# Polyurethane/Conducting Carbon Black Composites: Structure, Electric Conductivity, Strain Recovery Behavior, and Their Relationships

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ABSTRACT: The polyurethane composites with conducting carbon black (CB) were prepared by a solution-precipitation process, which was followed by melt compression molding. The polyurethane used has good shape memory effect. The morphology of CB fillers in polyurethane matrix and the resulting conductivity of the composites were investigated. It has been found that CB fillers exist in the forms of aggregates. The percolation threshold is achieved at the CB concentration of 20 wt %. The presence of CB fillers decreases the degree of crystallinity of polycaprolactone (PCL) soft segments of the polyure thane. However, the composites still have enough soft-segment crystals of polyurethane to fulfil the necessary condition for the shape memory properties. Dynamic mechanical data show that CB is an effective filler for the reinforcement of the polyurethane matrix, but does not deteriorate the stable physical cross-link structure of the polyurethane, which is necessary to store the elastic energy in the service process of the shape memory materials. Addition of CB reinforcement in the polyurethane has influenced the strain recovery properties, especially for those samples with CB concentrations above the percolation threshold. The response temperature of the shape memory effect  $T_{\rm r}$  has not been affected too much. Strain fixation  $S_{\rm fr}$  which expresses the ability of the specimens to fix their strain, has been improved in the presence of the CB fillers. The final recovery rates  $R_{f}$  and strain recovery speeds  $V_{r}$  of the shape memory measurements, however, have decreased evidently. It is expectedly ascribed to the increased bulk viscosity as well as the impeding effect of the inter-connective structure of CB fillers in the polymer matrix. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 68-77, 2000

**Key words:** polyurethane; composite; conducting carbon black (CB); shape memory properties; conductivity

## **INTRODUCTION**

Polymer composites with conducting carbon black (CB),<sup>1-6</sup> which may serve as polymer conductors

Journal of Applied Polymer Science, Vol. 75, 68–77 (2000) © 2000 John Wiley & Sons, Inc. CCC 0021-8995/00/010068-10 or semi-conductors or the media for heat transferring, have found a lot of applications in the fields of electric and electronics industry. The advantage of conductive polymeric composites is their plastic nature, which makes it easy to prepare various forms of products by using conventional processing techniques and hence reduces the manufacturing costs. The products generally are able to combine high electric conductivity with the favorable properties of polymer materials.

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tion of China (NNSFC).

Recently, we reported our research on a series of segmented polyurethanes with shape memory properties.<sup>7-11</sup> Shape memorable polymer is a special kind of functional material that may remember its original shape when it is deformed. This means the strain of shape memory polymers can be fixed after deformation and then recovered almost completely under appropriate conditions, for example, under heating. In this sense, they are thermally stimulated shape memory materials. We are herein interested in the composites of these functional polymers with CB fillers, which hopefully may display both the shape memory properties of the polyurethane and the conductivity of the CB fillers. These materials potentially can be used in a variety of industry applications where high conductivity and shape memory properties are the important parameters. So, we produced a series of such composites. Effect of the structures on the conductivity and shape memory properties was studied in this paper.

# **EXPERIMENTAL**

#### Materials

Segmented polyurethanes were obtained by a two-step method involving endcapping the hydroxy-terminated polycaprolactone (PCL) with 4,4'-diphenylmethane diisocyanate (MDI), followed by reaction in solution with the chain extender 1,4,-butadendiol (BDO). Samples of different soft and hard segment lengths were synthesized. Based on previous results,<sup>10,11</sup> the polyurethane chosen in this work has the PCL molecular weight of 7,000 and hard segment concentration of 18.7% by weight. The intrinsic viscosity is 1.01, which was measured in N,N'dimethylformide (DMF) at 30°C. Conducting carbon black (CB) (Sichuan Petro-gas Co. Ltd) used in this work has the average size of 50-90 nm, surface area of 240 m<sup>2</sup>/g, and pH value of 7–9 and was used as received.

