RSC Advances

RSC Publishing

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c3ra42704h

# Self-assembled carboxylic acid-functionalized carbon nanotubes grafting onto carbon fiber for significantly improving electrical actuation of shape memory polymers

Haibao Lu,*[a] Weilong Yin,[a] Wei Min Huang[b] and Jinsong Leng[a]

Received 3rd June 2013
Accepted 13th September 2013

DOI: 10.1039/c3ra42704h

**www.rsc.org/advances**

This study presents an effective approach to significantly reduce the electrical resistivity of thermally responsive shape memory polymer (SMP) nanocomposites that show Joule heating triggered shape recovery. Carboxylic acid-functionalized carbon nanotubes (CNTs) self-assembled and grafted onto the carbon fibers, were used to enhance the reliability in bonding between the carbon fiber and the SMP *via* van der Waals and covalent crosslinking, respectively. It was found that the electrical properties of SMP nanocomposites have been improved by the synergistic effect of carboxylic acid-functionalized CNTs and carbon fibers. Furthermore, the electrically responsive recovery behavior and temperature distribution were monitored and characterized. Finally, the molecular structure and temperature dependent electrical behavior were studied, and verified the electro-activated recovery performance of the SMP nanocomposites.

## 1. Introduction

Shape memory polymers (SMPs) having the ability to actively move upon applying an appropriate stimulus have found their way into several application areas such as biomedicine, automobile, aerospace and textiles.[1–4] The majority of historic shape memory materials (SMMs) are made of shape memory alloys (SMAs). While these materials are able to withstand large forces, they commonly will only deform a fraction of a percent.[5] In the late 1980s, it had been demonstrated that some SMPs could exhibit up to a 100% elastic strain, which is much more than any SMA.[6] A great deal of effort has been devoted to fundamental research in the last three decades. A large number of advantages of SMPs have been discovered and explored, such as their low weight, low cost, easy processing requirements, high extent of deformation *etc.*[7,8] Currently, SMPs are gradually attracting more and more scientific and technological attention. Tremendous progress in synthesis, analytics, characterization, actuation approach and modeling enables scientists today to develop SMPs in a knowledge based approach.[7–11] Fundamental research aims toward other stimuli different than heat (*e.g.* light, water, electric current, alternating magnetic fields, or ultrasound) and enabling more desirable requirements on demand.[12–16] In these approaches, additional functionalities are added for a successful realization of composites or nanocomposites based on SMPs.

The utilization of electrically Joule resistive heating to trigger the shape-memory effect of SMPs is desirable for practical applications where it would not be possible to use heat, and is another active area of research. Some current efforts use electrically conductive SMP composites with carbon nanotubes (CNTs),[17,18] short carbon fibers,[19] carbon black,[20,21] metallic Ni powder,[22] carbon fiber,[23] carbon nanofibers,[24,25] nanopaper,[26] graphene,[27] *etc.* Instead of improvement in electrical conductivity, these conductive fillers which enable remote actuation of shape transitions also enhance the thermal conductivity.[28] Furthermore, a synergic effect between two types of conductive fillers has been used with some degree of success. A synergistic effect of carboxylic acid-functionalized CNTs and carbon fiber is introduced in this study. The carboxylic acid-functionalized CNTs are self-assembled and grafted onto the carbon fibers to enhance the reliability in bonding between carbon fiber and SMP matrix *via* van der Waals and covalent crosslink, respectively. The combination of CNTs and carbon fibers is consequently used to significantly improve the electrical properties to achieve the actuation at a low electrical voltage for SMP composites.

