Electrical actuation and shape recovery control of shape-memory polymer nanocomposites

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Shape-memory polymers (SMPs) are one of the most popular smart materials due to their light weight and high elastic deformation capability. The synergistic effect of carbon nanofiber (CNF) and carbon nanofiber paper (CNFP) on the electro-actuation of SMP nanocomposites was studied. The electrical conductivity of SMPs was significantly improved by incorporating CNF and CNFP into them. The dynamic mechanical analysis result reveals good thermal stability of SMP nanocomposites even after they were mixed with CNFs. A vision-based control system is designed to precisely control the shape recovery of SMP composites. Any quasi-state shape between the permanent shape and a temporary shape can be achieved by adjusting the electrical energy input. Experimental results demonstrated that (1) compared with the baseline material, the full recovery time of the SMP nanocomposites was decreased by 1000% to less than 80 s; (2) a good repeatability was shown in the developed vision system in 10 experimental trials and the accuracy of the controlled deflection angle of SMPs was within a 5% error bound.

Keywords: shape control; electrical actuation; shape-memory polymer; carbon nanofiber paper

1. Introduction

Shape-memory polymer (SMP) is a kind of smart material which can be deformed into a temporary shape and then recover to its original permanent shape through external stimuli. Compared to shape-memory alloys, SMPs require lower recovery forces. However, SMPs also exhibit a number of considerable advantages such as the relative ease of fabrication, high elastic deformation capability, and tailored recovery temperature [1–3]. Therefore, SMP benefits a wide range of applications such as morphing structures of aircraft and spacecraft [4], textiles and clothing materials, biomedical engineering materials, and deployable structures [5,6].

Significant research has been carried out on the actuation for SMPs and SMP composites. Different kinds of actuation methods are explored including heat [7], light [8,9], electricity [10,11], magnetic field [12,13], or solvent [14–16]. Electrically actuating SMPs by electrical resistive heating has been intensively studied. By mixing carbon black and chopped short carbon fiber into styrene-based SMP, Lu et al. [17] successfully actuated the SMPs by electrical resistivity heat. Carbon nanofibers (CNFs) have also been used as conductive filler for the actuation of SMPs [18]. However, most of the previous works simply...
blended conductive fillers into pure polymers. This approach will cause many problems once the polymer is used as matrix for fiber-reinforced polymer composites and manufactured by the process of resin transfer molding (RTM), such as changing viscosity and cross-linking of the polymer matrix. Moreover, those traditional fabrication methods cannot achieve high-level nanoparticles loading, which is critical for enhancing the conductivity of SMP nanocomposites. Recently, a unique technique of pre-forming conductive CNFs as a sheet or paper has been explored for multifunctional material applications [16,17]. High-quality self-assembled CNFP is made by infiltrating the suspension of CNFs through a hydrophilic or hydrophobic membrane. Based on the excellent electrical properties of the CNFP, it is expected that the electrical conductivity of the SMP nanocomposites incorporated with a CNFP will be enhanced significantly.

To broaden the application of SMPs, such as biomedical or morphing structures, precisely controlling the shape change of SMPs is critical. The objective of the control system in this article is to precisely and repeatedly drive the deflection angle of the sample SMP to a desired value using the position information of the interested dots on the surface of the SMP and measured from the vision system.

In this study, we explored self-assembled CNFs paper incorporated with the epoxy-based SMP (Veriflex® E2; Sigma-Aldrich Inc., St. Louis, MO, USA) to fabricate the electro-induced SMP composites. The synergistic effect of CNF and carbon nanofiber paper (CNFP) on SMP nanocomposites actuation has been investigated. The deformation of SMPs sample has been detected and analyzed by a vision-based prediction system. The dynamic mechanical analysis (DMA) also been carried out in order to predict its thermal–mechanical properties. A number of control tests have been conducted to investigate the accuracy and repeatability of SMP nanocomposites.

2. Experiment

2.1. Materials

CNFs (Pyrograf®-III, PR-HHT-25) are provided in powder from Applied Sciences Inc., Cedarville, Ohio, USA. The nanofibers have a diameter of 50–100 nm and length of 30–100 µm. CNFs have excellent electrical (0.75 S/cm) and thermal conductivity (2000 W·K⁻¹·m⁻¹). Deionized water was used as solvent. Meanwhile, the nonionic surfactant (Triton X-100, Sigma-Aldrich Inc.) was used to aid the dispersion of CNFs. The epoxy-based SMP resin Veriflex® E2 was supplied from Cornerstone Research Group, Inc., Dayton, Ohio, USA. The Veriflex® E2 which comes as two-parts is a fully formable thermoset SMP resin system. The mixing ratio of parts A and B is 100:27.08. The Veriflex® E2 resin is engineered with a glass transition temperature (Tg) of 104°C, and the cured resin has unique ‘shape-memory’ properties and can be bent, stretched, and twisted, without the any loss of the shape-memory effect.

