Electrical conductivity of thermoresponsive shape-memory polymer with embedded micron sized Ni powder chains

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The electrical resistivity of a thermoresponsive polyurethane shape-memory polymer (SMP) filled with micron sized Ni powders is investigated in this letter. We show that, by forming conductive Ni chains under a weak static magnetic field (0.03 T), the electrical conductivity of the SMP composite in the chain direction can be improved significantly, which makes it more suitable for Joule heat induced shape recovery. In addition, Ni chains reinforce the SMP significantly but their influence on the glass transition temperature is about the same as that of the randomly distributed Ni powders. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2829388]

While shape-memory polymers (SMPs) can be actuated by various stimuli (e.g., light[1] and water[2]), an external heater is normally required for the shape recovery in thermoresponsive SMPs. In order to get rid of external heaters, SMP composites with different types of fillers have been developed,[3] so that they can be actuated by means of Joule heat (i.e., by passing an electrical current,[4–6] just like that of NiTi shape memory alloys[7]) or induction heat (e.g., by applying an alternating magnetic field to induce heat through hysteresis in magnetic particles[8–10]). While the latter approach has the advantage for wireless/remote operation, the former might be more of the interest in many engineering applications in which a bulk system to generate magnetic field is not appreciated.

Electrically conductive powders, fibers, and even nanowires/nanotubes have been utilized as the fillers to improve the electrical conductivity of polymers.[11–13] Although conductive fiber and nanowire/nanotube can significantly enhance the stiffness and strength of polymers,[14] their deformable strain is limited to within a few percent (at the most).[15,16] Since the recoverable strain in SMPs is normally on the order of hundred percent, there is a potential problem of deformation compatibility. As such, electrically conductive powders, such as, carbon black and Ni powder, should be better choice.

Previously, we have developed thin film SMPs with embedded magnetic powder (Fe_3O_4) chains inside. This work inspired us to use some other powders, which are both magnetic and electronically conductive, to form conductive chains for enhanced electrical conductivity. The purpose of this letter is twofold. One is to fabricate SMP thin films with embedded conductive powder chains and the other is to investigate their electrothermomechanical properties and compare them with those with randomly distributed powders.

The thermoresponsive polyurethane SMP solution from Diaplex Co. Ltd. (MS-5510) was used in this study. It consists of 30 wt % of SMP (glass transition temperature, T_g: about 40 °C) and 70 wt % of dimethylformamide (DMF). Its molecule chain consists of alternating sequences of soft segment with low molecular weight and hard segment built from diisocyanates and extenders to form the points for physical linking.[17] Ni powders, which are magnetic and electronically conductive, with an average size from 3 to 7 μm and a purity of 99.8%, were bought from Goodfellow, UK.

SMP thin films filled with different volume fractions of Ni powders were prepared in the following steps. First, Ni powders were mixed with the SMP/DMF solution and well stirred for a uniform dispersion. After that, the highly viscous mixture was poured into a 40 mm diameter Petri dish (to reach a final height about 1.5–2.0 mm) (Fig. 1). Two magnets and a Petri dish were placed in a way, as illustrated in Fig. 1. The whole setup was kept in an oven for 24 h at a constant temperature of 80 °C. After curing, a SMP thin film with Ni chains inside was obtained. The resulted thin film (about 0.5–0.7 mm thick) was kept in an oven at 160 °C for more than 8 h to fully remove any moisture absorbed during processing.[18] Various sized samples were cut out of the thin film for testing. This group of samples is named chained samples hereinafter. Another group of thin films was prepared in the same way but without applying the magnetic field. Hence, Ni particles were randomly distributed within the SMP matrix. This group is named random sample hereinafter.

