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Effects of moisture on the glass transition temperature of polyurethane shape memory polymer filled with nano-carbon powder

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Abstract

One simple approach to produce electrically conductive polymers is to fill them with conductive powders. This paper investigates the effects of moisture on the glass transition temperature of a polyurethane shape memory polymer (SMP) filled with nano-carbon powders. It is found that the SMP composites before immersion in water have a slightly lower glass transition temperature, and in the mean time, the moisture fraction at the saturation point upon immersion is also lower. On the other hand, the moisture can remarkably reduce the glass transition temperature of the composites. Heating to over 180 °C is an effective way to remove the moisture, which also results in the glass transition temperature back to the original. As the glass transition temperature can be greatly reduced by moisture, a novel feature, namely, the water actutable recovery of SMP composites is also proposed based on this study.

Keywords: Shape memory polymer; Glass transition temperature; Moisture; Carbon powder; Polyurethane; Functionally gradient; Electrically conductive

1. Introduction

Shape memory polymer (SMP) has drawn great attention from the research communities for its unique feature in the recovery of its original shape by heating [1,2]. One typical SMP is the polyurethane, which has a wide range of temperature for shape recovery, high recoverable strain (up to 400%) and low cost for manufacturing [3–5]. Previous researches on SMP polyurethane were mostly focused on its structure and thermomechanical properties [2–8]. More recently, Yang et al. [9] reported the moisture effects and based upon these findings, water actuated SMP polyurethane was proposed.

Conventionally, the shape recovery in a SMP is actuated by external heating. If the external heating process is not applicable, other mechanisms for triggering the shape recovery have to be considered. One of the possible choices is electrical current. However, since most polymers are electrically non-conductive, making them electrically conductive is the first task of all. Yang et al. [10] reported that a good conductivity could be achieved by filling SMP polyurethane with nano-sized carbon particles (cf. Fig. 1). As shown in our earlier study in [9], the moisture has a profound effect on the

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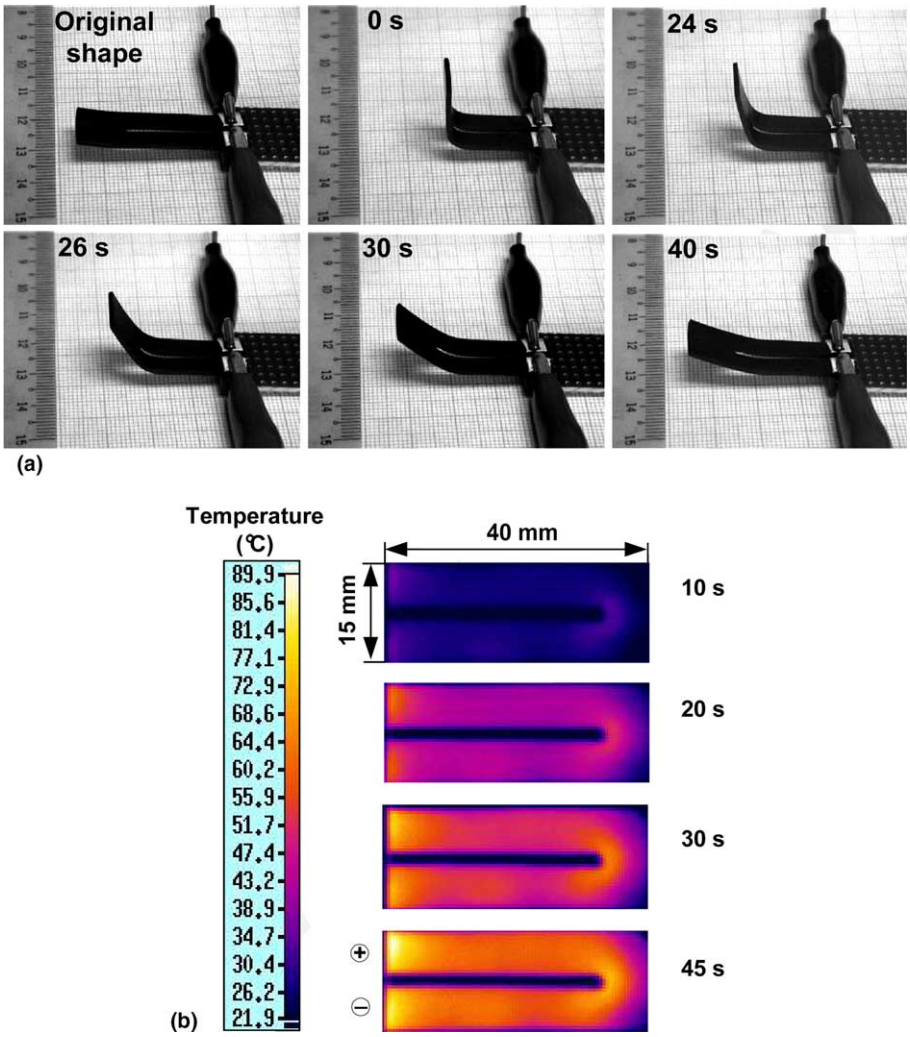

