]. Another example is the shape-memory polyurethane composites incorporating 5 wt.% surface-modified multi-walled carbon nanotubes, and the electrical conductivity about 10^{-3} S cm^{-1} was obtained [13]. Paik et al. [14], incorporating of shape-memory polyurethane with multi-walled carbon nanotubes, and the electrical conductivity was about 2.5×10^{-3} S cm^{-1}. It is proposed a novel approach to make shape recovery triggered more conveniently by passing an electrical current through SMP composite with carbon black (CB) nanoparticle and short carbon fiber (SCF) filled [19]. Leng et al. [21], demonstrate an approach to significantly reduce the electrical resistivity in polyurethane SMP filled with randomly distributed carbon black and Ni particles which are aligned into chains by applying magnetic field.

2. SMP filled with conductive fillers

2.1. SMP filled with carbon nanotubes

Goo et al. of Konkuk University firstly introduces the shape recovery of conducting SMP composites using carbon nanotubes by electrical current, not by applying thermal heating [12–14]. These achievements may lead to the application of SMPs as electro-activate actuators, which is important in many practical applications such as smart actuators for controlling micro-aerial vehicles. To obtain conducting SMPs, multi-walled carbon nanotubes (MWNTs) were used after being chemically surface-modified in a mixed solvent of nitric acid and sulfuric acid, for improvement of interfacial bonding between polymers and conductive fillers. These reports depict how to fabricate electro-activate SMP

* Corresponding author. Tel./fax: +86 451 86402328.
E-mail address: lengjs@hit.edu.cn (J. Leng).

0266-3538/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2008.08.016

nanocomposites and how to utilize the voltage-triggered shape memory for application as an actuator.

The electrical conductivity of composite films, measured by the four point probe method, was in the order of 10^{-3} S cm for samples of 5 wt.% modified MWNT content. With increasing the amount of modified MWNT content, the electrical conductivity also increased. And the effect of surface-modified MWNT on the electrical conductance was significant. The electrical conductivity of this surface-modified MWNT composite was lower than that of the composites filled with untreated MWNT, at the same filler content. This is attributable to the increased defects in the lattice structure of carbon–carbon bonds formed on the nanotube surface owing to the acid treatment. In practice, the severe modification of the nanotubes significantly lowered the electrical conductivity. As a result, both the mechanical and electrical properties were dependent on the degree of surface modification of the MWNTs, and the acid treatment at 90 °C gave desirable properties for shape memory.

Fig. 1 shows the typical relation between the surface temperature and applied voltage for the 5 wt.% surface-modified MWNT composite. The temperature of the samples was measured using digital multi-meters (M-4660, DM-7241, and METEX) with a non-contact temperature measuring system. Typically, with applied voltage (60 V), the sample heated above 35 °C in 8 s. It was, however, impossible to heat the sample above its transition temperature with a voltage lower than 40 V [12].

Though preparing electro-activate shape-memory composites and investigating their characteristics, the shape-memory effect could be shown to be dependant on the filler content and degree of surface-modification of the MWNTs. Composites made with surface-modified MWNTs had improved mechanical properties, and the modulus and stress at 100% elongation increased with improving surface-modified MWNT content. As a result, the electrical conductivity of the surface-modified MWNT composites was lower than that of the untreated MWNT composites. An order of 10^{-3} S cm^{-1} was obtained in the samples with 5 wt.% modified MWNT content. Consequently, the composites with surface-modified MWNTs could show electro-activate shape recovery with an energy conversion efficiency of 10.4% as well as improved mechanical properties.

Cho [14] blends shape-memory polyurethane block copolymer (SMPU) with carbon nanotube and carbon black. They are called SMP-CNT and SMP-CB composites, respectively. The SMP-CNT composite consists of SMPU and 3%, 5%, or 7% CNT, while the SMP-CB composite consists of SMPU and 20% or 30% CB. In their work, a conducting shape-memory polymer had been fabricated and tested.

