

Electroactive Shape Memory Cyanate/Polybutadiene Epoxy Composites Filled with Carbon Black

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Abstract Electroactive shape memory composites were synthesized using polybutadiene epoxy (PBEP) and bisphenol A type cyanate ester (BACE) filled with different contents of carbon black (CB). Dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), electrical performance and electroactive shape memory behavior were systematically investigated. It is found that the volume resistivity decreased due to excellent electrical conductivity of CB, in turn resulting in good electroactive shape memory properties. The content of CB and applied voltage had significant influence on electroactive shape memory effect of developed BACE/PBEP/CB composites. Shape recovery can be observed within a few seconds with the CB content of 5 wt% and voltage of 60 V. Shape recovery time decreased with increasing content of CB and voltage. The infrared thermometer revealed that the temperature rises above the glass transition temperature faster with the increase of voltage and the decrease of resistance.

Keywords: Electroactive shape memory behaviors; Cyanate ester; Carbon black; Electrical performance.

INTRODUCTION

Shape memory polymer (SMP) is a new type of intelligent polymer. It can rapidly recover from a temporary shape with an appropriate stimulus such as temperature, specific ions, electron, pH, magnetic field, or enzyme^[1–8]. Compared with shape memory alloy and shape memory ceramic, SMP possesses the merits of light weight, low cost, good processing, high deformation speed and tailored transition temperature^[9–13]. Since the 1990s, SMPs have been rapidly developed and widely applied in smart textiles and apparels^[14], intelligent medical treatments^[15, 16], and self-deployable structures in spacecrafts^[17].

Nevertheless, there are still some technical barriers which prevent wide spread applications of SMPs. For instance, SMPs have relatively low recovery stress due to low rubbery modulus (0.1 MPa to 10 MPa), low recovery rate primarily due to poor thermal conductivity and inertness to electrical and magnetic stimuli (in contrast with SMAs), due to the electrical insulation of most polymeric materials^[18]. A common and useful method to improve mechanical and shape recovery properties is introducing inorganic fillers, especially nanoparticles with high modulus into SMPs. Various inorganic fillers such as hydroxyapatite^[19], carbon nanotubes (CNTs)^[20–22], Fe₃O₄^[23–25], SiO₂^[26], nanoclay^[27] have been studied about their effects on the mechanical and shape memory properties of SMPs. Additionally, the electroactive shape memory composites filled with electrically conductive filler are much more popular because of their better controllability, remote drive and fast shape recovery rate. Jinsong Leng *et al.*^[28] prepared electroactive thermoset styrene based shape memory polymer (SMP) nanocomposites filled with nanosized (30 nm) carbon powders. The results showed that the SMP composites present good electrical conductivity with a percolation of about 3.8 vol%. And due to the

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relatively high electrical conductivity, a sample filled with 10 vol% nanocarbon powders shows good electroactive shape recovery performance when being heated by a voltage of 30 V.

It has been proven that bisphenol A type cyanate ester (BACE, Scheme 1a)/polybutadiene epoxy (PBEP, Scheme 1b) copolymer is of excellent shape memory effect^[29], and the reaction formulas between BACE and PBEP are shown in Scheme 1(c). Moreover, CB is considered as ideal reinforcing filler for high performance polymeric composites due to its excellent electrical properties. Therefore, various properties, especially electroactive shape memory effect of PBEP/BACE/CB composites are investigated in this paper. The results showed that the composites obtained exhibit excellent electroactive shape memory effect by passing electrical currents.

EXPERIMENTAL

Materials

The materials for preparing PBEP/BACE/CB composites were as follows. BACE was of white powder with purity of more than 99.5% and molecular weight of 278 g/mol, obtained from Zhejiang Victory Biological Chemical Co., Ltd. PBEP was of amber sticky liquid with the viscosity average molecular weight of 2500 g/mol and the epoxide number of 0.817, purchased from Wuhan ShiZiShan Paint Manufacture Co., Ltd. CB (Ketjenblack®, EC-600JD), with particle size less than 125 µm, was obtained from AkzoNobel. These materials were used without further purification.

