Advanced Materials Research Vols. 47-50 (2008) pp 714-717
online at http://www.scientific.net

Online available since 2008/Jun/12

Investigate of Electrical Conductivity of Shape-Memory Polymer Filled with Carbon Black

Xin Lan*, Jinsong Leng, Yanju Liu, Shanyi Du

P.O. BOX 3011, Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin150080, China

*E-mail: lanxin@hit.edu.cn; Tel/Fax: 86-451-86402328

Keywords: shape memory polymer, carbon black, electrical conductivity, shape recovery

Abstract. A new system of thermoset styrene-based shape-memory polymer (SMP) filled with carbon black (CB) is investigated. To realize the electroactive stimuli of SMP, the electrical conductivity of SMP filled with various amounts of CB is characterized. The percolation threshold of electrically conductive SMP filled with CB is about 3% (volume fraction of CB), which is much lower than many other electrically conductive polymers. When applying a voltage of 30V, the shape recovery process of SMP/CB(10 vol%) can be realized in about 100s. In addition, the thermomechanical properties are also characterized by differential scanning calorimetery (DSC).

1. Introduction

As a promising smart material, shape memory polymer (SMP) has been a promising field under intensive investigation in recent years. SMP is able to recover their original shape upon applying an external stimuli[1,2], such as heat[3,4], light[5], and moisture[6,7]. Among these SMPs, the thermo-responsive SMP is common. In order to get rid of external heaters, SMP composites with different types of fillers have been developed[1,2], so that they can be actuated by means of Joule heat (i.e., by passing an electrical current[8-10], just like that of NiTi shape memory alloys). To date, most of the researches regarding electroactive SMP are focus on thermoplastic SMP polymers [8-10]. However the relatively poor mechanical properties (e.g. strength, stiffness) of thermoplastic SMP can not meet the practical applications. By contrast, the thermoset SMPs show better mechanical properties than thermoplastic SMP [10]. However, the study in electrical conductivity of thermoset SMP received little attentions.

In this study, a new system of thermoset styrene-based SMP filled with carbon black is investigated. In order to realize the electroactive stimuli of SMP, styrene-based SMP filled with carbon black (CB) is fabricated, and then its electrical conductivity is characterized. Finally, the shape recovery demonstration of SMP/CB(10%) composite is performed by passing an electrical current.

2. Sample preparation

The polymer matrix used in current study is a thermoset styrene-based SMP polymer. Carbon back (CB), bought from the Degussa, is nano-carbon particles. The technical data of CB includes, average powder size: 30 nm; specific gravity: 1.85; purity: 98.4%; DBP absorption: 420ml/100 g; BET surface area: 1000 m^2/g.

The composites were prepared by mixing the styrene-based shape-memory resin with the cross-link agent in a proper proportion at room temperature. Certain amount of carbon particles was blended in together with an additional solvent to reduce the viscosity of the mixture. Mechanical stirring was applied for 30 min, followed by ultrasonic processing at a power of 150 W (Sonics & Materials, VCX750) for 20~40 min. And then, the solution was placed in a vacuum oven for 30~60 min to dispose bubbles. Subsequently, the mixture was poured into an open mold, and cured for 36 h at 55~75 °C in an oven. After solidification, the SMP composite filled with CB was obtained. Various sized samples were cut out of the thin film for testing. Five types of materials were fabricated, namely pure SMP (CB0), composite with 2 vol% CB (CB2), composite with 4 vol% CB (CB4), composite with 6 vol% CB (CB6), and composite with 10 vol% CB (CB10).

3. Experimental results and discussions

3.1 DSC test

DSC tests were carried out on these samples with a DSC 2920 (TA Instruments) to examine the evaluation in transition temperature (T_g) with various amounts of CB. The samples for testing weigh around 10 mg and the constant heating/cooling rate is 5°C/min. T_g was defined as the temperature at the median point in the range of glass transition during the heating process.