2.2. SMP filled with electromagnetic filler

It is found that by adding of surface-modified super-paramagnetic nanoparticles into shape-memory polymer matrices, remote actuation of complex shape transitions by electromagnetic fields is possible. The thermosetting composite being made from oligo (e-caprolactone)dimethacrylate/butyl acrylate contain between 2 and 12 wt.% magnetite nanoparticles serving as nano-antennas by magnetic field heating. The specific loss power of the particles is determined to be 30 W g^{-1} at 300 kHz and 5.0 W. During the shape transition at 43 °C, no further temperature increase is observed.

In Fig. 2(a), a photo series impressively documents the electromagnetically induced shape-memory effect of sample. The used specimen is cut from the composite film as a rectangular strip (about 15 × 2 × 0.5 mm), referred to as the permanent shape. After heating the sample to 70 °C, it is deformed to a helix and cooled to fix this temporary shape by the formation of oligo(e-caprolactone) crystallites. After this programming process, the sample holds the helical shape in the absence of external forces as can be seen from Fig. 2(b) (0 s). The shape transition in the AC field of 300 kHz was documented with a digital camera. After 10 s, the starting conversion of the helix was observed, taking another 10 s to be completed. The final shape was close to the original rod with some remaining flexion due to friction between the soft polymer and the glass plate. The observed time window is in good agreement with the experimental sample temperature in the induction heating experiment with temperature control described above, and the temperature of the sample's environment (the open aired system inside the coil is shown to be hardly affected by the process [17].

2.3. SMP filled with Ni chain

Leng and Huang adds magnetic particles into SMP, these particles formed chains by applying magnetic field in the cured process. Electrical resistance is significantly reduced in this way. SEM images reveal that single chains start to be formed at 1 volume fraction percent of Ni. With the increase of Ni content, multi-chains (bundles) are resulted, and eventually no clear Ni chain can be recognized (Fig. 3, left column). In addition, after five stretching-shape recovery cycles, the Ni chains still exist (Fig. 3, right column), which indicates the possibility of using chained SMPs for cyclic actuation [21].

Fig. 4 plots the electrical resistivity of the random and chained samples against the volume fraction of Ni powders. The volumetric electrical resistivity ρ is calculated by

$$\rho = \frac{RA}{L} \tag{1}$$

where R is the measured resistance, A is the cross-sectional area of sample, L is the length between two aluminum electrodes (refer to the right insert in Fig. 4 for the setup for the resistivity measurement). As expected, ρ of the random sample is the highest, while ρ of random samples is lower. ρ of chained samples in the chain direction is always the lowest. For example, at 10 volume fraction percent of Ni powder, ρ of random sample is 2.36×10^4 Ω cm; while in the chained sample, it is 2.93×10^6 Ω cm in the transverse direction, and only 12.18 Ω cm in the chain direction. However, at a high Ni content, ρ of all types of samples is close. This is due to that the Ni chains become unrecognizable at a high Ni content, as revealed in Fig. 4. At 10 volume fraction percent of Ni, the chained sample (with a dimension of 16 × 5 × 0.6 mm) can be heated from room temperature 20–55 °C by applying a voltage of 6 V (refer to infrared image in Fig. 4, bottom-left insert), which is enough to trigger the shape recovery. However, for the same setup and configuration, it is only about 26 °C in the random sample. No shape recovery can be actuated, as it is far below the actuation temperature [21].

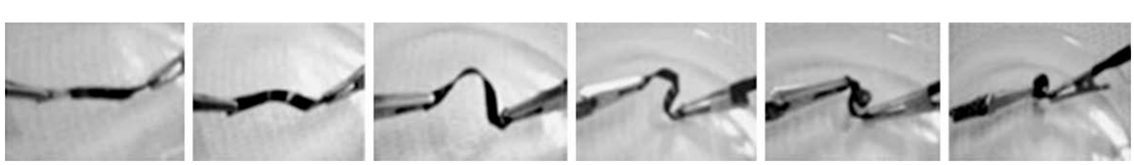

Fig. 1. Electro-activate shape recovery behavior of PU-MWNT composites (MWNT content of 5 wt.%). The sample undergoes the transition from temporary shape (linear, left) to permanent (helix, right) within 10 s when a constant voltage of 40 V is applied.