Optical microscopic observation revealed the formation of clear chain structure in chained samples, in particular, at a small Ni content. A scanning electron microscopy (SEM) (JEOL 5600LV) was used to observe the details of Ni chains
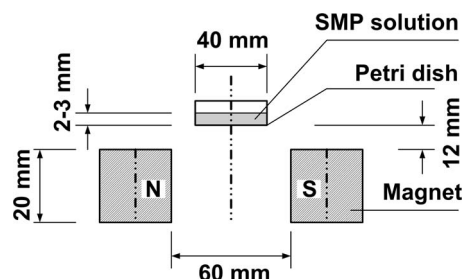

FIG. 1. Illustration of setup for sample preparation. The strength of magnetic field was measured as 0.03 ± 0.003 T in the area underneath the Petri dish.

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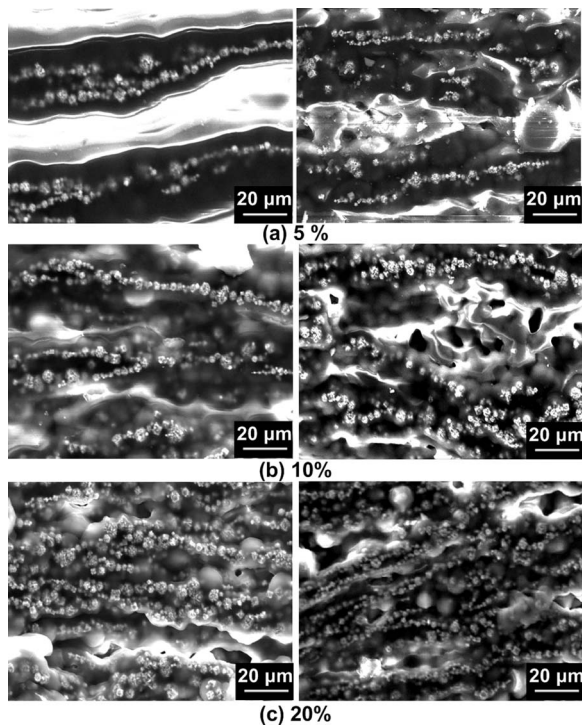
FIG. 2. Typical SEM images before (left column) and after (right column) five stretching (at 50% strain)-shape recovery cycles.

before and after five stretching (50% strain)-shape recovery cycles. The volumetric electrical resistance of random and chained samples was measured by a multimeter (IDM91E). An infrared video camera (AGEMA, Thermovision 900) was used to monitor the temperature distribution in samples upon Joule heating. Differential scanning calorimetery (DSC) (modulated DSC, DSC-2920), and dynamic mechanical analysis (DMA) (DMA 2980 TA Instrument) were used to determine the thermomechanical properties of chained and random samples.

SEM images reveal that single chains start to be formed at 1% volume fraction of Ni. With the increase of Ni content, multichains (bundles) are resulted, and eventually no clear
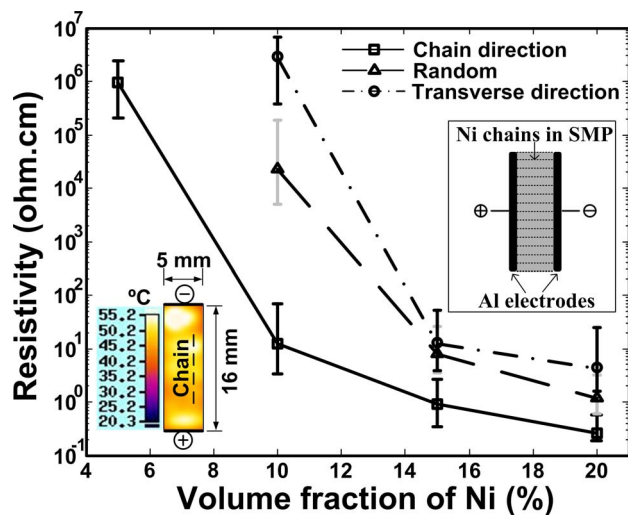

FIG. 3. (Color online) Electrical resistivity vs volume fraction of Ni powder. Right inset: illustration of setup for the resistivity measurement along the chain direction. Bottom-left inset: infrared image of temperature distribution in chained sample (10% Ni, 6 V).
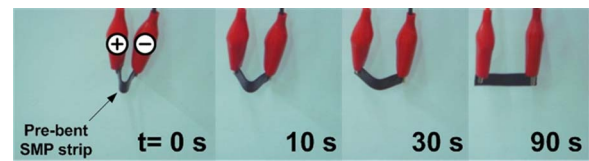

FIG. 4. (Color online) Shape recovery sequence in a chained sample ($30 \times 7 \times 1$ mm^3, 10% Ni, 20 V).