#### **Sample Preparation**

A solution-precipitation process was used to mix polyurethane and CB.<sup>12</sup> Polyurethane was first dissolved in its solvent DMF at 60°C. Then a certain amount of CB was added into the polyurethane under stirring at 600 rpm. After 30 min, the suspension solution was poured into a surplus of distilled water. The mixture of polyurethane/CB was able to promptly precipitate from the water. The precipitated mixture was palletized and dried under vacuum. The composite samples were subsequently made by compression molding of the dried pellets at 180°C. The specimens were stored in a dessicator at room temperature prior to measurements. The samples are generally named PU-CBXX, which means the composites are made of polyurethane (PU) and conducting carbon black (CB) with the filler content of XX% by weight. PU-CB00 refers to the pure polyurethane.

#### Characterizations

The melting and crystallization behavior was studied by using a Perkin-Elmer DSC-4 apparatus purged with nitrogen in a cooling and heating process. The scanning rate was 20°C/min. The temperature was calibrated by indium. The degree of crystallinity was calculated from the enthalpy datum  $\Delta H_{\rm C}$  of the crystallization peak for the PCL component of the polyurethane in the composites by using an enthalpy value for fusion of 100% crystalline PCL, 32.5 cal/g, given by Crescenzi et al.<sup>13</sup>

Dynamic mechanical data were obtained at 10 Hz in a tension mode by using a Dynamic Mechanical Thermal Analyzer MK III of Rheometric Scientific Ltd. Thin sheet specimens of 20 mm length and 3 mm width were used, and their thickness was about 0.3 mm. The measurements were carried out at a heating rate of  $3^{\circ}$ C/min purged with N<sub>2</sub>.

The fracture topography and the dispersed structure of the fractured specimens were studied using a scanning electron microscope (SEM S-530). The composite specimens were fractured in liquid nitrogen. The surfaces of the specimens were coated with gold prior to SEM observations.

The room temperature conductivity measurements were performed on the composites using the four-point probe technique.<sup>14</sup> The cross-sectional area of each test piece was measured. A known current was then passed through the outer two electrodes, and the voltage drop across the middle two electrodes was measured.

Specimens for strain recovery measurements were prepared according to a diagram given in Figure 1. The compression molded film (point A) is first heated to temperature  $T_{\rm D}$  (80°C in this work), above the melting point of PCL crystals in the polyurethane (point B). The film is stretched at this temperature to a strain  $\varepsilon_1$  (point C) and



**Figure 1** Diagram of preparation procedure of specimens for strain recovery measurements and recovery curves.

then cooled down immediately to a setting temperature  $T_{\rm s}$  under constrained conditions of constant length. That corresponds to the point D in the graphic. In this work, room temperature,  $T_{\rm rt}$ , was chosen as the setting temperature. When the external force is withdrawn, a contraction may occur, and the strain changes from  $\varepsilon_1$  to  $\varepsilon_2$ .  $\varepsilon_2$  is the fixed strain, which means that the film specimen moves from point D to point E. The specimen at point E is then used for studying the strain recovery behavior in a process of constant heating rate.

The strain recovery effect of the specimens in a heating process was directly measured under an Olympus BHSP polarizing microscope equipped with a hot stage. The heating rate was about  $2.7^{\circ}$ C/min. The recovery process can be expressed by the temperature dependence of the strain  $\varepsilon(T)$ or the recovery rate R(T), the percentage of the recovered strain at temperature T in the total fixed strain (see Figure 1).

$$R(T) = \frac{\varepsilon_2 - \varepsilon(T)}{\varepsilon_2} \tag{1}$$

Some important parameters are usually obtained from these measurements to characterize the shape memory behavior of the specimens. The strain fixation  $S_{\rm f}$  expresses the ability of the specimens to fix their strain and is defined as  $S_{\rm f}$ =  $\varepsilon_2/\varepsilon_1$ . As shown in Figure 1, the final recovery rate  $R_{\rm f}$  shows the recovery ability of the sample. The temperature  $T_r$  related with 50%  $R_f$  is called the response temperature, and a parameter  $V_r$  is used to characterize the speed of the recovery process, which is defined as

$$V_{\rm r} = \frac{0.8R_{\rm f}\varepsilon_2}{T_{90} - T_{10}} \cdot \frac{dT}{dt}$$
(2)

where  $T_{10}$  and  $T_{90}$  are the temperatures corresponding to the recovery rate of 0.1  $R_{\rm f}$  and 0.9  $R_{\rm f}$  in the recovery curve, and dT/dt is the average heating rate of the recovery measurements.