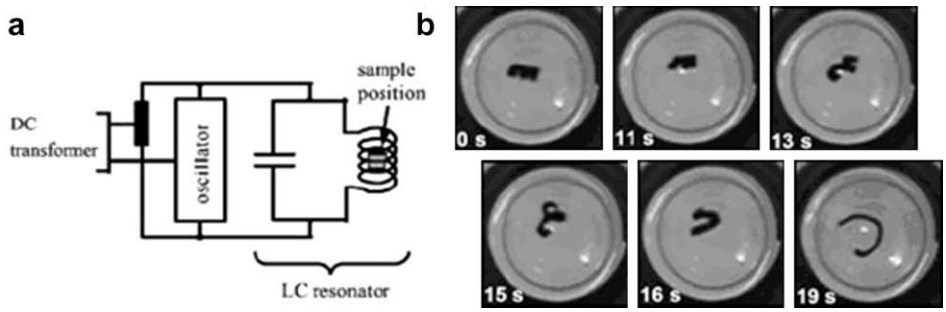

Fig. 2. (a) Schematic diagram of the LC resonant circuit-based HF generator used for induction heating experiments, and sample positioning; (b) photo series demonstrating the shape-memory transition induced by the impact of an HF electromagnetic field, measured from the topside of the induction coil. The shape of the sample is changed from helical (temporary shape) to a rectangular strip (permanent shape).

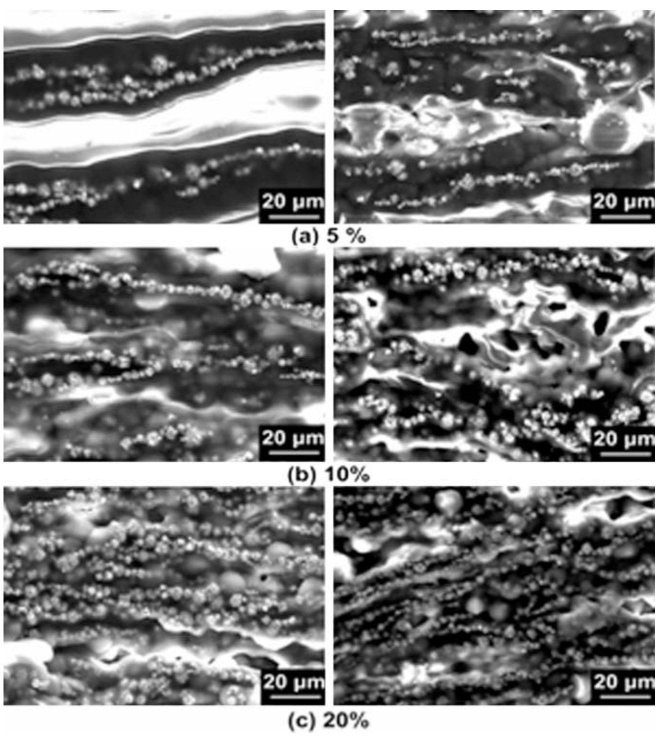

Fig. 3. Typical SEM images before (left column) and after (right column) five stretching (at 50% strain) shape recovery cycles.

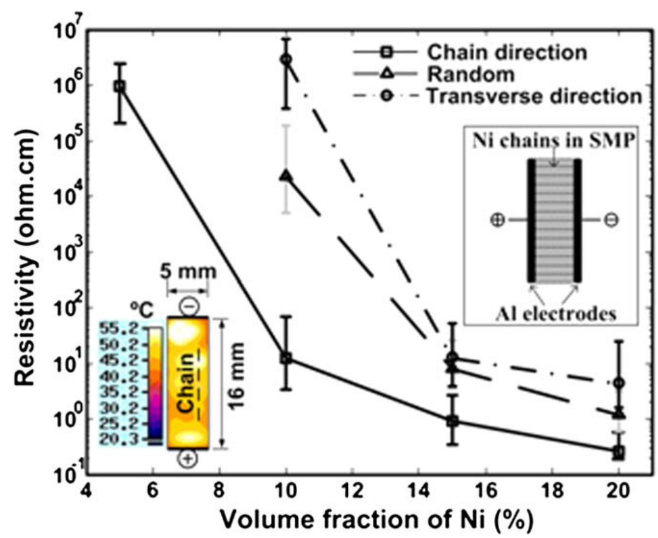

Fig. 4. Electrical resistivity vs. volume fraction of Ni powder. Right insert: illustration of setup for the resistivity measurement along the chain direction. Bottom-left insert: infrared image of temperature distribution in chained sample (10 volume fraction percent Ni, 6 V).