Fig. 1. Shape recovery in a SMP composite (with 13% nano-carbon powder in volume) by electrical current. (a) Shape recovery; (b) temperature distribution (taken by an infrared camera).

physical properties of polyurethane SMP. The main purpose of this paper is therefore to study the moisture effects on the thermal properties of carbon powder filled polyurethane SMP.

2. Materials and sample preparation

The polymer used in this study is SMP MM 5520 in pellet form bought from the Mitsubishi Heavy Industry (MHI). It is a thermoplastic polyurethane SMP prepared from diphenylmethane-4,4′-diisocyanate, adipic acid, ethylene glycol, ethylene oxide, polypropylene oxide, 1,4-butanediol and bisphenol A. According to the data provided by MHI, it has the glass transition temperature around 55 °C, melting temperature around 200 °C, and a bulk density of 1.25 g/cm^3. The carbon powders were made by the Degussa with an average diameter of 30 nm and density around 1.85 g/cm^3.

Before blended with carbon powders, the polyurethane SMP pellets were dried in a vacuum oven at 80 °C for 12 h. The polyurethane SMP pellets were then melted at 200 °C inside the mixing head of a Haake Rheocord 90. Carbon powders were added in and uniformly blended with the SMP. After mixing, the SMP composite was hot-pressed at 200 °C into sheets with a thickness of 2.0 mm. The SMP composites with volume fractions of 4%, 7%, 10%, 13% and 15% carbon powders were all prepared in this way. In this paper, we use CBX to denote the volume fraction of X% carbon powder. The volume fraction (φ_f) is determined by the following equation,

$$\varphi_f = \frac{1}{1 + (M_m/\rho_m)\cdot(\rho_f/M_f)} \cdot 100\% \quad (1)$$

where M_m, ρ_m, M_f, and ρ_f are the mass and bulk density of polyurethane SMP and carbon powder, respectively.

3. Thermal properties before immersion in water

The thermal stability of carbon powder filled polyurethane SMP composites was tested by the thermogravimetric analysis (TGA) using the Perkin Elmer TGA 7. The samples weighing 20–25 mg were heated at a constant heating rate of 20 °C/min in nitrogen atmosphere. The results are plotted in Fig. 2. It shows that the decomposition of pure polyurethane SMP (CB0) starts at about 260 °C. In general, with the addition of carbon powders the onset of decomposition temperature increases slightly and the full decomposition is increased to a higher temperature. It has been reported that the incorporation of nano-particles could improve the thermal stability of some polymer composites [11,12].

Differential scanning calorimetry (DSC) tests were carried out at a constant heating/cooling rate of 20 °C/min on the DSC 2920 (TA Instrument) to measure the glass transition temperature. The samples for DSC test were around 10 mg. Fig. 3 plots the DSC results of samples upon heating with the glass transition temperatures being marked. Noted that the glass transition temperature is taken at the median point in the range of glass transition. It reveals that the glass transition temperature decreases slightly with the increase of the carbon powder in volume fraction. A similar phenomenon has been reported in other polymer composites filled with nano-particles e.g. [13]. A possible explanation is that the added nano-particles change the kinetics of the glass transition and make it easier to proceed [13].