### **RESULTS AND DISCUSSION**

Figure 2 shows the dependence of the room temperature conductivity on the CB content of the composites. In the samples with lower level of CB fillers, e.g., less than 10 wt %, the electric conductivity is beyond the measurements of this technique.<sup>14</sup> Generally, the conductivity increases slowly at low loading of CB fillers. There is a dramatic increase in the electric conductivity at the filler content of approximately 20 wt %, which corresponds to the percolation threshold as the conducting pathways throughout the polymer are being established. When the CB concentration further increases, the electric conductivity levels off. The percolation threshold for the conductivity



**Figure 2** Relationship between room temperature electric conductivity and the CB concentrations in the composites.



**Figure 3** Temperature dependence of electric conductivity of the specimen PU-CB30.

of nonpolar polymer composites with CB, such as polyolefins,<sup>1</sup> is about 10-25 wt %.<sup>1-6,15-17</sup> Because of the difference in sample preparation and the relatively poor wetability between polar polyurethane and CB fillers,<sup>5</sup> relatively high loading of CB is necessary for the conductive pathways to form throughout the composites, i.e., the percolation threshold is a little high in this study.

The electric conductivity of some carbon-black loaded polymers is found to decrease sharply as the composite is heated toward its melting point,  $T_{\rm m}$ . This effect is commonly referred to as the positive temperature coefficient of resistance (PTCR).<sup>15</sup> Figure 3 gives the temperature dependence of electric conductivity for the composite

PU-CB30. The temperature range is about 25-80°C, which corresponds to the service temperature region of shape memory polyurethanes.<sup>10,11</sup> The normal PTCR effect is not observed in this case. The electric conductivity shows a slight drop at temperatures near or even above the melting point of PCL crystals of the polyurethane. This phenomenon can be elucidated in terms of the physical cross-linking nature in the polyurethane matrix. The PTCR mechanism might be suggested as follows.<sup>15</sup> The conducting filler forms a network of conductive chains at temperatures below  $T_{\rm m}$ . As the polymer is heated, the sudden expansion, which takes place at the crystalline melting point, results in the breakup of the conducting chains, with a consequent anomalous decrease in conductivity. This mechanism can explain why amorphous polymers show very much smaller PTCR effect,<sup>18</sup> and the PTCR effect also can be eliminated by cross-linking.<sup>19</sup> In this study, the PCL crystals melt at 80°C, but the hard segmental domains, which are able to serve as physical crosslinks, are still stable.<sup>10,11</sup> So, the conductive pathways are not influenced too much as the result of the melting of the PCL crystals in the polyurethane.

Deformation, which is necessary for the characterization of the shape memory properties, has an effect on the conductivity of the composites. Table I lists the results of room temperature conductivity of different samples after being stretched. The samples PU-CB15 and PU-CB20 have the room temperature conductivity of  $2.4 \times 10^{-4}$  and  $4.9 \times 10^{-4}$  s/cm, respectively. However, after deformation, no conductivity was detectable along the stretching direction. It follows that the conductive pathways in the composites were de-