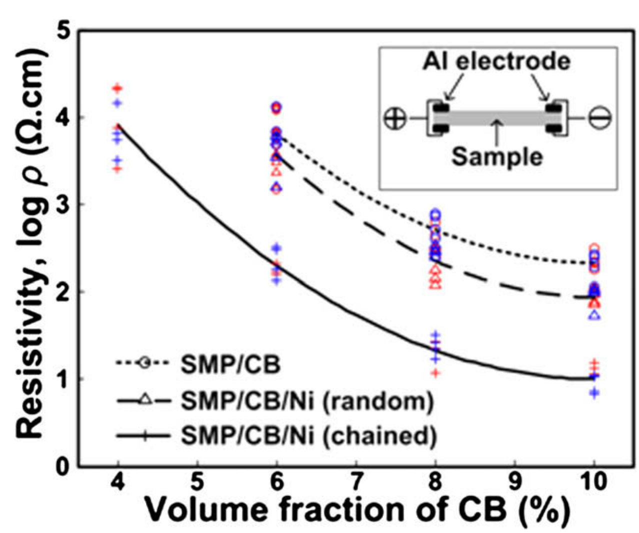

Fig. 5. Resitivity vs. volume fraction of CB with/without 0.5 volume fraction percent of Ni. Red symbol: right after fabrication; blue symbol: 1 month later. Inset figure illustrates how the resistance was measured. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Fig. 5 reveals the relationship between CB content and electrical resistivity of SMP/CB/Ni (chained), SMP/CB/Ni (random) and SMP/CB. It is clear that the additional 0.5 volume fraction percent of Ni, if distributed randomly, only slightly reduces the resistivity of the composites. However, at the same amount of Ni particles, if well-aligned to form chains, can significantly reduce the electrical resistivity by more than 10 times. Obviously, the remarkable reduction in the electrical resistivity is the result of the conductive chains, which serve as conductive channels to bridge those small isolated CB aggregations. This bridging effect is more significant in composites loaded with a low amount of CB in which the CB aggregates are relatively small in size and more isolated. As shown in Fig. 6, almost full recovery is observed in 120 s [22].

2.4. SMP filled with hybrid fibers

Fig. 7 shows the typical relation between the resistivity of composites against fillers content. The curves of SMP filled with micro-carbon powder and SMP filled with micro-carbon powder and SCF

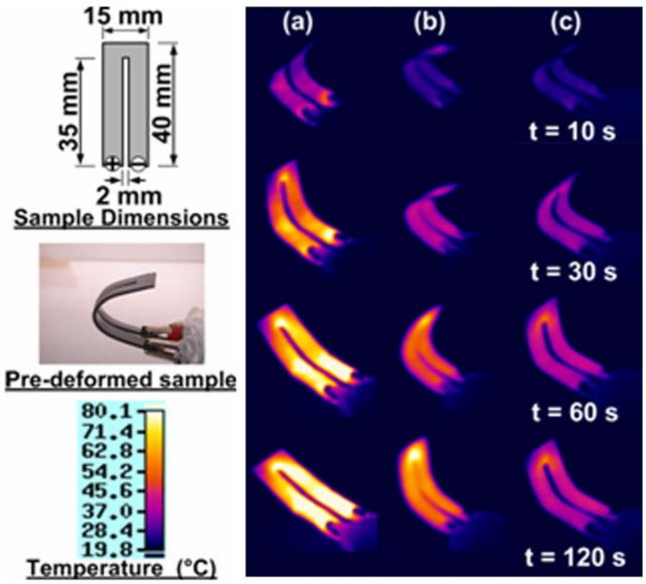

Fig. 6. Sequence of recovery and temperature distribution. Top-left inset: dimensions of sample; middle-left inset: pre-bent shape; bottom-left inset: temperature bar (in °C). Sample (a) 10 volume fraction percent of CB, 0.5 volume fraction percent of chained Ni; sample (b) 10 volume fraction percent of CB, 0.5 volume fraction percent of randomly distributed Ni; and sample (c) 10 volume fraction percent of CB only. The tests were repeated for more than five times on each sample.

are served as comparison [16]. Through comparison, the composites containing nanoparticles have a better conductivity than that blended with micro-size conductive filler that is why CB was selected. As the amount of filler content increasing, the volume resistivity decreased, and a synergy effect reduces the resistivity of CB/SCF system. At the same time, the resistivity of the composite filled with CB is 10^4 times higher than that of the composite with CB/SCF at the same filler content of 7 wt.%. This can be attributed to the fact that the inherent fibrillar form of SCF has a higher tendency to form a three-dimensional network in the composites, ensuring better electrical response than that of particulate fillers.