## 2. Experimental

Carboxylic acid-functionalized CNTs are available with diameters ranging from 50 to 100 nm and lengths of 5 to 15 μm. Distilled water was used as a solvent. The raw CNTs of 0.6 g were

---

[a] *Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin 150080, China. E-mail: luhb@hit.edu.cn*

[b] *School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore*

mixed with 600 ml of distilled water to form a suspension. The surfactant $C_{14}H_{22}O(C_2H_4O)_n$ of 2 ml was introduced to aid the dispersion of the CNTs. The CNT suspension was then sonicated with an ultrasound power level of 300 W for 30 min. After which, the suspension was filtered under a high pressure to self-assemble and graft onto the carbon fibers with the aid of a hydrophilic polycarbonate membrane. Consequently, the carbon fibers grafted with carboxylic acid-functionalized CNTs were dried in an oven at 120 °C for 2 h to further remove the remaining water and surfactant. CNT assembly has a macroscale dimension and can be handled as conventional carbon fiber mats to attain controllable reinforcement dispersion and content.

The polymer matrix is an epoxy-based fully formable thermoset SMP resin. The resin is engineered with a glass transition temperature ($T_g$) of 110 °C. Cured epoxy-based SMP has a unique shape memory effect. When heated above or approximate to $T_g$, it could change from a rigid plastic to an elastic rubber. A resin transfer molding technique was applied to construct the SMP nanocomposites. 0.6 g of carbon fibers were grafted with 0.08, 0.10, 0.12, 0.14, 0.16, 0.18 and 0.20 g of carboxylic acid-functionalized CNTs and placed on the bottom of the metallic mold. The SMP mixture was then injected into the mold. The relative pressure of the resin transfer molding was kept at approximately 6 bars. After filling the mold, the mixture was cured at a ramp of approximately 1 °C min$^{-1}$ from room temperature to 100 °C and kept for 5 h before being ramped to 120 °C at 20 °C per 180 min. Finally, it was ramped to 150 °C at 30 °C per 120 min to produce the final SMP composites.

## 3. Results and discussion

### 3.1 Morphology of CNT assemblies onto carbon fibers

Scanning electron microscopy was used to study the surface morphology and structure of CNT functionalized carbon fibers. Fig. 1 shows the typical surface view of the raw CNT arrays at an accelerating voltage of 20.00 keV. The CNTs have a diameter ranging from 10 to 50 nm, and are entangled with each other. No large aggregates of nanotubes were observed. The bright lines correspond to individual nanotubes and the dark areas correspond to the carbon fiber. It is shown that the CNTs stick to the carbon fibers along the outer edges of the grooves with different angles due to the high specific surface area of the individual nanotube. The CNTs were grafted onto and uniformly deposited on the carbon fiber *via* the membrane filtration process. The CNTs appeared to be tightly associated with the carbon fiber surface. A synergistic effect of CNTs and carbon fibers confirms a continuously conductive network.

### 3.2 Raman spectra characterization

Raman spectra were obtained with a Horiba HR 800 spectrometer. The 632 nm radiation from a 20 mW air-cooled Argon ion laser was used as the exciting source. As shown in Fig. 2, Raman spectra were dominated by CNTs, but its actual intensity is proportional to the amount of CNT grafted onto the carbon fiber. Here, Raman spectroscopy is shown to provide a powerful tool to differentiate sp$^2$ carbon nanostructures of CNTs which have many properties in common and others that differ. The D bonding and G bonding of C═C shifts lower from 1349 to 1326 cm$^{-1}$ and 1588 to 1573 cm$^{-1}$, respectively, with the concentration of carboxylic acid-functionalized CNTs from 0.0 to 1.2 g, which reveal that the interaction force between carboxylic acid-functionalized CNTs and raw carbon fibers is improved. With that the G′ peak is therefore shown.

### 3.3 Electrical resistivity measurement

The electrical resistivity was determined with a van der Pauw four-point probe apparatus. This approach is an electrical impedance measuring technique that uses separate pairs of current-carrying and voltage-sensing electrodes to make more accurate measurements than the traditional two-terminal sensing method. In order to reduce experimental errors from many previous measurements, it is preferable that the tested sample is symmetrical. The apparatus has four probes with an adjustable inter-probe spacing. A constant current passed through two outer probes and an output voltage was measured across the inner probes with a voltmeter. The electrical resistivity of the SMP nanocomposites with a variety of weight