Ni chain can be recognized (Fig. 2, left column). In addition, after five stretching-shape recovery cycles, the Ni chains still exist (Fig. 2, right column), which indicates the possibility of using chained SMPs for cyclic actuation.

Figure 3 plots the electrical resistivity of the random and chained samples against the volume fraction of Ni powders. The volumetric electrical resistivity ρ is calculated by

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

where R is the measured resistant, A is the cross-sectional area of sample, L is the length between two aluminum electrodes (refer to the right inset in Fig. 3 for the setup of the resistivity measurement). Although limited by the measuring range of the multimeter, as we expected, ρ of the chained sample in the transverse direction (i.e., perpendicular to the chain direction) is the highest, while ρ of random samples is lower. ρ of chained samples in the chain direction is always the lowest. For example, at 10% volume fraction of Ni powder, ρ of random sample is 2.36×10^4 Ω cm; while in the chained sample, it is 2.93×10^6 Ω cm in the transverse direction, and only 12.18 Ω cm in the chain direction. However, at a high Ni content, ρ of all types of samples is close. This is due to that the Ni chains become unrecognizable at a high Ni content, as revealed in Fig. 2. At 10% volume fraction of Ni, the chained sample (with a dimension of $16 \times 0.6 \times 5$ mm^3) can be heated from room temperature (20 °C) to 55 °C by applying a voltage of 6 V (refer to infrared image in Fig. 3, bottom-left inset), which is enough to trigger the shape recovery. However, for the same setup and configuration, it is only about 26 °C in the random sample. No shape recovery can be actuated, as it is far below the actuation temperature. The recovery sequence of a chained sample upon Joule heating is shown in Fig. 4. According to the DSC results in Fig. 5, with the increase of Ni
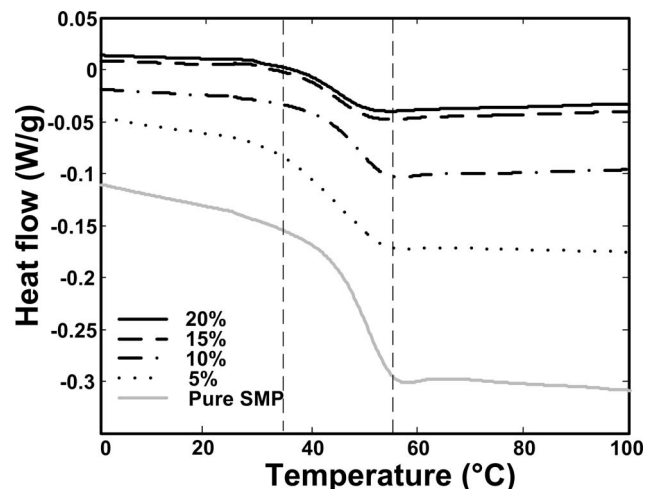

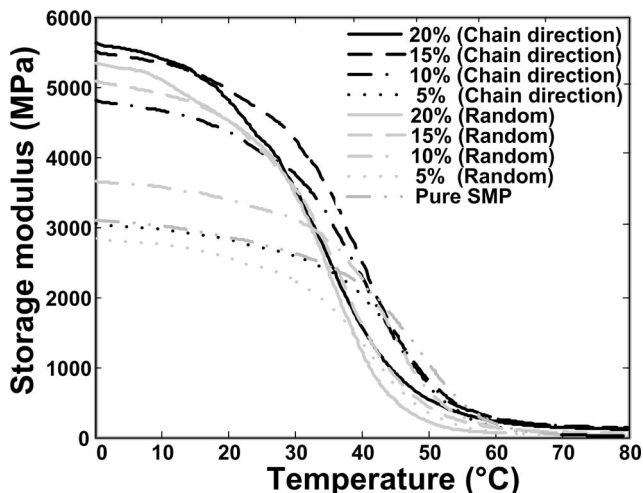FIG. 5. DSC results of random samples.