The characteristic volume resistivity curves for the SMP/CB/SCF composite (shown in Fig. 7) indicate that SMP filled with 5 wt.% CB and 0.5 wt.% SCF, of which the resistivity is 128.32 Ω cm, where insulator to conductor transition presents; while the resistivity of composite containing 5 wt.% CB and 2 wt.% SCF is 2.32 Ω cm which can be defined as conductor.

The electrically induced shape-memory effect is exemplarily demonstrated for SMP with dimension of 112 × 23.2 × 4 mm filled with 5 wt.% CB and 2 wt.% SCF shown in Fig. 8, where a change in shape from temporary flexural shape to permanent plane stripe shape occurring within 50 s is shown, when a constant voltage of 24 V is applied. The rate of shape recovery was strongly dependent on the magnitude of the applied voltage and the electrical resistivity of SMPC [19].

As shown in Fig. 9, the short fibers are dispersed randomly; however, there are many interconnections between fibers. These interconnections form the conductive networks which can be used to explain the excellent electrical conductivity of composites filled with SCF. However, the dispersion of SCF is normally inhomogeneous within composites. As a result, the electrical conductivity of composites filled with only SCF may not be good.

Two microstructure images in Fig. 9 show the formation of co-supporting conductive networks. Such conductive networks could improve the electrical properties of SMP composites. The dispersion of particles and short fibers in the SMP composites are evaluated by investigating the cross-section of samples.

From Fig. 9, it is found that there is a distinct difference between fibrous and particulate filler in influencing conductivity of the composites. SCFs may be considered as a rigid long aggregate of carbon, leading to easy formation of continuous conductive networks, and the amount of the networks generally determines the effectiveness of conductivity. The increase of filler content would increase the number of filler particles in the composite interacting with incident conductive networks, although normally the aggregates are separate from each other. Thus, the conductivity of composites including particulate filler is poor, unless, very high filler content is used. However, the particulate filler plays an important role in SMPCs. There are two major reasons being used to account it. First, its aggregate is the node of conductive network which makes orientation of short fiber improves on; second, there are many particles and their aggregates adsorbed on the surface of SCF, enlarge surface of conductive fillers and improve the electrical properties of polymer which ranged as one of the worst conductors.

3. Summary and conclusions

In the past decade, numerous researches have been conducted on the mechanism, shape recovery and electrical properties of SMP filled with conductive filler and the corresponding applications. The electro-activate SMP has been mature attributed to the works done at the early stage. This review regarding shape-memory polymer continues its recent development in undergoing electro-induced shape recovery, summarizes the growth of

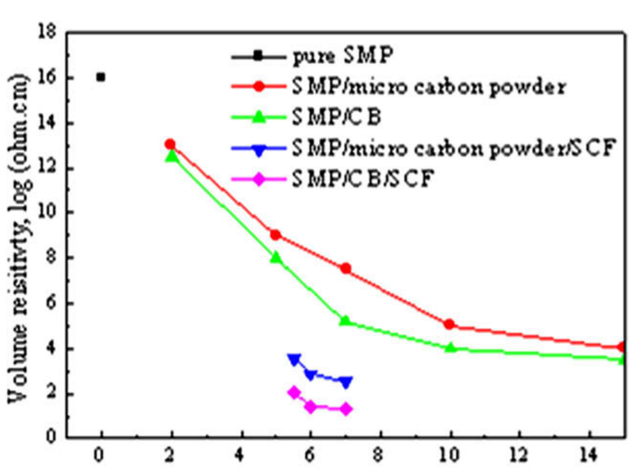

Fig. 7. Resistivity of SMP matrix filled with MCP, CB, MCP/SCF and CB/SCF systems versus filler content.