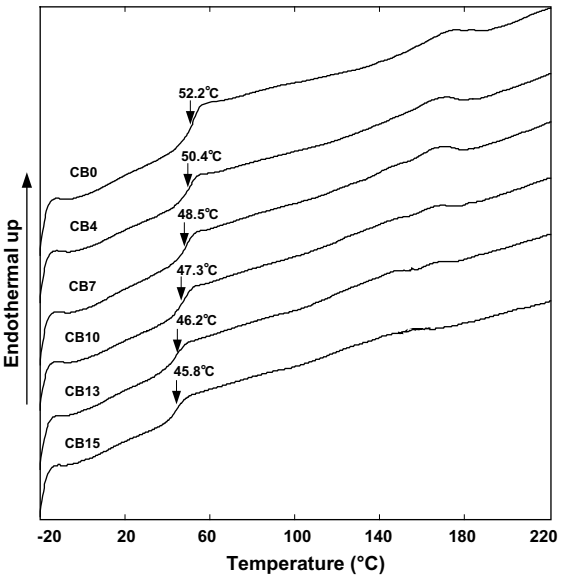

Fig. 3. DSC results of dry SMP composites upon heating.

4. Water absorption

In order to study the water absorption in the SMP composites, the hot pressed SMP composite sheets were immersed in room temperature water (about 25 °C). After different hours of immersion, these sheets were cut into small pieces for TGA test in order to determine the moisture fraction in them.

Fig. 4 presents one set of TGA results (CB13) after different hours of immersion. As we can see, a major weight loss is found in the range between 100 °C and 240 °C before decomposition. The weight-loss can be attributed to the evaporation of water absorbed in the SMP composite. For simplicity, we took the percentage

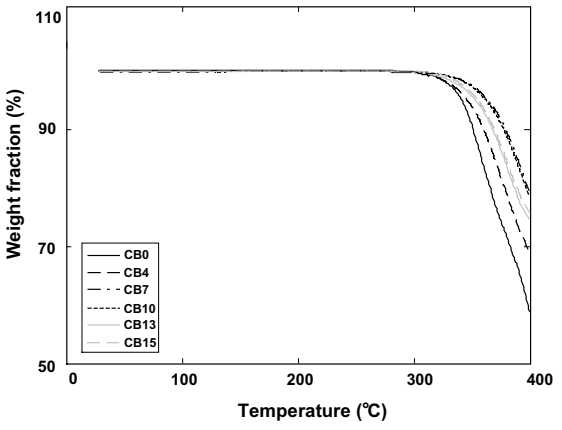

Fig. 2. TGA results of dry SMP composites with different volume fractions of carbon powders.

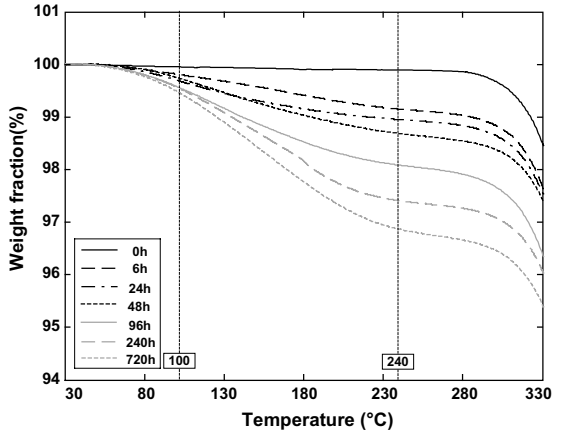

Fig. 4. TGA results of CB13 after different immersion hours in water.

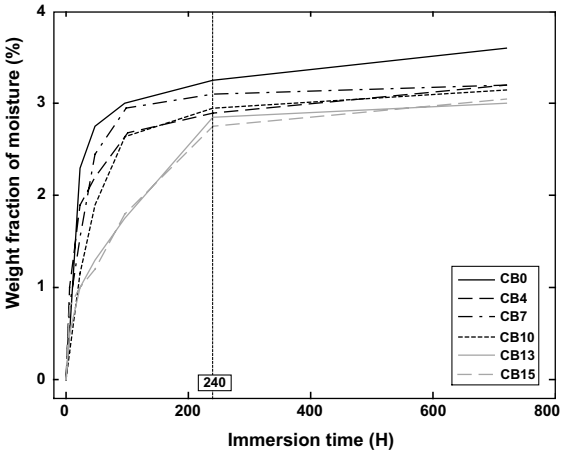

Fig. 5. Moisture fraction in weight % vs. immersion time.

of weight-loss at 240 °C as the total weight percentage of moisture being absorbed. It is also obvious that the moisture content in a SMP composite increases with longer immersion time.

Fig. 5 further summarizes the moisture fraction in weight % vs. immersion time of samples with carbon powders in different volume fractions. It shows that the increase of carbon powder tends to have less moisture loss in the SMP composites and the loss becomes relatively minor as the immersion exceeds 240 h. Note that the maximum moisture absorption (in weight %) in the pure polyurethane SMP is found at about 3.5% for CB0.