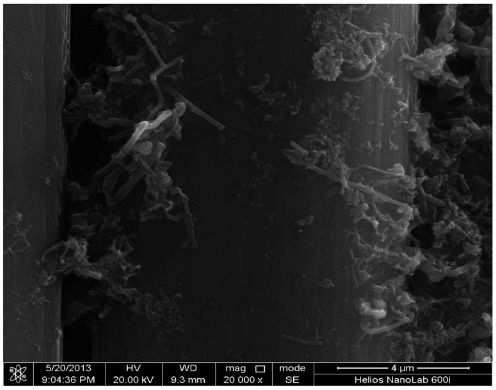

**Fig. 1** The typical surface view of the CNTs grafted onto the carbon fibers at an accelerating voltage of 20.00 keV.

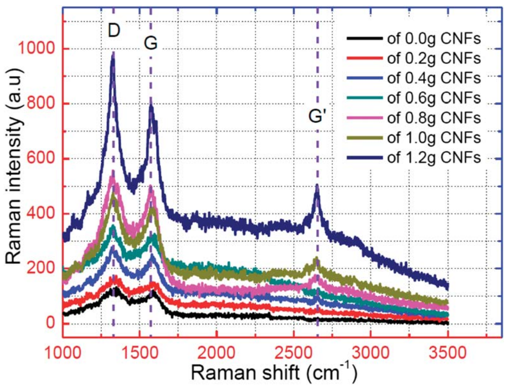

**Fig. 2** Raman spectra of tested samples with 632 nm excitation.

content of carboxylic acid-functionalized CNTs was plotted, as shown in Fig. 3.

Four electrodes were embedded into a disc-like sample. When a Kelvin connection was used, the electrical current was supplied with a pair of force connections. The electrical resistances of two modes are therefore used to calculate the electrical resistivity of the tested sample according to the van der Pauw expression. In the experiments, it was found that the average value of electrical resistivity decreased from 0.09284 to 0.08643 Ω cm, as the weight content of carboxylic acid-functionalized CNTs increased from 0.08 to 0.20 g.

Furthermore, the temperature range in a practical engineering application of polymers and their composites are ranged from room temperature to 100 °C. Thus, the temperature dependent electrical characteristics of carbon fiber grafted with CNTs in this range should be considered. It is determined by measuring the electrical resistivity while heating the specimen to a desired temperature. Fig. 4 shows the temperature dependent electrical resistivities of three tested samples (0.6 g of carbon fibers grafted with respectively 0.08 g, 0.10 g and 0.20 g of carboxylic acid-functionalized CNTs) as their temperatures increased from room temperature (approximate 25 °C) to 100 °C. As presented from these curves, the electrical resistivity value decreased with an increase in temperature. The initial and final values of electrical resistivity for carbon fibers grafted with 0.2 g carboxylic acid-functionalized CNTs are 0.13931 Ω cm (at 24.2 °C) and 0.12896 Ω cm (at 100 °C), respectively. In comparison of these three curves, the electrical resistivity of the tested sample (0.6 g carbon fibers grafted with 0.08 g CNTs) decreased from 0.15424 to 0.13751 (0.01673) Ω cm with a temperature increase from 30 to 100 °C. On the other hand, the electrical resistivity decreased from 0.14312 (at 30 °C) to 0.13071 (0.01241) Ω cm for the 0.6 g of carbon fibers grafted with 0.10 g of CNTs. Furthermore, the electrical resistivity decreased from 0.13837 to 0.12896 (0.00941) Ω cm for the 0.6 g of carbon fibers grafted with 0.20 g of CNTs. The decrease ratio was 10.98%, 8.67% and 6.80% for the carbon fibers with 0.08 g, 0.10 g and 0.20 g of CNTs, respectively. This phenomenon could also be attributed to electron movement in the electrical circuit. As temperature increases, the micro-Brownian motion of an individual CNT will become more significance. Therefore, with a higher amount of CNTs, more nanotubes will be involved in preventing or postponing the beamed electrons motion in the electrical circuit. On the other hand, an increase in temperature results in the electrons in the conductive network picking up energy, thus the electron flow becomes accelerated. The velocity of cyclic electron flow in an electrical circuit will hence be accelerated, resulting in a shorter period of cyclic electron flow. This approach would therefore lower the electrical resistivity of the bulk. In summary, the above mentioned reasons synergistically influence the electrical properties of carbon fibers grafted with CNTs in response to temperature.