		$\sigma  ({ m s} \cdot { m cm}^{-1})$						
Sample	CB wt %	$\lambda = 0$	$\lambda = 1.5$	$\begin{array}{c} T_m \\ (^{\circ}\mathrm{C}) \end{array}$	Crystallinity (c %)	$E_{Trt}{}^{\mathrm{a}}$	$E_{T_D}{}^{\mathbf{a}}$	$E_{Ttr}/E_{T_D}$
PU-CB00	0	b	_	62.3	53.1	$1.60 imes10^8$	$8.90 imes10^6$	17.9
PU-CB05	5		_	60.8	52.0	$3.55 imes10^8$	$8.41 imes10^6$	42.2
PU-CB10	10			58.3	50.2	$2.81 imes10^8$	$9.55 imes10^6$	29.4
PU-CB15	15	$2.4 imes10^{-4}$		58.2	50.4	$3.88 imes10^8$	$1.20 imes10^7$	32.3
PU-CB20	20	$4.9 imes10^{-4}$						
PU-CB25	25	$5.2 imes10^{-2}$	$2.0 imes10^{-2}$	57.0	49.9	$5.37 imes10^8$	$2.88 imes10^7$	18.6
PU-CB30	30	$8.4 imes10^{-2}$	$3.2 imes10^{-2}$	57.1	50.1	$6.45 imes10^8$	$4.07 imes10^7$	15.8

Table I Characteristics of Polyurethane-Conducting CB Composites

<sup>a</sup> Storage modulus at room temperature  $(T_{\rm rt})$  and deformation temperature  $(T_{\rm D})$ .

<sup>b</sup> —, Conductivity is too low to be measured by this technique.



**Figure 4** SEM micrograph of the cryogenically fractured surfaces of the pure polyurethane.

stroyed by means of unilateral stretching along the elongation direction. In those samples with more than 20 wt % CB, high conductivity is still observed at the stretching ratio of 1.5 along the elongation direction. But the values are lower than those of the original samples. In these cases, unilateral stretching does influence, but not completely destroys the networks of conductive pathways throughout the polymer along the deformation direction of the high CB loaded composites.

Figure 4 shows SEM micrograph of the cryogenically fractured surface of the pure polyurethane. A single phase is observed with evidently brittle fracture behavior. Figure 5 (a and b) shows the SEM micrographs of the cryogenically fractured surfaces of two typical composite samples. The compositions of the samples PU-CB05 and PU-CB30 are below and above the percolation threshold, respectively. The general topograph of the fracture surfaces of the composites is the polyurethane matrix mixed with the CB aggregates. However, SEM technique is not able to get detailed information on the finer distribution of CB fillers in the polyurethane matrix that is generally found in other conducting polymer composites.<sup>18-20</sup> Based on the electric conductivity results, the inter-connective structure of CB fillers is expected to form throughout the polymer matrix in this system. But only those aggregates containing more spherical CB particles are observed. This is shown in Figure 6 by high magnification. When the CB content is lower than the percolation threshold, the fillers exist in the form of isolated inclusions (Fig. 5[a]), which is the reason why the conductivity is not measurable.<sup>14</sup> As the percolation threshold is achieved, such as PU-CB30, the concentration of the CB is expectedly

high enough to form inter-connective pathways, which results in good conductivity of the composites. However, the network of the inter-connective CB morphology is not observed, except for those large aggregates of the fillers in Figure 5(b). Compared with polypropylene/CB composites,<sup>1</sup> the aggregates in this system contain more CB particles. There are two possible reasons for the appearance of large CB aggregates in the polyurethane matrix. One is the relatively poor wetability between CB and polar polymers such as the polyurethane used in this study. The other reason is due to the sample preparation. Unlike melt extrusion, solution-precipitation method has lower shearing force. It also should be noted that carbon black particles are present only in amorphous regions between crystallites, since they are excluded from the crystallites themselves during the processing. Polyurethane used in this study contains both hard segmental and soft segmental crystallites. So, the CB particles are not able to disperse into the polymer matrix as identical, as we had expected.

