Significantly reducing electrical resistivity by forming conductive Ni chains in a polyurethane shape-memory polymer/carbon-black composite

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We demonstrate an approach to significantly reduce the electrical resistivity in a polyurethane shape-memory polymer (SMP) filled with randomly distributed carbon black (CB). With an additional small amount of randomly distributed Ni microparticles (0.5 vol %) in the SMP/CB composite, its electrical resistivity is only reduced slightly. However, if these Ni particles are aligned into chains (by applying a low magnetic field on the SMP/CB/Ni solution before curing), the drop of the electrical resistivity is significant. This approach, although demonstrated in a SMP, is applicable to other conductive polymers. © *2008 American Institute of Physics*.
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Conductive polymer composites have many remarkable advantages as compared to metallic conductors in terms of, for instance, easy processing, low density/cost, and wide range of electrical conductivity.[1] To achieve good electrical conductivity, conductive fillers, e.g., carbon black (CB), carbon fiber (CF), graphite, and metallic particle, are often incorporated into polymers. The conductive paths/chains, which are essential for good electrical conductivity,[2] enable the transport of electron along the direction of electrical field. In most of the previous works, conductive fillers are randomly dispersed, so that the formation of the conductive channels is not well under control but more or less depends on the dispersion and geometrical parameters of fillers.[1,3]

Carbon nanotubes can be aligned inside polymers under a magnetic field for good electrical conductivity.[4,5] However, the intensity of required magnetic field is extremely strong (7–26 T) and difficult to achieve in real engineering applications. As well known, magnetic particles suspended in a liquid medium can align into chains under a magnetic field.[6,7] The previous investigation on the influence of these chains is largely on the rheologic response, while the electrical conductivity receives little attention. Recently, we demonstrated the possibility of Joule heating at a low voltage for shape recovery in a polyurethane shape-memory polymer (SMP) with embedded micron sized Ni particle chains.[8] However, the required amount of Ni particles for good conductivity is still high. CB and CF have been used together for conductive SMPs.[9] Since the recoverable strain in SMPs is normally in the order of 100%,[10–17] a potential deformation compatibility problem raises between polymer and continuous fiber.

Instead of using only Ni particles, here, we propose to use a small amount of Ni particles to form chains inside polymers with randomly distributed conductive powders. The same Ni micropowders (average size of 3–7 μm) and polyurethane SMP (glass transition temperature T_g of about 40 °C) as in Ref. 8 were used. The conductive powder was CB (same as in Ref. 18). As reported, e.g., in Ref. 18, CB is aggregated and can be distributed reasonably uniformly within polymers. Ni chains (formed under a weak magnetic field before curing) serve as conductive channels to bridge CB aggregations, so that the electrical conductivity can be significantly increased, while other properties are more or less the same if the amount of Ni is small.

Three types of thin films were fabricated, namely, SMP/CB/Ni (chained), SMP/CB/Ni (random), and SMP/CB (i.e., without Ni). Within each type of thin films, the volume fraction of CB varies from 4% to 10%. However, in all thin films with Ni particles, Ni is always 0.5 vol %.

SMP/CB/Ni (chained) was produced in the following steps. First, CB and Ni (0.5 vol %) were mixed with the SMP/DMF (dimethylformamide) solution and well stirred. After that, the mixture was poured into a 50 mm diameter Petri dish. The Petri dish was placed above two magnets, as illustrated in Fig. 1 of Ref. 8. The strength of magnetic field at the bottom of the Petri dish was measured as 0.03 ± 0.003 T by a Gauss meter (Hirst, GM05). Subsequently, the whole setup was placed in an air-tightened box and kept in an oven for 24 h at a constant temperature of 80 °C for solidification. After the volatilization of DMF, a thin film embedded with Ni chains inside was obtained. The cured thin films were about 0.6–1 mm thick. SMP/CB/Ni (random) and SMP/CB films were prepared in a similar way but without the magnetic field.

After mixing, Ni powders suspend randomly within the SMP/CB mixture. At a low Ni content, 0.5 vol % in this study, many short Ni single chains, i.e., the Ni particles aligned one after another in one line, are formed instantly upon applying a weak magnetic field. After solidification, these chains are fixed (Fig. 1). Given that the length of chains ranging from 100 to 200 μm and the size of Ni particle is about 3–7 μm, the aspect ratio of Ni chains is about 14–70, which is comparable to short microfibers.

In order to determine the resistivity of these composites, samples ($1 \times 5 \times 20$ mm^3) were cut out of the thin films and connected to aluminum electrodes (refer to inset in Fig. 2). The resistance was measured by a digital multimeter

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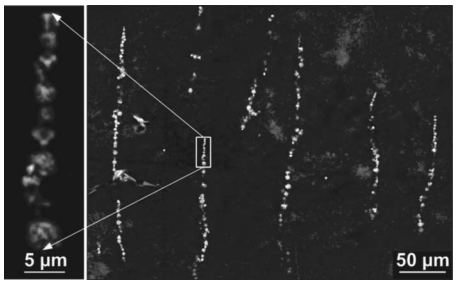

FIG. 1. SEM images of conductive SMP with 10 vol % of CB and 0.5 vol % of chained Ni. Inset: Zoom-in view of one Ni chain.

(IDM91E). Given the geometrical dimensions of samples, the corresponding electrical resistivity was derived. Four readings from four different pieces of samples of the same type of film were obtained. One month later, the samples were remeasured in order to check the stability.