5. Glass transition temperature after immersion

The DSC tests were carried out as well on these samples immersed in water for different hours to examine the change of their glass transition temperatures. Fig. 6 plots the DSC results of CB13. It reveals that the glass transition temperature decreases remarkably with longer immersion time. Furthermore, the temperature range of glass transition is widened.

Relationships between the glass transition temperature of the SMP composites with different carbon powder contents and immersion time are summarized in Fig. 7. It shows that the glass transition temperature of all samples falls with the increase of immersion time following a similar trend. The decrease is significant at the beginning and then becomes mild for immersion over 240 h, which is consistent with the increase of moisture shown in Fig. 5.

The absorbed moisture can interact with the polymer acting as the plasticizer, which improves the mobility of polymer chains and results in the decrease of glass transition temperature [14]. With more moisture absorbed

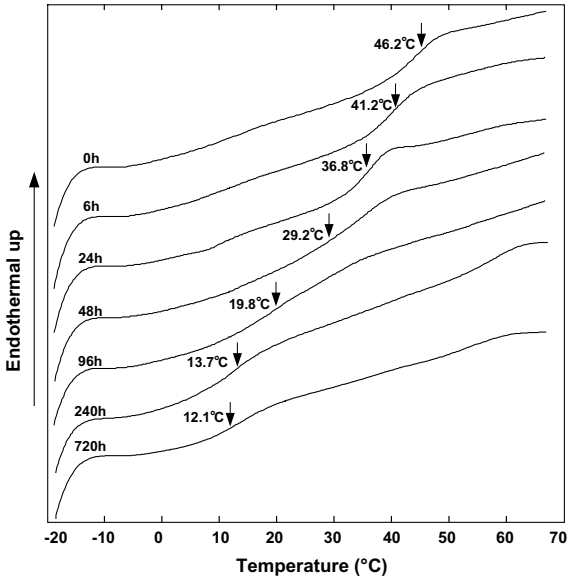

Fig. 6. DSC results of CB13 after different immersion hours in water.

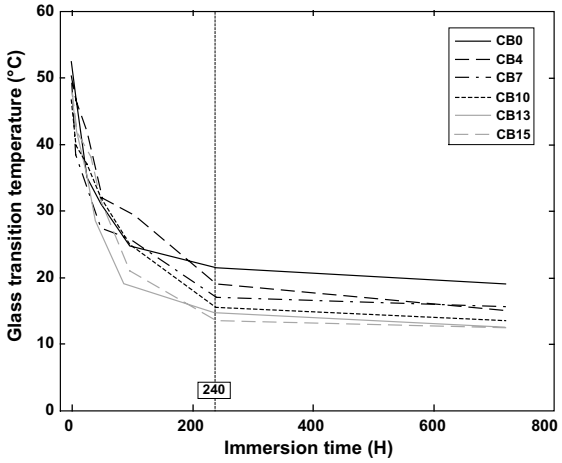

Fig. 7. Glass transition temperature vs. immersion time.

into the polymers, the glass transition temperature decreases further. This phenomenon holds valid until the polymer is saturated by water.

Fig. 7 also demonstrates that the added carbon powders have the tendency to lower the glass transition temperature. This is more obvious if the water content is high enough. For instance, the glass transition temperature of pure polyurethane SMP (CB0) at the saturation point (720 h) is about 20 °C higher than all other samples. The mechanism playing behind is complicate and beyond the scope of this study. However, it should surely involve the interactions among polymer chains, water molecules and carbon powders.

6. Recovery of glass transition temperature by thermal cycling

A very important question in materials processing and applications is whether the glass transition temperature can be reversed back to the original value of a dry condition by dehydrating as reported in [9]. In order to answer this question, cyclic DSC tests were carried out on the saturated SMP composites (720 h immersion). In each cycle, the sample was heated from −20 °C to a selected temperature and then cooled back to −20 °C at a constant rate of 20 °C/min. In each test, six temperatures, 80 °C, 100 °C, 140 °C, 160 °C, 180 °C and 240 °C, were selected for heating in an increase order.