Figure 7(a and b) shows the SEM micrographs of the cryogenically fractured surfaces of the sample PU-CB05 and PU-CB30 after being stretched. The stretching direction is vertical in the photographs. In Figure 7(a), it is clearly shown that CB aggregate elongates along the stretching direction. For the sample PU-CB30 in Figure 7(b), stretching breaks up the CB aggregates, but does not destroy the networks of conductive pathways throughout the polymer. So, electric conductivity is still detectable along the stretching direction, which has been discussed above. The empty holes in Figure 7(b) resulted from the collapsed CB aggregates during fracture. Because stretching is able to increase the inter-distance among individual conductive particles or break some inter-connective structures, the conductivity, therefore, is lowered after being stretched.

It has been found that the high degree of crystallinity of the soft segment regions at room temperature is one of the necessary conditions for a segmented copolymer to show shape memory behavior.<sup>8–11</sup> The polyurethane chosen as the binder of the composites is a typical material with good shape memory properties.<sup>10,11</sup> Therefore, it is very important to study the effects of the addition of CB fillers on the soft segment crystallization and melting behavior in the polyurethane. Figure 8 shows the relationship between the CB concentration and the crystallization and melting characteristics of the PCL segment in the poly-



(a) PU-CB05



(b) PU-CB30

**Figure 5** SEM micrographs of the cryogenically fractured surfaces of the composites. (a) PU-CB05 and (b) PU-CB30.

urethane. Addition of CB fillers decreases the degree of crystallinity of PCL segment crystals as well as the subsequent melting temperatures. When the CB fillers increase up to 10 wt %, both the degree of crystallinity and melting temperatures are almost unchanged as the amount of CB is increased. The degree of crystallinity of PCL segment in the composites also is able to reach as high as 50%, which is high enough for fulfilling the shape memory conditions. The melting temperatures of the soft segment crystals are about  $57^{\circ}$ C after adding CB fillers.

Formation of stable hard segment domains as physical cross-links above the melting point of PCL crystals of the polyurethane is also one of the necessary conditions for the segmented copolymers to show shape memory effect.<sup>10,11</sup> Figure 9 gives the temperature dependence of the storage modulus E' of the polyurethane composites. The dynamic modulus of these specimens at room temperature is between  $2.8 \times 10^8$  Pa and 6.5imes 10<sup>8</sup> Pa, in the same order of magnitude of conventional plastics, but starts dropping at 50°C and decreases slightly after 60°C. Then the curves reach a plateau, which indicates the existence of physical cross-links in these specimens.  $^{10,11}$  The shapes of the elastic plateaus of the dynamic modulus after melting of PCL crystals are very similar to each other, independent of their compositions, which implies that the presence of CB fillers does not influence the existed physical cross-links formed by hard segment domains in the polyurethane. This may be the main reason for the absence of normal PTCR effect of this conducting composite as has been discussed in the previous section. Figure 10 shows the dependence of storage modulus at 80°C on the CB content in the composites. The dynamic modulus monotonously increases with CB content. The increase of modulus as a function of CB concentration means that carbon black serves as the effective filler to strengthen the elastic polymers. Furthermore, two distinctive trends have been found. Below 20 wt % of CB, the dynamic modulus increases slowly, which corresponds to the morphology of separate CB inclusions in the composites. After that, i.e., above 20 wt % of CB fillers, there is a sharp increase in the modulus, when CB networks of conductive pathways throughout the polymer are established. It means that the morphology of the composite might have a great influence on the mechanical properties of the composites.



**Figure 6** High magnification of SEM micrograph of CB aggregate in the composite PU-CB05.



(a) PU-CB05



# (b) PU-CB30

**Figure 7** SEM micrographs of the cryogenically fractured surfaces of the composites. (a) PU-CB05 and (b) PU-CB30 after being stretched.