Preparation

The method for preparing PBEP/BACE/CB composites was as follows. BACE and PBEP were mixed with the mass ratio of 1:0.8 to form a polymer matrix. 3 wt% CB was added to form a homogeneous mixture. After stirred in oil bath equipped with a magnetic stirrer for 40 min at 80 °C, the mixture was put into the oven at 80 °C for 4 h to obtain prepolymer. The prepolymer were cured in a PTFE mould at elevated temperatures, *i.e.* 80 °C/30 min +100 °C/2 h +120 °C/1 h +160 °C/30 min. During the first two hours of molding process, the pressure was slowly raised to 8 MPa. Then PBEP/BACE/CB composites samples were obtained with the thickness of approximately 4.0 mm. BACE/PBEP/CB composites with CB of 5 wt%, 8 wt% and 10 wt% were fabricated in the same way. For comparison, a pure SMP specimen was prepared under the same conditions.

Characterization

Electrical conductivity tests

The volume resistivity of all types of samples was investigated using a simple circuit. A modern digital multimeter (UT61E) was applied directly on the samples.

The volume resistivity is calculated by:

$$\rho = R \frac{A}{L}$$

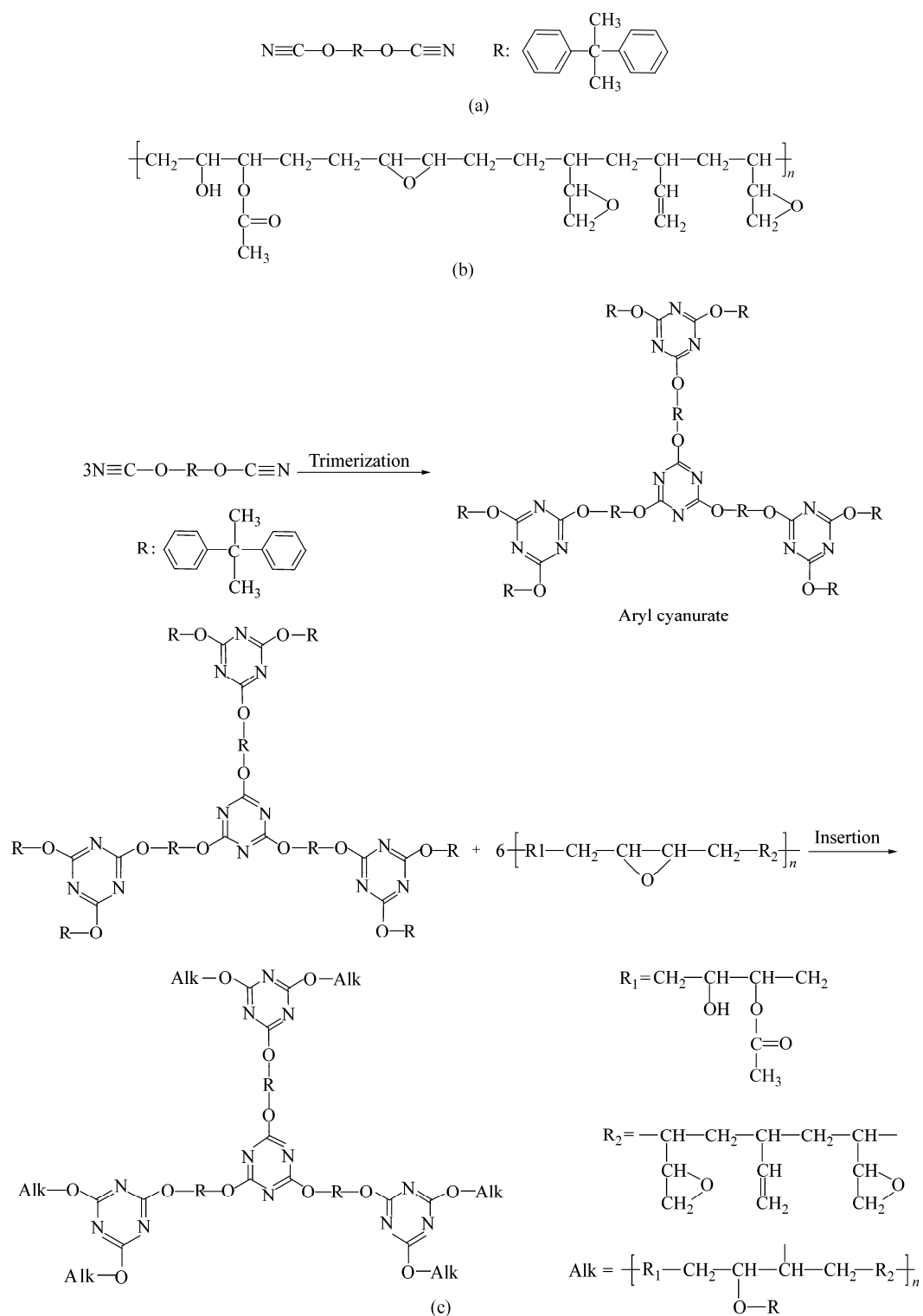
where R is the resistance, L is the length of the sample (8 cm), A is the contact area between the electrode and composites (1.5 cm × 0.4 cm), and ρ is the volume resistivity.