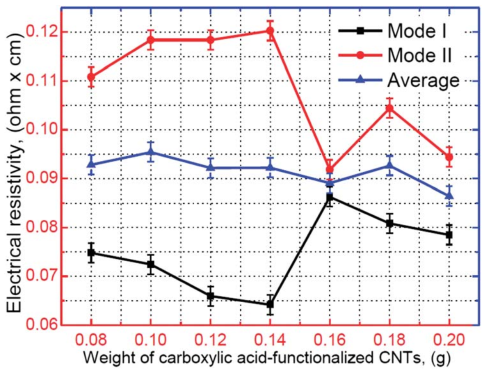

**Fig. 3** Electrical resistivity of carbon fibers grafted with different weight of carboxylic acid-functionalized CNTs. Each experimental data was repeated twenty times.

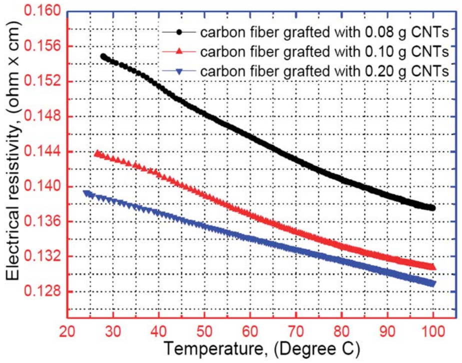

**Fig. 4** Electrical resistivity of carbon fibers grafted with different weight concentration of carboxylic acid-functionalized CNTs.

### 3.4 Thermomechanical property analysis

Dynamic mechanical analysis (DMA) is a most useful technique to characterize the viscoelastic behavior for polymeric materials. One important application of DMA is the measurement of the $T_g$ of amorphous polymers. In the epoxy-based SMP, the $T_g$ is responsible for the shape-memory effect. Exceeding it activates the polymer segments and thereby allowing the material to regain its permanent (or original) form. Therefore, the $T_g$ is a critical parameter and is necessary for characterizing the shape recovery performance of amorphous SMPs. Therefore, $T_g$ is a base for future characterizing the shape-memory behavior of SMPs and their nanocomposites in this study. The temperature of the sample or the frequency of the stress is often varied, leading to variations in the complex modulus. The determination of the dynamic mechanical properties was performed on a Netzsch DMA 242C (Netzsch, Germany) apparatus. All experiments were performed in the single cantilever mode at a constant heating rate of 10 °C $\text{min}^{-1}$. The oscillation frequency was 1.0 Hz and temperature interval ranged from room temperature to 200 °C. Consequently, the storage modulus, tangent delta and $T_g$ of the SMP nanocomposites incorporated with 0.08 g, 0.10 g and 0.12 g CNTs were determined in this manner. The storage modulus and tangent delta data were recorded as a function of temperature. As shown in Fig. 5, the $T_g$ is defined as the intersection point of storage modulus and the tangent delta curves. In this manner, the $T_g$ of SMP nanocomposites incorporated with 0.08 g, 0.10 g and 0.12 g CNTs

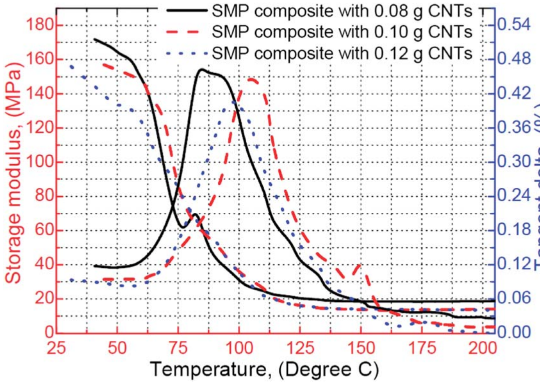

**Fig. 5** $T_g$ of SMP nanocomposites incorporated with carbon fibers and carboxylic acid-functionalized CNTs of 0.08 g, 0.10 g, 0.12 g and 0.20 g, respectively.