The thermally stimulated strain recovery curves of the composite specimens are given in Figure 11. The stretching ratio used in the measurements is about 1.5. The specimen of pure polyurethane displays a typical shape recovery behavior.<sup>11</sup> But, the existence of CB fillers in the polymer does influence the shape memory effects. Table II summarizes the results of the strain recovery measurements, which are graphically shown in Figure 12. The response temperature  $T_{\rm r}$ , which is related to the melting of PCL crystals, slightly decreases from 46°C to 40°C when CB fillers are added. But the CB concentrations seem to have little effect on these feature temperatures of the composites. This is consistent with the previous DSC results as listed in Table I. The



**Figure 8** DSC results of polyurethane and the corresponding CB composites.

heating rate in the strain recovery measurements is only 2.7°C/min, so it is reasonable that the  $T_r$ values are almost 18°C lower than those of  $T_m$  by



**Figure 9** Temperature dependence of storage modulus E' of the polyurethane and its composites.



**Figure 10** Effect of CB concentration on the storage modulus at 80°C for the polyurethane and its composites.

DSC. The final recovery rate  $R_f$  of the pure polyurethane can reach as high as 98%. However, the results of the composites decrease, evidently to approximate 85%. The final recovery rates further go down below 70% in the high loading of CB fillers of the composites, i.e., above the percolation threshold. The variations of the average recovery speed  $V_r$  are also obvious in the same manner.

In the deformation of viscoelastic polymer materials, the total strain  $\varepsilon_0$  can be defined as follows<sup>21</sup>:

$$\varepsilon_0 = \varepsilon_{\rm E} + \varepsilon_{\rm RE} + \varepsilon_{\rm IR} \tag{3}$$

where  $\varepsilon_{\rm E}$  is the elastic strain;  $\varepsilon_{\rm RE}$  is the rubber elastic strain; and  $\varepsilon_{\rm IR}$  corresponds to the irreversible strain. For shape memory polymers,  $\varepsilon_{\rm RE} \geq \varepsilon_{\rm E}$  and  $\varepsilon_{\rm IR}$  when it is deformed at  $T_{\rm D}$ . So,

$$\sigma_0 = E_{\rm app} \cdot \varepsilon_0 = E_{\rm app} \cdot \varepsilon_{RE} \tag{4}$$

where  $\sigma_0$  is the average internal stress in the specimen. Here the apparent modulus  $E_{\rm app}$  is approximately equivalent to the storage modulus at  $T_{\rm D}$  in this case. After the crystallization of the soft segments at room temperature, the force is removed. The specimen will shrink by  $\varepsilon'_0$  under the internal stress  $\sigma_0$ .

$$\varepsilon_0' = \frac{\sigma_0}{E_{T_{\rm rt}}} = \frac{E_{\rm app}}{E_{T_{\rm rt}}} \cdot \varepsilon_0 = \frac{E_{T_{\rm D}}}{E_{T_{\rm rt}}} \cdot \varepsilon_0 = \frac{\varepsilon_0}{A} \tag{5}$$

where  $A = E_{T_{rt}} / E_{T_{D}}$ . So, the fixed strain  $\varepsilon_{0.app}$  can be defined as:

$$\varepsilon_{0.\text{app}} = \varepsilon_0 - \varepsilon'_0 = (1 - A^{-1})\varepsilon_0 \tag{6}$$

The strain fixation is then expressed in formula (7):

$$S_{\rm f} = \frac{\varepsilon_{0.\rm app}}{\varepsilon_0} = 1 - A^{-1} \tag{7}$$

which means  $S_{\rm f}$  is only determined by the modulus ratios at  $T_{\rm D}$  and  $T_{\rm r}$ .

Table II gives both the theoretically calculated and experimental  $S_{\rm f}$  values. It has been found that for pure polyurethane and the composites below percolation threshold, the experimental values are consistent with the calculated values. However, for those composites, especially with high CB loading levels, large divergences are observed. Noticeably, different trends have been found from those values as the result of CB concentration. The calculated values decrease with an increase in CB content, while the experimental results increase with the increase of CB concentration.