Scanning electron microscopy (SEM)

The samples were frozen in nitrogen for 30 min and then quickly impact fractured. The freshly broken surfaces were sputter coated with gold and then observed with SEM (INCA-ACT).

Dynamic mechanical analysis (DMA)

DMA sample dimensions were 3 mm × 10 mm × 35 mm. The glass transition temperature (T_g) and storage modulus (E') were determined using an instrument TA Q800 in single cantilever clamping fixture. The temperature was ranged from 25 °C to 260 °C at a frequency of 1 Hz and a heating rate 3 K/min.



Scheme 1 Schematic chemical structures of (a) BACE, (b) PBEP, (c) Curing chemistry of shape memory BACE/PBEP copolymer

Electroactive shape memory tests

The specimens (80 mm × 10 mm × 4 mm) were used to evaluate the electroactive shape memory properties of BACE/PBEP/CB composites. Electroactive shape memory tests were conducted under the following procedures. (i) Heat up the specimen to the transformation temperature (T_{trans} , $T_{\text{trans}} = T_g + 20\text{ }^{\circ}\text{C}$) above the T_g in an oven for 5 min for full heating. (ii) As it is shown in Fig. 1, the samples were deformed to an angle θ_i ($\theta_i = \Pi$) and rapidly quenched in cold water. Consequently, the deformation was restored. (iii) The electroactive shape memory effect was observed when a constant voltage was applied. When the angle did not change any more, the shape recovery time was recorded and the applied voltage was removed. The shape recovery rate at corresponding temperature is defined as $(\theta_i - \theta_f)/t \times 100\%$, and the shape recovery ratio is defined as $(\theta_i - \theta_f)/\theta_i \times 100\%$.

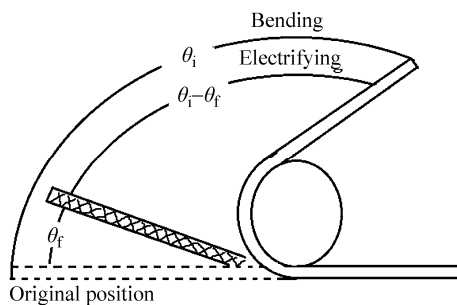


Fig. 1 Deformation model of shape memory effect

Thermo-gravimetric analysis (TGA)

The thermo-gravimetric analysis (TGA) was performed using the TGA Q50 thermo-gravimetric analyzer. The samples were about 10 mg. The temperature was ranged from 20 °C to 500 °C with a heating rate 10 K/min.