Figure 1 plots the DSC results of these samples. It reveals that T_g decreases slightly with the increase of CB volume fraction. For a better illustration, T_g (together with the onset and end point of glass transition is summarized in Figure 2. The T_g of pure SMP, defined as the medium point of glass transition, is about 69 °C. The corresponding onset point and end point temperature of the glass transition of pure SMP is about 66 °C and 73 °C. According to the DSC results in Figure 1and Figure 2, with the increase of CB content, the glass transition shifts a little bit toward a lower temperature range, that is, T_g decreases slightly from 69 °C (CB0) to 56 °C (CB10). It indicates the slight chemical interaction between CB powders and SMP.

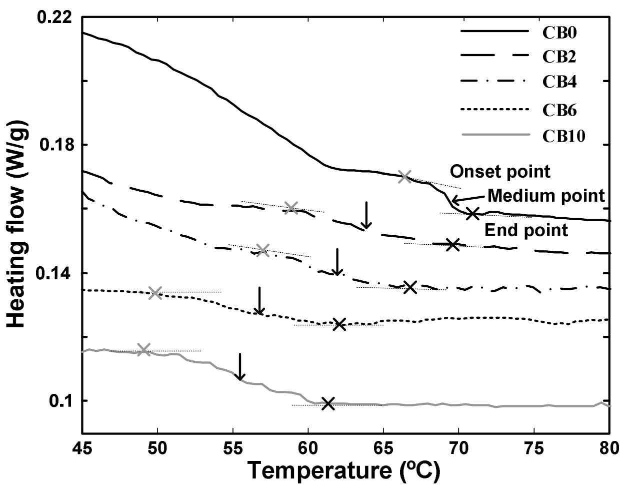

Figure 1 DSC results of SMP with various amount of CB

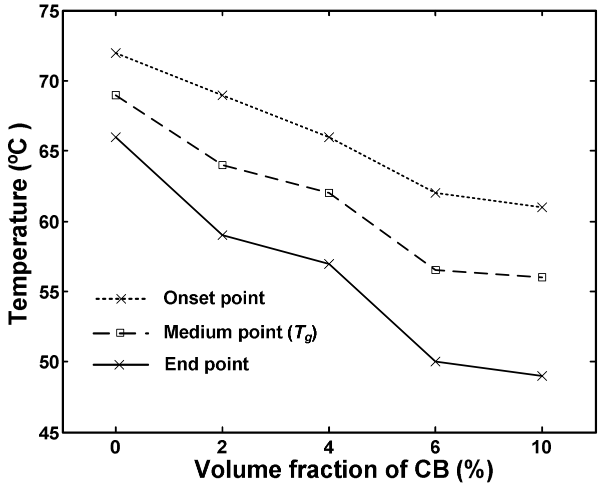

Figure 2 T_g against CB content

3.2 Electrical resistivity

In order to determine the electrical resistivity of thin films, samples were cut into the same dimensions (0.5×5×20 mm) with two copper electrodes clamped tightly on both ends along the length direction. The resistance was monitored by a digital multimeter (IDM91E). Subsequently, given the geometrical dimensions of samples, the corresponding electrical resistivity ρ is calculated by,

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

where R is the measured resistant, A the cross-sectional area of sample, L the length between two copper electrodes (refer to the top insert in Figure 3 for the setup of the resistivity measurement).

Figure 3 presents the electrical resistivity of SMP composites filled with different volume fractions of CB. It shows that the electrical resistivity in composite with less than 2% (volume fraction) of CB is extraordinary high. During this range, the SMP/CB composite can be treated as electrically insulating materials. By contrast, a sharp transition occurs between 2% to 6%, which is called the percolation threshold range [10]. The percolation threshold is a critical value, which indicates the transition of the material from insulating to conductive. For the SMP composites with a low volume fraction of CB (e.g., <3%), the carbon aggregates in the SMP matrix are relatively more separated, so that almost no conductive channel can be formed in the material. Hence, the electrical resistivity is very high. As the volume fraction of conductive filler approaches the percolation threshold (~3 vol% CB content), some carbon aggregates even directly contact with each other. Thus, the composite becomes much more electrically conductive. It results in a sharp decrease in the electrical resistivity with the increase of nano-carbon powder content. A further increase of volume fraction of carbon powders (>6%) reduces the gap slightly, and only a few more conductive channels are formed. Hence, reduction in resistivity is in a much gradual manner. For the practical application of SMP/CB composite, the high and stable electrical conductivity is required. Consequently, the SMP filled with CB at a higher content than 6 vol% is usually employed in the shape recovery test in our study.