Generally, cross-linked polymers do not show much  $\varepsilon_{\text{IR}}$ . If  $\varepsilon_{\text{IR}} = a\varepsilon_0$ , *a* is generally less than 5%. The final recovery rate  $R_f$  can be defined as:



**Figure 11** Strain recovery curves of the polyurethane and its composites.

Sample		$S_{\mathrm{f}}$ (%	${S}_{ m f}\left(\% ight)$			
	λ	$S_{ m f}^{ m exp}$	$S_{ m f}^{ m cal}$	$T_{\rm r}(^{\rm o}{\rm C})$	$R_{ m f}\left(\% ight)$	$V_{\rm r}~({\rm min}^{-1})$
PU-CB00	1.56	94.6	94.4	45.7	98.0	0.77
PU-CB05	1.54	95.8	97.6	41.5	89.4	0.76
PU-CB10	1.55	95.8	96.6	41.1	82.6	0.74
PU-CB15	1.53	97.0	96.9	40.4	80.0	0.71
PU-CB25	1.54	$\sim 100$	94.6	40.2	70.0	0.42
PU-CB30	1.52	$\sim 100$	93.7	40.1	65.2	0.35

(8)

 Table II
 Thermally Stimulated Strain Recovery Characteristics of Polyurethane Polymer

 and Its Composites With CB

$$egin{aligned} R_{\mathrm{f}} &= rac{arepsilon_{0.\mathrm{app}} - arepsilon_{\mathrm{IR}}}{arepsilon_{0.\mathrm{app}}} = rac{(1 - A^{-1}) \cdot arepsilon_0 - a arepsilon_0}{(1 - A^{-1}) \cdot arepsilon_0} \ &= 1 - rac{a}{1 - A^{-1}} pprox 1 - a \end{aligned}$$

This means the final recovery rate  $R_{\rm f}$  is mainly determined by the irreversible strain. In fact, *a* is a characteristic of polymer itself. If the physical cross-link structure is intact with the addition of CB fillers, the final recovery rate should be similar, since the same polymer has been used. However, from Table II, the  $R_{\rm f}$  decreases with the increase of CB fillers. The value is much lower when the percolation threshold is achieved.

From the previous results, it is known that the presence of CB does not influence the physical cross-links structure significantly. But the existence of the fillers is able to increase the bulk viscosity of the material after the melting point of PCL crystals,<sup>20,22</sup> subsequently greatly increasing the relaxation time of the PCL segments of the polyurethane. It makes it difficult for the measurements to reach the thermodynamic equilibrium. Thus, the recovery speed is relatively low and the high recovery rate cannot be easily achieved during the experimental time period. The above explanation also accounts for the divergence of the experimental and calculated strain fixation values  $S_{\rm f}$ . In the cases of high loading levels of CB, inter-connective morphology of the fillers throughout the polymer has been established in the bulk of the composites. This kind of structure is able to impede the movements of the PCL segments greatly both below and above the melting point of the soft segment crystals. Hence dramatic changes of the shape memory parameters have been observed.

So, unlike pure polyurethane, with a high degree of crystallinity of soft segments and stable physical cross-links, its composites with CB do not necessarily show good shape memory behavior.<sup>10,11</sup> The priority herein is therefore to generate good electric properties and while sacrificing the strain recovery properties to the least extent. In this study, polyurethane composites can be obtained with good electric conductivity and more than 60% shape recovery rate. High loading of CB results in good electric properties; however, it influences the strain recovery effects. So, decreasing the percolation threshold is effective to achieve the goal. Recently, we reported our newly developed shape memory materials based on nonpolar polymers,<sup>23–25</sup> which are expected to have good wetting properties with the CB fillers. The



**Figure 12** Shape memory parameters of the polyurethane and its composites as a function of CB concentrations.

percolation threshold is supposed to be lower when nonpolar polymers are used.

#### CONCLUSIONS

Polyurethane composites with CB have displayed the combination of both shape memory properties and electric conductivity. Higher CB concentration is necessary for the percolation threshold, which may be due to the poor wetting property between the reinforcing fillers and the polymer binder. It has been found that higher CB concentration has not influenced the crystallization and melting behavior of the polymers in the composites. The physical cross-links have not been affected too much either. However, the addition of CB increases the bulk viscosity of the polymer, which results in the slow strain recovery speed and low final recovery rate. The composites, which are satisfactory in both shape memory behavior and electric conductivity, can be produced within appropriate composition range.

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