were 72.8 °C, 83.4 °C and 79.8 °C, respectively. Experimental results could be attained from the carboxylic acid-functionalized CNTs that enhance the bonding strength between carbon fiber and the SMP matrix, resulting in improved thermo-mechanical properties. However, with an increase in weight content of CNTs above a certain value, the bonding strength would be decreased due to an increase in separation distance among carbon fibers and the SMP matrix. Meanwhile, the dispersion and bonding of CNTs with both SMP and carbon fiber also play a critical role in influencing the dynamic mechanical behavior of the composites.

### 3.5 Electrically triggered shape recovery and temperature distribution

The tested SMP nanocomposite originally had a flat shape. After the sample was heated above its $T_g$, it could be deformed into a desirable shape upon application of an external force. Cooling back to room temperature, the SMP nanocomposite with a temporary (deformed) shape was subsequently fixed. The synergistic effect of carbon fiber (0.6 g in weight) and carboxylic acid-functionalized CNT (0.2 g in weight) on the actuation was studied on a "Π" shaped SMP nanocomposites (7.2 g in weight) sample. The flat sample with a dimension of 30 × 4 × 3 mm$^3$ was bent into a "U" shape at 110 °C. Images were taken with a digital camera at a constant frame rate of 30 Hz, and with an appropriate visual range to detect the sample's curvature. Snapshots of the shape recovery sequence of the SMP nanocomposite sample is shown in Fig. 6. A constant 10 V DC voltage was applied to the SMP nanocomposite. It took 40 s to complete the shape recovery. It showed very little recovery ratio during the first 20 s, but then exhibited a faster recovery behavior until 35 s. Finally, the SMP nanocomposite sample regained its original (permanent) shape. Simultaneously, an infrared video camera was used to monitor the shape recovery behavior and temperature distribution. Nine snap-shots of the tested SMP nanocomposite sample were presented in Fig. 7.

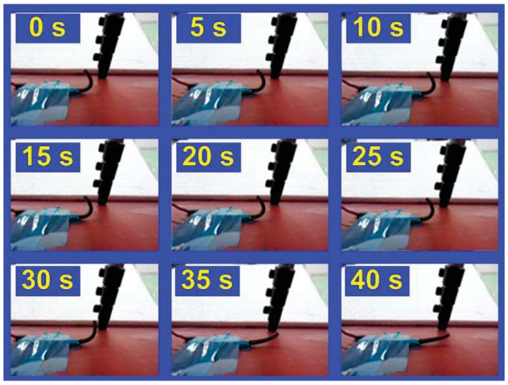

**Fig. 6** Electrically resistive heating-induced shape memory effect of SMP nanocomposites with 0.6 g carbon fibers and 0.2 g carboxylic acid-functionalized CNTs.

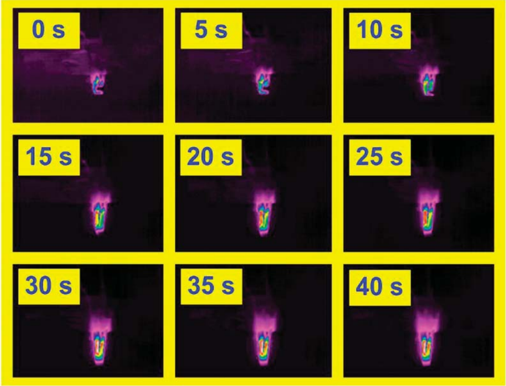

**Fig. 7** Snap shots of shape recovery and temperature distributions of SMP nanocomposite incorporated with 0.6 g carbon fibers and 0.2 g carboxylic acid-functionalized CNTs.