Figure 2 reveals the relationship of CB content versus electrical resistivity of SMP/CB/Ni (chained), SMP/CB/Ni (random), and SMP/CB. It is clear that the additional 0.5 vol % of Ni, if distributed randomly, only slightly reduces the resistivity of the composites. However, the same amount of Ni particles, if well aligned to form chains, can significantly reduce the electrical resistivity by more than ten times. Obviously, the remarkable reduction in the electrical resistivity is the result of the conductive chains, which serve as conductive channels to bridge those small isolated CB aggregations. This bridging effect is more significant in composites loaded with a low amount of CB in which the CB aggregates are relatively small in size and more isolated. It should be pointed out that for the same sample, the resistance measured one month later is about the same as before. Hence, the resistivity of these samples is stable.

In order to demonstrate the shape recovery by Joule heating, three samples [namely SMP/CB/Ni (chained), SMP/CB/Ni (random), and SMP/CB], all with 10 vol % of CB, 1 mm thick, and in a shape as illustrated in Fig. 3 (left-top inset), were bent by about 150° at 80 °C, and then cooled to room temperature (22 °C) (refer to Fig. 3, left-middle inset). Subsequently, a 30 V of power was applied (Fig. 3, left-top inset for the setup). An infrared video camera (AGEMA, Thermo-vision 900) was used to monitor the temperature distribution and shape recovery simultaneously. Fig. 3 (right) presents four snap shots of each sample. We can see clearly that sample (a) [SMP/CB/Ni(chained)] reaches the highest

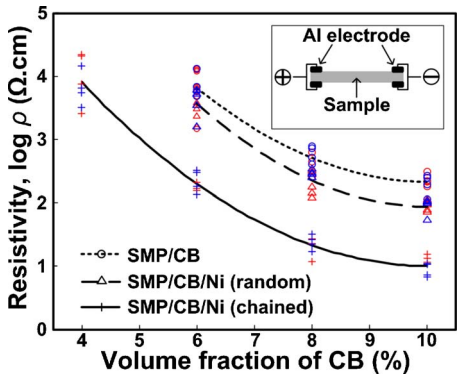

FIG. 2. (Color online) Resistivity vs volume fraction of CB with/without 0.5 vol % of Ni. Red symbol, right after fabrication; blue symbol, one month later. The inset figure illustrates how the resistance was measured.

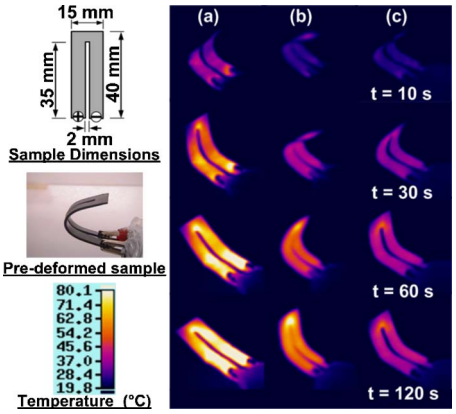

FIG. 3. (Color online) Sequence of shape recovery and temperature distribution. Top-left inset, dimensions of sample; middle-left inset, prebent shape; bottom-left inset, temperature bar (in °C.) Sample (a), 10 vol % of CB, 0.5 vol % of chained Ni; sample (b), 10 vol % of CB, 0.5 vol % of randomly distributed Ni; sample (c), 10 vol % of CB only. The tests were repeated for more than five times on each sample.

temperature (about 80 °C everywhere, which is much higher than the T_g of the SMP, so that almost full recovery is observed in 120 s), while the temperature of sample (c) [SMP/CB] is the lowest (about 45 °C only, slightly higher than the T_g of the SMP; hence, the shape recovery is small). Sample (b) [SMP/CB/Ni (random)] reaches around 65 °C and the shape recovery is not completed after 120 s. In terms of power consumption, it is about 1.2 W for sample (a). In addition, we investigated the evolution of resistivity after up to 20 shape recovery cycles (20% prestrained). Figure 4 reveals that the degradation of electrical conductivity in sample (a) is relatively more significant than the others. As the recovery in a SMP is normally not 100%,[8–10,14,19] the conductive paths in Ni chain/CB may be degraded upon thermomechanical cycling, which causes the degradation of its conductivity.

In summary, we propose a convenient and cheap way to significantly reduce the electrical resistivity of SMP composites. By adding in a small amount of Ni micropowders (0.5 vol %) and aligning them into chains in a SMP filled with CB, the resistivity is reduced by over ten times, as compared to the same sample but with randomly distributed Ni particles. The short Ni chains can be easily formed in SMP/CB solution under a low magnetic field (0.03 T only) to enhance conductivity. This effect is more significant in SMPs with lightly loaded CB. We demonstrate that a piece of composite $(40\times15\times1\ \mathrm{mm}^3)$ with 10 vol % of CB and

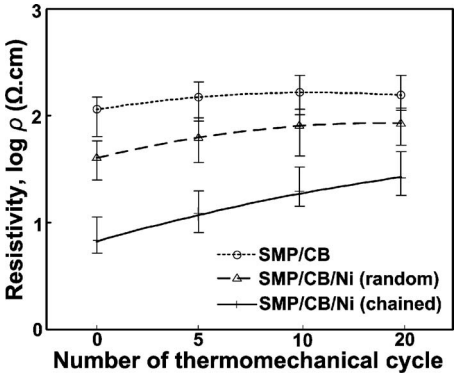

FIG. 4. Evolution of resistivity upon shape-memory cycling.

0.5 vol % of Ni (chained) can be heated to 80 °C for shape recovery at 30 V (1.2 W) of power.

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