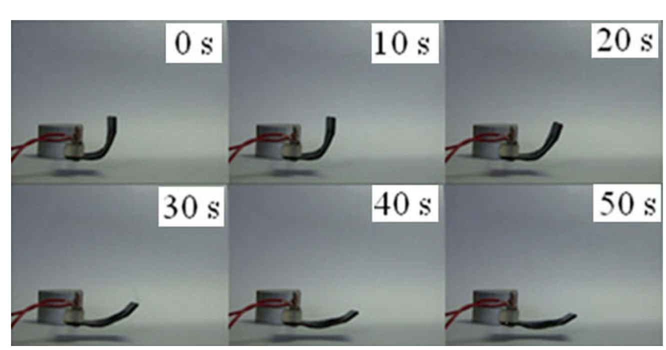

Fig. 8. Electro-activate SMP filled with CB/SCF induced by applying 25 V.

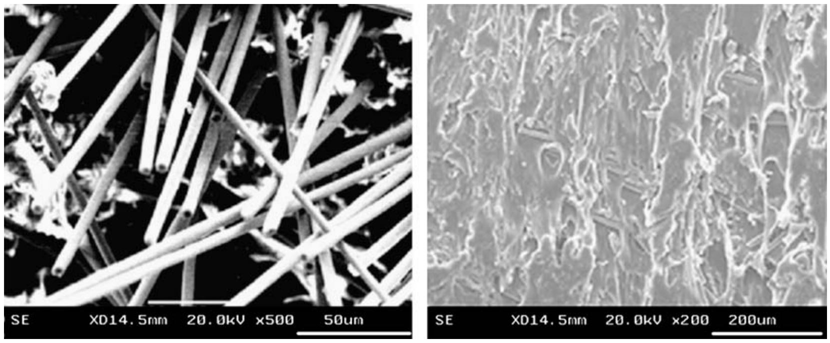

Fig. 9. Morphology of short carbon fibers (the left one) and sectional observation (the right one).

electro-activate shape-memory polymer investigation by our group and other academic groups. Electricity as a stimulus enables resistive actuation of shape-memory polymer filled with conductive fillers. In this way, external heating, which is unfavorable for many applications and is used to stimulate conventional shape-memory polymers, can be avoided. The electric triggering of shape-memory polymer composites enlarges their technological potential.

Acknowledgements

We would like to thank the Program of Introducing Talents of Discipline to Universities, PR China. We also wish to acknowledge the funding provided by The National Natural Science Foundation of China (NSFC 90505010) and Harbin Institute of Technology.