Fig. 8(a) and (b) plot the cyclic DSC results of saturated CB13 and the zoom-in details. It is found that the glass transition temperature changes distinctly for both heating and cooling in the temperature range from 140 °C to 180 °C. Using the median point in the range of glass transition as, for instance, in Fig. 8(b), Fig. 9 summarizes the evolution of glass transition temperature upon thermal cycling for all composites. It shows that the most significant recovery occurs in the temperature range from 140 °C to 180 °C. Further heating beyond the melting point (~200 °C) can bring the glass transition temperature almost back to the original value, i.e., 55 °C in a dry condition. The added carbon powders lower down the glass transition temperature.

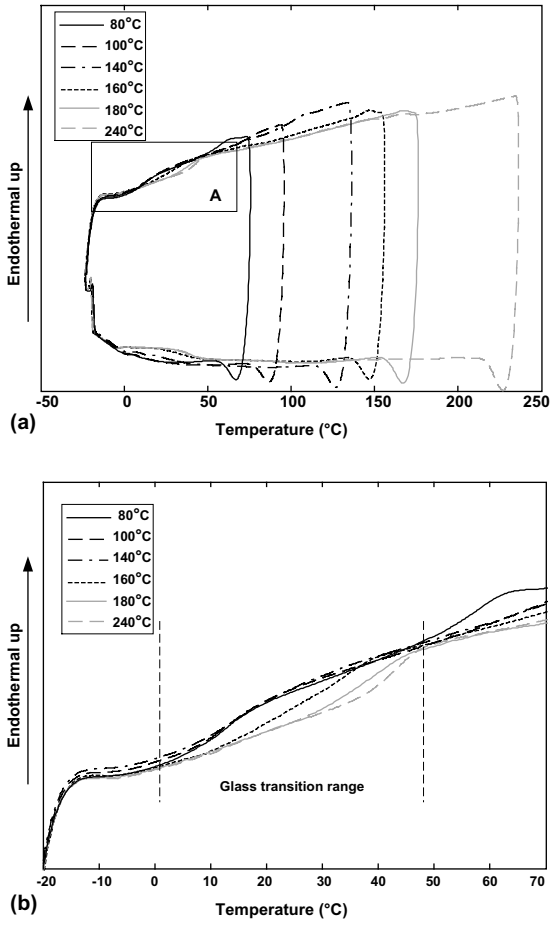

Fig. 8. Cyclic DSC results of saturated CB13. (a) Overall view; (b) zoom-in of A in (a).

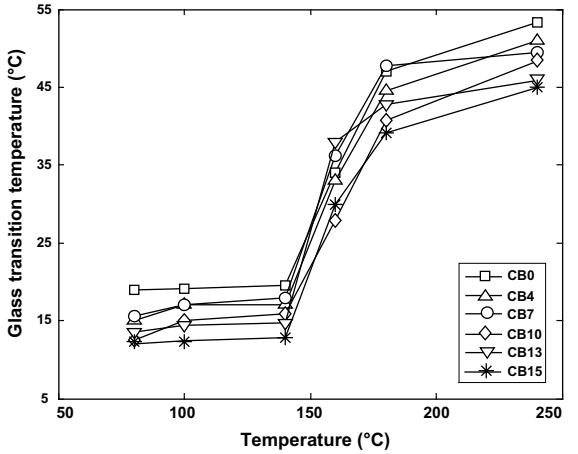

Fig. 9. Evolution of glass transition temperature upon thermal cycling.

Note that there is a significant part of moisture being removed at a temperature above 140 °C (Fig. 4). Since the moisture is removed only through evaporation, the whole process is reversible even for heating to near the melting point, i.e. the transition temperature can be reduced if samples are immersed in water again.

7. Application: water actuatable SMP composite

Since the glass transition temperature of the polyurethane SMP composites can be reduced by water immersion, we can therefore utilize this feature to design water actuatable SMP composites. The basic idea is to lower the glass transition temperature of SMP composites by moisture and to make them more flexible. Fig. 10 presents the recovery of a deformed dry sample (cut from the CB7 sheet with a thickness of about 0.15 mm) upon immersion in room temperature water. The sample was straightened corresponding to the decrease of glass transition temperature after 2 h of immersion. It demonstrates that a recovery can be actuated solely by water. Such mechanism can be further extended into designing functionally gradient SMP composites, which have a gradient glass transition temperature in various parts withheld by different content of moisture. The recovery of such material can thus be artificially controlled.