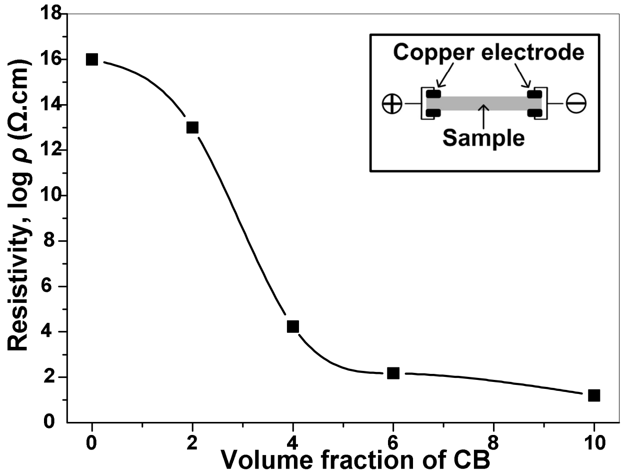

Figure 3 Resitivity vs. volume fraction of carbon black

3.4 Effects of temperature on the electrical resistivity

Normally, the temperature range in a practical engineering application of the SMP and its conductive composites is in the rage from room temperature to about 100°C. In the study, the electrical resistivity of SMP/CB composite (CB4, CB6, and CB10) was recorded against temperature (20~80 °C) measured by digital multimeter. The result is plotted in Figure 4. In the composite of CB6 and CB 10, there is no apparent evaluation in the electrical resistivity within this temperature range. By contrast, for the composite of CB4, the resistivity rises significantly when the temperature increases.

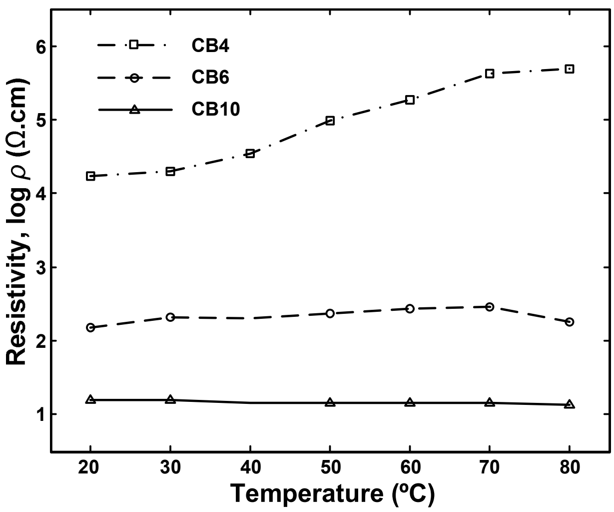

Figure 4 Evolution of resistivity upon heating

3.5 Demonstration of shape recovery by passing an electrical current

The SMP composite CB10 was cut into an ‘n’ shape for demonstrating the shape memory effect upon heating by passing an electrical current through it. The sample was cut into an ‘n’ shape. The sample can be easily bended at 70°C (above T_g). After switching off the electrical power and cooling back to room temperature of 22°C, the temporary pre-deformed shape was formed. Then, the sample was applied a voltage of 30 V through two conductive clampers. The sample began to deploy about 5 seconds right after heating by the electrical current. The whole deployment process lasts about 100 seconds. It obvious that the deployment velocity of sample in the range of 40~60 seconds is relatively higher than these in other time range.