FIG. 6. Typical storage modulus vs temperature curves obtained from DMA test.

FIG. 8. T_g of chained and random samples.

content, the glass transition shifts a little bit toward a low temperature range, which indicates the slight chemical interaction between Ni powders and SMP.

From the measured storage modulus versus temperature curves of random and chained samples (Fig. 6), we plot the storage modulus (at 0 °C) against the volume fraction of Ni for both random samples and chained samples (chain direction only) in Fig. 7. At around 10% volume fraction of Ni content, the composite is already significantly strengthened. For the same amount of Ni content, the storage modulus of chained samples in the chain direction is always much higher than that of random sample. This indicates that the reinforcement is more effective by forming Ni powder chains.

T_g is one of the major characteristics of SMPs. Traditionally, T_g can be defined in various ways. Here, we differential the storage modulus curve with regard to temperature, and then define the peak temperature as T_g. Figure 8 plots T_g against the volume fraction of Ni powders for both random samples and chained samples (chain direction only). As we can see, with the increase of Ni content, T_g decreases in a more or less same linear fashion in both types of samples. At 20% Ni content (this is extremely high), T_g drops by about 15 °C, to 35 °C only, which confirms the slight chemical interaction between SMP and Ni powders.

In conclusion, we demonstrate a simple way to produce SMPs with embedded micron sized Ni powder chains by application of relatively weak magnetic field. Due to these
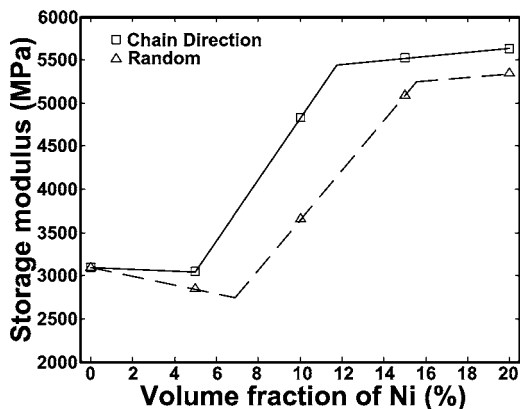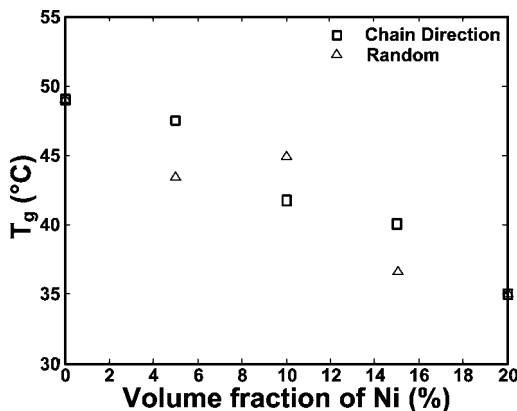
conductive Ni chains, the electrical resistivity of SMP composite is greatly reduced in the chain direction, so that Joule heating is possible at a low electrical voltage. In addition, the alignment of Ni powder chains efficiently reinforces the SMP. The slight chemical interaction between Ni powder and SMP results in a lower T_g. This approach, i.e., to form conductive particle chains in SMPs for enhanced electrical conductivity, is easy for implementation. It should be applicable to other types of polymers. Multilayered electrically conductive polymer composites can also be realized by, for instance, bonding a few such layers together.

FIG. 7. Storage modulus vs volume fraction of Ni at 0 °C.

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