RESULTS AND DISCUSSION

Electrical Properties

The influence of carbon black on the resistance and volume resistivity of BACE/PBEP/CB composites was investigated, and the results are displayed in Table 1. As expected, the volume resistivity of BACE/PBEP/CB composites decreased progressively with increasing carbon black loading. The volume resistivity of composites with 3% weight fraction of carbon black is extraordinary high ($216 \times 10^3 \Omega \cdot \text{cm}$). In contrast, a sharp transition of volume resistivity occurs between 5 wt% and 8 wt%. Meanwhile, it is noted that the conductivity of composites is dependent on many factors, the size, shape, and type of hybrid fillers. But, the amount of the conductive filler is the most important influential factor in this study.

In order to further the analysis of conductive network of the composites, the SEM was used to observe the dispersion of CB. As shown in Fig. 2. The carbon black particles in the BACE/PBEP/CB composites with 3 wt% carbon black are more separated, so very few conductive channels formed in the composites. As the mass ratio of carbon black is increased, some carbon black aggregates even directly contact with each other and have a higher tendency to form conductive networks in the composites. Thus, the composites become much more electrically conductive.

Table 1. Resistance and volume resistivity of the composites

Samples	$R (\Omega)$	$\rho (\Omega \cdot \text{cm})$
3 wt% CB/CE/PBEP	3×10^6	216×10^3
5 wt% CB/CE/PBEP	2×10^3	150
8 wt% CB/CE/PBEP	305	23
10 wt% CB/CE/PBEP	150	11

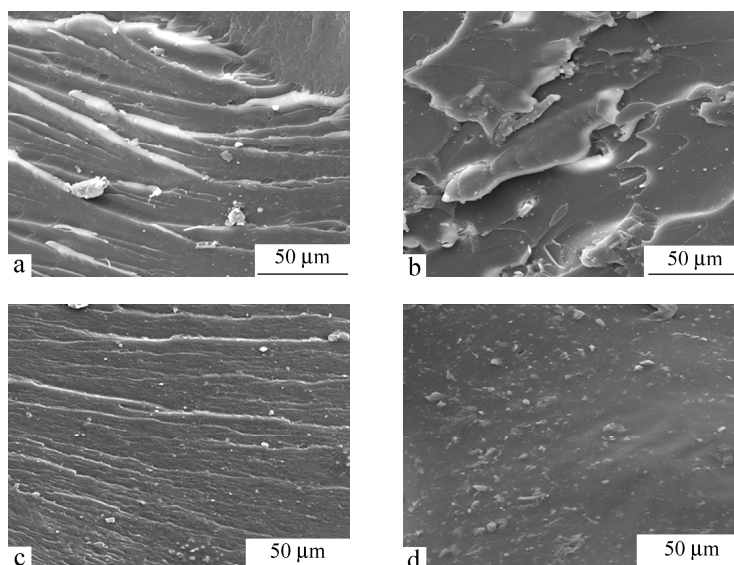


Fig. 2 SEM images of the distribution of carbon black in the SMP matrix: (a) CB, 3 wt%, (b) CB, 5 wt%; (c) CB, 8 wt% and (d) CB, 10 wt%

DMA

In order to determine the T_{trans} for electroactive shape memory test, T_g of different samples was investigated by DMA, and DMA curves of BACE/PBEP/CB composites are shown in Figs. 3 and 4. The curves showed that the T_g shifted toward higher temperatures with increasing content of CB. The obtained T_g of 3 wt%, 5 wt%, 8 wt% and 10 wt% BACE/PBEP/CB composites are 135, 141, 143 and 147 °C, respectively. On the one hand, it is the increasing stiffness effect of CF that enhances the rigidity of the composites. There is a certain free volume in the polymer according to free volume theory^[30]. The free volume was occupied incorporating CB and the movement of molecular chain was hindered. On the other hand, as increasing content of CB, adhesion/sorption of the molecular chains hampered the mobility of the molecular chains. Therefore, the T_g increased. However, the T_g of BACE/PBEP/CB composites change slightly.