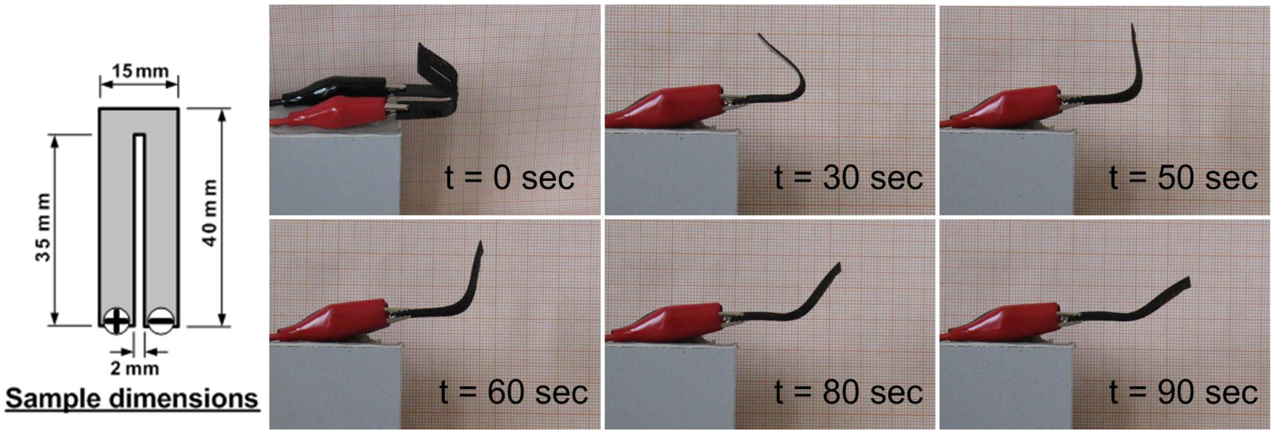

Figure 5 Sequences of shape recovery of CB10 by passing an electrical current (voltage, 30V)

4. Conclusions

A new system of thermoset styrene-based shape-memory polymer incorporated with different amounts of carbon black is fabricated. DSC test results indicated that the glass transition temperature shifts a little bit toward a low temperature range with the increasing of CB content. The SMP/CB composite shows good electrical conductivity with a percolation threshold about 3 %, which is much lower than many other polymer-based conductive composites. During the shape recovery demonstration, SMP/CB with 10 vol% CB shows good shape recovery performance by applying a voltage of 30 V.

References

[1].M. Behl and A. Lendlein, Mater. Today vol. 10, (2007), p. 20
[2].D.Ratna and J. Karger-Kocsis, J. Mater. Sci. vol. 43, (2008), p. 254
[3].Y. Liu, K. Gall, M. L. Dunn and P. McCluskey, Mechanics of Materials vol. 36, (2004), p. 929
[4].F. Ji, Yong Zhu, J. Hu, Y. Liu, L. Yeung and G. Ye, Smart Mater. Struct. vol. 15, (2006), p. 1547
[5].A. Lendlein, H. Y. Jiang, O. Junger and R. Langer, Nature vol. 434, (2005), p. 879
[6].W. M. Huang, B. Yang, L. An, C. Li and Y. S. Chan, Appl. Phys. Lett. vol. 86, (2005), 114105
[7].J. S. Leng, H. B. Lv, Y. J. Liu and S. Y. Du, Advanced Engineering Materials (In press).
[8].J. S. Leng, H. B. Lv, Y. J. Liu, and S. Y. Du, Appl. Phy. Lett. vol. 91, (2007), 144105
[9].J. S. Leng, W. M. Huang, X. Lan, Y. J. Liu, N. Liu, S. J. Phee, Q. Yuan and S. Y. Du, Appl. Phy. Lett. vol. 92, (2008), 014104
[10]. J. S. Leng, W. M. Huang, X. Lan, Y. J. Liu and S. Y. Du, Appl. Phy. Lett. (In press).