Meanwhile, the temperature distribution along the tested sample (70 selection points were set) was plotted in Fig. 8. High temperatures were found where internal strains were higher than the local resistivity. With electricity being applied, the resistive Joule heating resulted in the gradually increased in temperature. At 35 s, the maximum temperature of the sample reached approximately 135 °C, and the external electricity was turned off to avoid thermal degradation of the polymer. Consequently, the temperature on the tested sample lowered to room temperature.

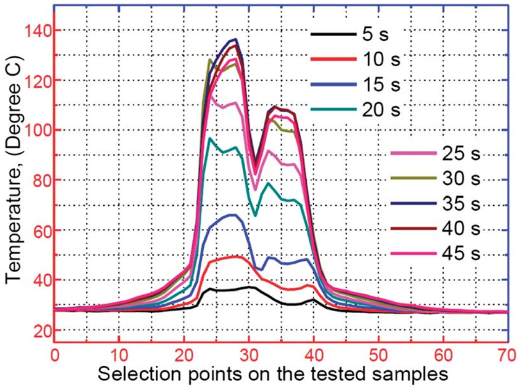

**Fig. 8** Temperature distribution curves of the SMP nanocomposite driven by loading an electric voltage of 10 V at various heating times.

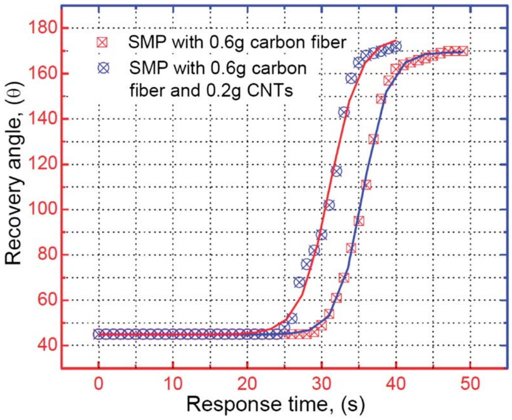

**Fig. 9** A comparison in actuation of pristine SMP composite (incorporated with carbon fiber) to SMP nanocomposite (incorporated with the carbon fiber grafted with 0.2 g carboxylic acid-functionalized CNTs).

To further characterize the effect of CNTs on the electrical actuation of SMP nanocomposites, a comparison of the actuation of a pristine SMP composite (incorporated with carbon fiber) with an SMP nanocomposite (incorporated with carbon fiber that was grafted with 0.2 g carboxylic acid-functionalized CNTs) is carried out to identify improvement in the performance at the electric voltage of 25 V, as shown in Fig. 9. Experimental results indicate that the SMP nanocomposite shows a faster heating speed of 40 s by loading with CNTs, while that of the SMP composite is 49 s. Therefore, it is determined that the carboxylic acid-functionalized CNTs improve the electrical actuation of SMPs.

## 4. Conclusions

A series of experiments were conducted to study the synergistic effect of carbon fibers and carboxylic acid-functionalized CNTs on the SMP nanocomposites, of which the actuation was achieved by electrically resistive Joule heating. These carboxylic acid-functionalized CNTs were grafted onto the carbon fiber to significantly enhance the reliability in bonding, and helped to transfer the resistive Joule heating between the carbon fiber and the SMP. The electrically driven recovery behavior was characterized at an electric voltage of 10 V. Furthermore, temperature distribution of the SMP nanocomposite with 0.2 g of CNTs was monitored in the recovery process by electricity. We demonstrated a simple way to produce electro-activated SMP nanocomposites by application of deposition of carboxylic acid-functionalized CNTs onto carbon fibers, and that Joule heating was possible at a low electrical voltage.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC) (Grant no. 51103032) and Fundamental Research Funds for the Central Universities (Grant no. HIT.BRETIV.201304).