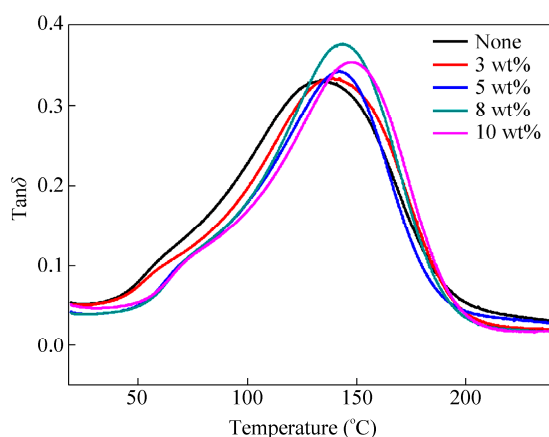


Fig. 3 Tanδ versus temperature of BACE/PBEP/CB composites

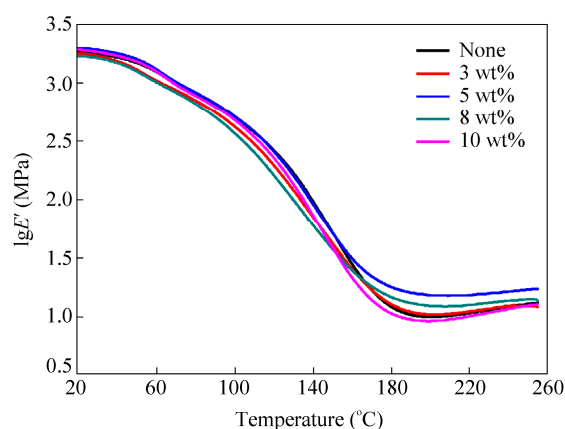


Fig. 4 Storage moduli versus temperature of BACE/PBEP/CB composites

Moreover, it was generally recognized that the prominent shape memory materials must have a stable high-elastic state, and the storage modulus usually changes by about two orders of magnitude when the ambient temperature varied^[31]. Figure 4 illustrates that the storage moduli of BACE/PBEP/CB composites below T_g are

about two orders of magnitude larger than that above T_g . For instance, the 3 wt% BACE/PBEP/CB composites exhibit the storage modulus of 1796 MPa at 40 °C, while it is just 15 MPa at 200 °C. Moreover, compared to the neat resin system, slight increase of storage moduli is observed at low temperatures (below T_g), meaning that the incorporation of CB increases the storage moduli of the composites in glass state. The effect of storage moduli may be attributed to the stiffness effect of CB.

Electroactive Shape Memory Properties

The detailed electroactive shape memory performances including shape recovery time and shape recovery ratio versus the cycling times are revealed in Fig. 5 and Table 2. Figure 5 shows a whole and clear shape recovery procedure of BACE/PBEP/CB composites with 8 wt% CB. The sample began to deploy within about 5 s under voltage of 40 V. It undergoes the transition from the temporary shape ($t = 0$ s) to the permanent shape ($t = 68$ s) within 68 s. In addition, it was obvious that the shape recovery rate of SMP composites in the range of 0–25 s was relatively higher than that in other time ranges. This simple shape deformation and fast recovery process demonstrate excellent shape memory effect and it can be used in electro-sensitive actuators.