References

[1] Behl M, Lendlein A. Shape-memory polymers. Mater Today 2007;10(4):20–8.
[2] Dietsch B, Tong T. A review—features and benefits of shape memory polymers (SMPs). J Adv Mater 2007;39(2):3–12.
[3] Ratna D, Karger-Kocsis J. Recent advances in shape memory polymers and composites: a review. J Mater Sci 2008;43:254–69.
[4] Gall K, Kreiner P, Turner D, Hulse M. Shape-memory polymers for microelectromechanical systems. J Microelectromech Syst 2004;13(3):472–83.
[5] Gall K, Dunn ML, Liu YP, Finch D, Lake M, Munshi NA. Shape memory polymer nanocomposites. Aata Mater 2002;50:5115–26.
[6] Hu JL, Ji FL, Wong YW. Dependency of the shape memory properties of a polyurethane upon thermomechanical cyclic conditions. Polym Int 2005;54(3):600–5.
[7] Lendlein A, Kelch S. Shape-memory polymers. Angew Chem Int Edi 2002;41(12):2034–57.
[8] Liu C, Qin H, Mather PT. Review of progress in shape-memory polymers. J Mater Chem 2007;17(16):1543–58.
[9] Everhart MC, Nickerson DM, Hreha RD. High-temperature reusable shape memory polymer mandrels. In: White EV, editor. Procceeding of 11th international symposia on smart structures and materials, vol. 6171. San Diego: SPIE; 2006.
[10] Lendlein A, Jiang HY, Junger O, Langer R. Light-induced shape-memory polymers. Nature 2005;434(7035):879–82.
[11] Jiang Hy, Kelch S, Lendlein A. Polymers move in response to light. Adv Mater 2006;18(11):1471–5.
[12] Goo NS, Paik IH, Yoon KJ, Jung YC, Cho JW. Actuation of MAV control surface using conducting shape memory polymer actuator. In: Alison BF, editor. Proceeding of 11th international symposia on smart structures and materials. Bellingham, WA, USA: SPIE; 2004. p. 194–201.
[13] Cho JW, Kim JW, Jung YC, Goo NS. Electroactive shape-memory polyurethane composites incorporating carbon nanotubes. Macromol Rapid Commun 2005;26(5):412–6.
[14] Paik IH, Goo NS, Jung YC, Cho JW. Development and application of conducting shape memory polyurethane actuators. Smart Mater Struct 2006;15(5):1476–82.
[15] Yang B, Huang WM, Li C, Li L, Chor JH. Qualitative separation of the effects of carbon nano-powder and moisture on the glass transition temperature of polyurethane shape memory polymer. Scripta Mater 2005;53(1): 105–7.
[16] Leng JS, Lv HB, Liu YJ, Du SY. Electroactivate shape-memory polymer filled with nanocarbon particles and short carbon fibers. Appl Phys Lett 2007;91:144105.
[17] Schmidt AM. Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles. Macromol Rapid Commun 2006;27(14):1168–72.
[18] Koerner H, Price G, Pearce N, Alexander M, Vaia RA. Remotely actuated polymer nanocomposites-stress-recovery of carbon-nanotube-filled thermoplastic elastomers. Nat Mater 2004;3(2):115–20.
[19] Lv HB, Leng JS, Du SY. Electro-induced shape-memory polymer nanocomposite containing conductive particles and short fibers. In: Procceedings of 15th international symposia on smart structures and materials, vol. 6932. San Diego: SPIE; 2008.
[20] Buckley PR et al. Inductively heated shape memory polymer for the magnetic actuation of medical devices. IEEE Trans Biomed Eng 2006;53(10):2075–83.
[21] Leng JS et al. Electrical conductivity of thermoresponsive shape-memory polymer with embedded micron sized Ni powder chains. Appl Phys Lett 2008;92:014104.
[22] Leng JS, Huang WM, Lan X, Liu YJ, Du SY. Significantly reducing electrical resistivity by forming conductive Ni chains in a polyurethane shape-memory polymer/carbon-black composite. Appl Phys Lett 2008;92:204101.
[23] Yang B, Huang WM, Li C, Li L. Effects of moisture on the thermomechanical properties of a polyurethane shape memory polymer. Polymer 2006;47(4):1348–56.
[24] Lv HB, Leng JS, Liu YJ, Du SY. Shape memory polymer in response to solution. Adv Eng Mater 2008;10(6):592–5.
[25] Huang WM, Yang B, An L, Li C, Chan YS. Water-driven programmable polyurethane shape memory polymer: demonstration and mechanism. Appl Phys Lett 2005;86:114105.
[26] Leng JS, Lv HB, Liu YJ, Du SY. Comment on "Water-driven programmable polyurethane shape memory polymer: demonstration and mechanism" [Appl. Phys. Lett. 86, 114105, (2005)]. Appl Phys Lett 2008;92:206105.
[27] Velasco-Santos C, Martinez-Hernandez AL, Fisher FT, Ruoff R, Castano VM. Improvement of thermal and mechanical properties of carbon nanotube composites through chemical functionalization. Chem Mater 2003;15(23):4470–5.
[28] Geng HZ, Rosen R, Zheng B, Shimoda H, Fleming L, Liu J, et al. Fabrication and properties of composites of poly(ethylene oxide) and functionalized carbon nanotubes. Adv Mater 2002;14(19):1387–90.
[29] Lin Y, Zhou B, Fernando KAS, Liu P, Allard LF, Sun YP. Polymeric carbon nanocomposites from carbon nanotubes functionalized with matrix polymer. Macromolecules 2003;36(19):7199–204.
[30] Drubetski M, Siegmann A, Narkis M. Electrical properties of hybrid carbon black/carbon fiber polypropylene composites. J Mater Sci 2007;42(1): 1–8.