## Notes and references

1 A. Lendlein and R. Langer, *Science*, 2002, **296**, 1673.
2 J. S. Leng, H. B. Lu, Y. J. Liu, W. M. Huang and S. Y. Du, *MRS Bull.*, 2009, **34**, 848.
3 W. M. Huang, Z. Ding, C. C. Wang, J. Wei, Y. Zhao and H. Purnawali, *Mater. Today*, 2010, **13**, 44.
4 J. Hu, *Advances in shape memory polymers*, Woodhead Publishing Limited, 2013.
5 C. Liu, H. Qin and P. T. Mather, *J. Mater. Chem.*, 2007, **17**, 1543.
6 T. Xie, *Polymer*, 2011, **52**, 4985.
7 P. T. Mather, X. F. Luo and I. A. Rousseau, *Annu. Rev. Mater. Res.*, 2009, **39**, 445.
8 I. A. Rousseau, *Polym. Eng. Sci.*, 2008, **48**, 2075.
9 W. Wolfgang, K. Karl, H. Matthias and A. Lendlein, *Adv. Polym. Sci.*, 2010, **226**, 97.
10 M. C. Serrano and G. A. Ameer, *Macromol. Biosci.*, 2012, **12**, 1156.
11 J. L. Hu, Y. Zhu, H. H. Huang and J. Lu, *Prog. Polym. Sci.*, 2012, **37**, 1720.
12 H. Koerner, G. Price, N. A. Pearce, M. Alexander and R. A. Vaia, *Nat. Mater.*, 2004, **3**, 115.
13 W. M. Huang, B. Yang, L. An, C. Li and Y. S. Chan, *Appl. Phys. Lett.*, 2005, **86**, 114105.
14 J. S. Leng, H. B. Lv, Y. J. Liu and S. Y. Du, *J. Appl. Phys.*, 2008, **104**, 104917.
15 R. Mohr, K. Kratz, T. Weigel, M. Lucka-Gabor, M. Moneke and A. Lendlein, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 3540.
16 G. Li, G. Fei, H. Xia, J. Han and Y. Zhao, *J. Mater. Chem.*, 2012, **22**, 7692.
17 J. W. Cho, J. W. Kim, Y. C. Jung and N. S. Goo, *Macromol. Rapid Commun.*, 2005, **26**, 412.
18 R. Mohan, A. M. Shanmugharaj, S. H. Ryu and J. Subha, *Mater. Chem. Phys.*, 2011, **129**, 925.
19 J. S. Leng, H. B. Lv, Y. J. Liu and S. Y. Du, *Appl. Phys. Lett.*, 2007, **91**, 144105.
20 H. H. Le, O. Osazuwa, I. Kolesov, S. Ilisch and H. J. Radusch, *Polym. Eng. Sci.*, 2011, **51**, 500.
21 H. H. Le, A. Zulfiqar, U. Mathias, S. Ilisch and H. J. Radusch, *J. Appl. Polym. Sci.*, 2011, **120**, 2138.
22 P. R. Buckley, G. H. McKinley, T. S. Wilson, W. Small, W. J. Benett, J. P. Bearinger, M. W. McElfresh and D. J. Maitland, *IEEE Trans. Biomed. Eng.*, 2006, **53**, 2075.
23 X. Lan, Y. J. Liu, H. B. Lv, X. H. Wang, J. S. Leng and S. Y. Du, *Smart Mater. Struct.*, 2009, **18**, 024002.
24 I. S. Gunes, G. A. Jimenez and S. C. Jana, *Carbon*, 2009, **47**, 981.
25 Z. Tang, D. Sun, D. Yang, B. Guo, L. Zhang and D. Jia, *Compos. Sci. Technol.*, 2013, **75**, 15.
26 H. B. Lu, F. Liang and J. Gou, *Soft Matter*, 2011, **7**, 7416.
27 H. B. Lu and J. Gou, *Nanosci. Nanotechnol. Lett.*, 2012, **4**, 1155.
28 J. Morshedian, H. A. Khonakdar and S. Rasouli, *Macromol. Theory Simul.*, 2005, **14**, 428.