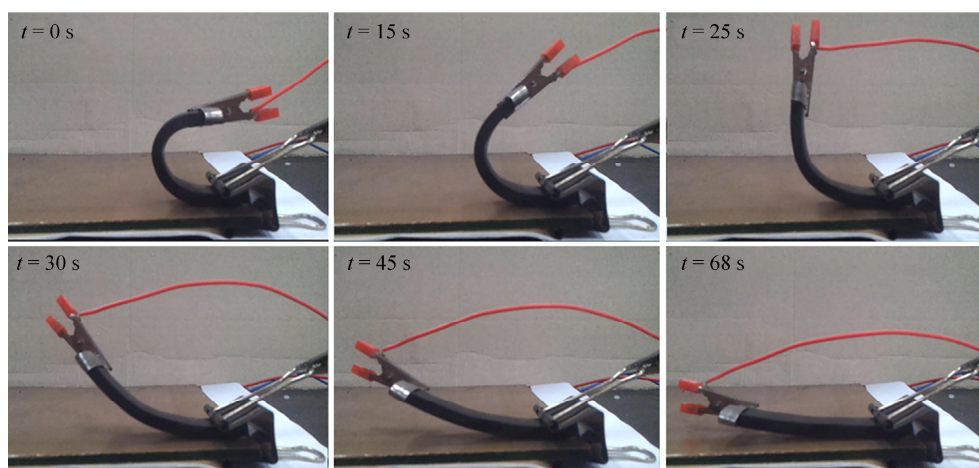


Fig. 5 Electroactive shape-recovery behavior of composites with 8 wt% CB on passing an electrical current (voltage-40 V)

Table 2. Shape recovery time of the composites under different voltages

Samples	20 V	40 V	60 V	80 V	100 V	120 V
3 wt% CE/PBEP/CB	—	—	—	—	—	—
5 wt% CE/PBEP/CB	—	—	299 s	143 s	91 s	62 s
8 wt% CE/PBEP/CB	371 s	109 s	43 s	27 s	11 s	4 s
10 wt% CE/PBEP/CB	209 s	98 s	30 s	21 s	6 s	2 s

Earlier reports revealed that electroactive shape memory behavior was triggered at lower weight percentages on loading rigid long aggregate carbon nanostructures such as carbon nanofibers or carbon nanotubes due to the formation of conductive network^[32–35]. When passing an electrical current, The SMP composites exhibit the shape memory effect upon heating generated by the CB conductive network. Therefore, as shown in Table 2, the composites with 3 wt% content of carbon black cannot recover to the initial shape under any voltage. Because the heat generated is not sufficient to trigger the shape memory recovery. Similarly, the composites with 5 wt% CB exhibit shape recovery effect when the voltage is more than 60 V. Moreover, it can be found that the shape recovery time of the composites decreases with the increment of the voltage. The 10 wt% BACE/PBEP/CB composites undergo the shape recovery within 21 s when the voltage rises to 80 V. And, it can recover instantaneously within 6 s when the voltage rises to 100 V.

What's more, in order to analyze the changes of temperature with changes of the voltage and the resistance in electroactive shape memory tests, we test temperature changes of samples with different resistances under

different voltages using infrared thermometer, as shown in Figs. 6, 7 and 8. It can be seen from the figures, all the temperature changes showed the same trend of slow increase first and rapid linear increase later. And with the increase of voltage and the decrease of resistance, the temperature rises above the glass transition temperature faster. According to Joule's law, the heat generated by the conductor is in the direct ratio with the square voltage and the time, and is inversely proportional to the resistance, as shown by the following formula:

$$Q = \frac{U^2 t}{R}$$

where Q is the heat (J), U is the voltage (V), R is the resistance of the material (Ω) and t is the time (s). As you can see from the formula, within the same time and the increase of applied voltage, the heat generated by the composites of the same resistance increased, so the temperature of the sample rises quicker and easier to be above the glass transition temperature. At the same time, the electrical resistance will decrease with increasing the content of carbon black, which also can generate more heat and raise the temperature much faster.

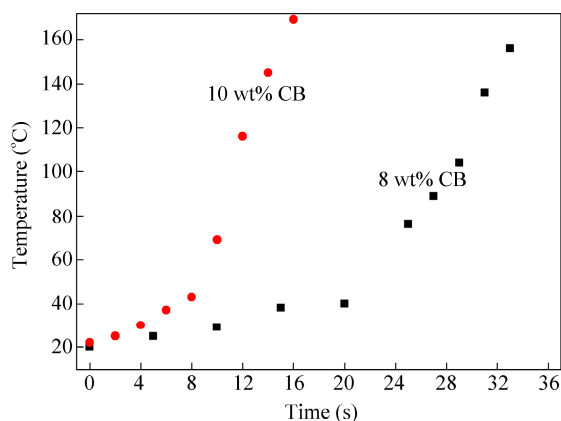


Fig. 6 Temperature of shape memory composites versus time (voltage-60 V)