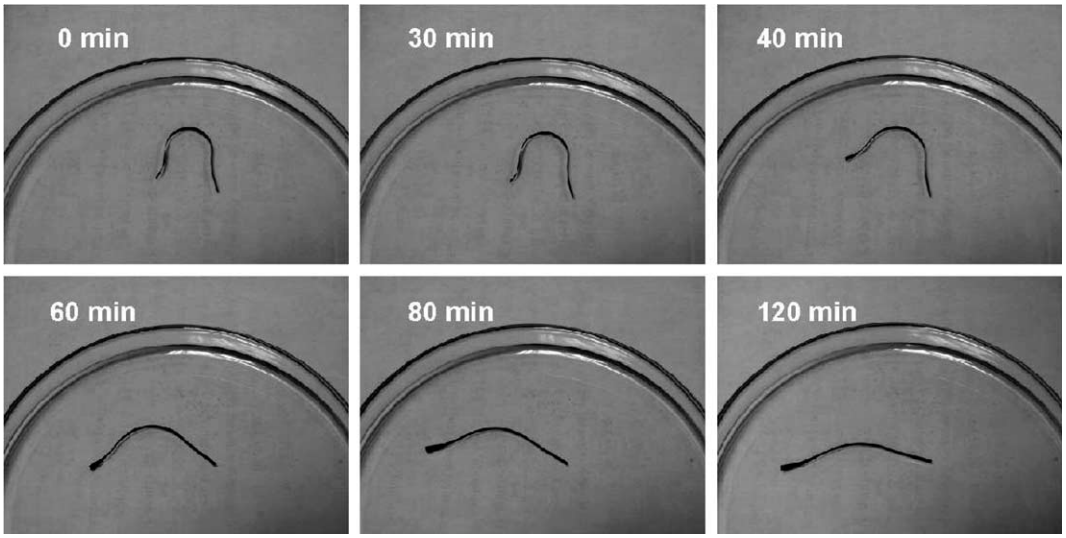

Fig. 10. Recovery of a CB7 sample actuated by room temperature water.

8. Conclusions

Electrically conductive SMPs can be fabricated by filling SMPs with nano-sized carbon powders. In this paper, we investigate the effects of moisture on the glass transition temperature of such composites. Experimental results show that the glass transition temperature can be reduced effectively by water immersion. The absorbed moisture interacts with the polymer chains and thus improves their mobility, resulting in the decrease of glass transition temperature. This phenomenon holds valid until the polymer is saturated by water. Moreover, results indicate that the added carbon powders have the tendency to lower the glass transition temperature. We also found the change of transition temperature is reversible by heating or dehydrating since the removal/absorption of moisture is only a physical process. As the glass transition temperature can be remarkably reduced by water immersion, a novel feature, namely, the water actutable recovery of SMP composites can be realized as shown in our demonstration. This feature can be further extended into the fabrication of SMP composites with a gradient transition temperature.

Acknowledgments

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References

[1] Lendlein A, Langer R. Science 2002;296:1673.
[2] Lee BS, Chun BC, Chung YC, Sul KI, Cho JW. Macromolecules 2001;34:6431.
[3] Yang JH, Chun BC, Chung YC, Cho JH. Polymer 2003;44:3251.
[4] Tobushi H, Yamada E, Hayashi S. Smart Mater Struct 1996;5:483.
[5] Tobushi H, Okumura K, Hayashi S, Ito N. Mech Mater 2001;33:545.
[6] Cho JW, Lee SH. Eur Polym J 2004;40:1343.
[7] Maitland DJ, Lee AP, Schumann DL, Silva LD. US Patent specification 2000: 6,102,917.
[8] Chiodo JD, Billett EH, Harrison DJ. In: Proc 7th IEEE Int Symp Electron Environ. Danvers, MA: IEEE Computer Society; 1999. p. 151.
[9] Yang B, Huang WM, Li C, Lee CM, Li L. Smart Mater Struct 2004;13:191.
[10] Yang B, Huang WM, Li C. Nano carbon powder filled shape memory polymer. In: The 1st International Symposium of Nanotechnology, Singapore, 13–17 July 2004.
[11] Zenga J, Saltysiakb B, Johnsonb WS, Schiraldic DA, Kumara S. Compos Part B Eng 2004;35:173.
[12] Gilman JW, Jackson CL, Morgan Jr AB, Manias E, Giannelis EP, Wuthenow M, et al. Chem Mater 2000;12:1866.
[13] Gall K, Dunn ML, Liu YP, Finch D, Lake M, Munshi NA. Acta Mater 2002;50:5115.
[14] Sperling LH. Introduction to physical polymer science. New York: Wiley; 1986.