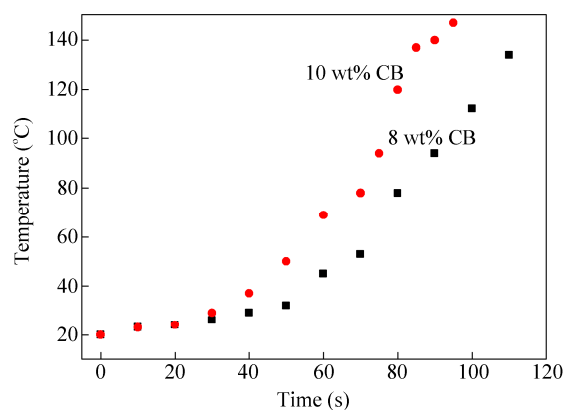


Fig. 7 Temperature of shape memory composites versus time (voltage-40 V)

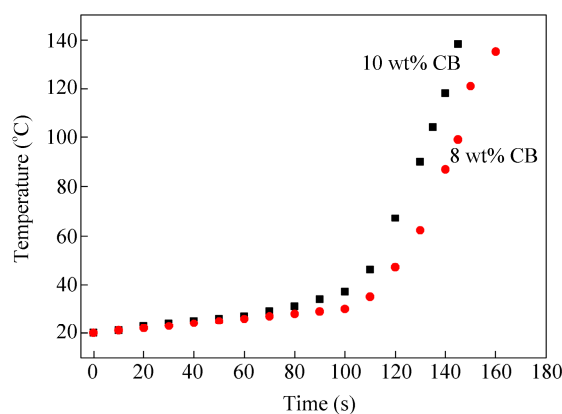


Fig. 8 Temperature of shape memory composites versus time (voltage-20 V)

TGA

The heat resistant properties of the BACE/PBEP/CB composites were evaluated by TGA, and the results are shown in Fig. 9. The TGA curves show that the initial decomposing temperature and maximum decomposing temperature of the BACE/PBEP/CB composites are about 350 °C and 450–500 °C. With increasing the content of CB, both the initial decomposing temperature and the maximum decomposing temperature shifted toward

higher temperatures. This result indicates excellent heat resistant properties of the composites. In addition, it can be seen from the figure that the char yield increased and the thermal decomposition rate at higher temperatures reduced. Therefore, the heat resistance was improved by incorporation of carbon black.

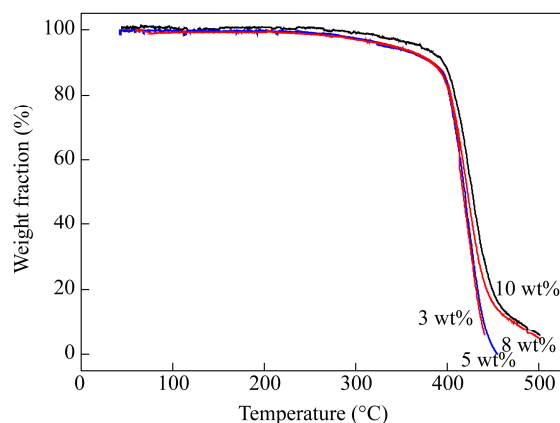


Fig. 9 The TGA curves of BACE/PBEP/CB composites

CONCLUSIONS

In this work, electroactive shape memory BACE/PBEP/CB composites were fabricated. The mechanical, thermal, electrical properties and electroactive shape memory performance were investigated systematically. With increasing content of CB, the glass transition temperature of the SMP composites shifted slightly toward high temperature range. And the similar trend is observed in their storage moduli. Due to the electrical conductivity and well dispersion of CB in the matrix, the composites show good electrical conductivity, which in turn results in the excellent electroactive shape memory behaviors. And the shape recovery rate of the composites increases with increasing content of CB and voltage but the shape recovery ratio decreases slightly with increasing cycling times. The polymer synthesized in this study is suitable for processing good electroactive shape memory composites and is potentially applicable in manufacturing intelligent materials and sensors.

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