2.2. Fabrication of CNFs paper and the CNFP-based SMP nanocomposites

The CNFs were divided into several parts evenly and then transferred into 1000-ml beakers and 400 ml deionized water was added in each beaker. In order to disperse the CNFs even into the water, 4 ml surfactant Triton-X100 was added into the solution. The solution was subsequently sonicated using a high-intensive probe sonicator for with 30 min. After that, the solution was cooled down to room temperature and 10 drops of surfactant were added into the solution. Then the solution was sonicated twice again with 30 min interval and
was cooled down to room temperature. Finally, the as-prepared suspensions were sonicated to 2 min and immediately transferred into filtration system. The CNF paper was made by filtering the suspension through 0.4 µm hydrophilic polycarbonate membrane under a high-pressure (0.689 MPa) filtration system. Once the paper was made, the filter with the carbon nanopaper was carefully removed and placed onto a piece of paper where the filter was detached. The remaining paper was put into oven at a temperature of 120°C for 2 h. RTM process was used to fabricate the SMP nanocomposites. In order to increase the thermal and electrical conductivity, CNFs were added into SMP resin. Two parts of Veriflex® E2 resin were first mixed together using a high shear mixer. The CNFs were blended into the SMP resin with 1% weight fractions. The resulting mixture was degasified in a vacuum oven. To further investigate the effect of the thickness of the CNFPs, different thicknesses of CNFPs (0.5 mm, 1 mm) were placed on the inside bottom of the mold. The SMP resin modified with CNFs was then injected into the mold. The curing cycle for the resin is as follows: ramping to 120°C and hold for 4 h, and then again ramping to 150°C and hold for another 4 h. Table 1 shows the composition of samples.

### Table 1. The composition of samples.

| Group | CNFP thickness (mm) | CNF wt.% |
|-------|---------------------|----------|
| G1    | 0.5                 | 0        |
| G2    | 1.0                 | 0        |
| G3    | 0.5                 | 1.0      |
| G4    | 1.0                 | 1.0      |

3. Results and discussion

3.1. Morphological characterization of CNF paper and its SMP composites

In order to study their morphologies and network structures, the CNFPs and its composites were characterized with scanning electron microscope (SEM) (ZEISS Ultra-55, at 5 kV; Carl Zeiss Microscopy GmbH Inc., Oberkochen, Germany). The samples were coated with about 10 nm of gold (Au) on its surface in order to enhance SEM imaging. The SEM images of CNFPs and CNFPs infused with SMP resin are shown in Figure 1. The CNFs are homogeneously dispersed without any aggregation. CNFs are one of the best conductive materials, each individual CNF is the conductive path for electrons. The continuous network structure further enhances the conductivity of CNFPs. Figure 1(b) shows the cross-section of CNFPs after resin infusion and the network structure still remained which transformed the nonconductive polymer to be a conductor through the conductive network, which facilitated electro-actuation of the SMP nanocomposites.

3.2. Electrical resistivity of CNFPs incorporated SMP composites

The electrical resistivity of the neat SMP and their hybrid filler filled composites were measured by a standard four-probe method (SIGNATONE QUADPRO system) using a precision multimeter incorporated with a four-point cylindrical probe. The electrical resistance was calculated as

\[ \rho = R_s \times t = 4.53 \times \frac{V}{I} \times t \]  

(1)
Figure 1. SEM images of (a) CNFPs and (b) CNFPs infused with SMP resin.
where $\rho$ is the bulk resistivity, $R_s$ is the electrical resistance, $V$ is the voltage applied on the outer two probes, $I$ is the electrical current passed through inner two probes, and $t$ is the thickness of the samples. The resistivity of different groups of SPM samples is shown in Figure 2. The resistivity of G1 (group 1) is 0.54 Ohm-cm, which is about $2 \times 10^{16}$ times less than the pure SMP (about 1016 Ohm-cm). As mentioned before, due to intrinsic excellent conductivity of CNFs, more efficient conductive path for electrons are provided. The network structure of CNFP further improves the conductive structure and enhances the conductivity of SMP composite. Compare G1 with G2 (group 2), the resistivity decreases as the thickness of CNFP increases due to more conductive paths were involved. After blended with CNFs into the resin system, the resistivity of SMP composites is even less, and the value is 0.340 Ohm-cm for G3 (group 3) and 0.307 for G4 (group 4). This indicates the CNFs blended into the SMP resin system increased the free electron density in SMP nanocomposites, which made the conductive path shorter and more efficiency.

3.3. Dynamic mechanical analysis

In order to investigate the dynamic mechanical property of SMP composites, DMA was carried out using TA Instruments DMA Q800 (TA Instruments, New Castle, DE, USA). Dynamic mechanical properties refer to the response of a material as it is subjected to an oscillating load. These properties may be expressed in terms of a storage modulus, a loss modulus, and a tangent delta (damping ratio). The testing temperature ranges from 60°C to 170.00°C and the heating rate is 10.00°C/min. The frequency is 1.0 Hz. The testing results are presented in Figure 3. The storage modulus, loss modulus and tangent delta of four groups of SMP samples are plotted versus temperature. Storage modulus describes elastic property of SMP composites which is related to the Young’s modulus. The loss modulus stands for the viscous property which associated with energy dissipation in the form of heat upon deformation. The peak value of tangent delta indicates the glass
transition temperature ($T_g$) of the SMP composites. The peak values of four groups of samples are quite similar which tells good thermal stability of SMP composites after mixed with CNFs.

3.4. Characterization results of shape recovery effect of SMPs by a vision-based coordinate measurement system

In order to obtain the information related to deformation of arbitrary points on the polymer material with the applied current and voltage, a low-cost vision-based measurement system is designed. Figure 4 shows the experimental setup in which a material sample marked with different colors in different locations is placed in front of two webcams of known orientations. The projection to the camera system allows a reconstruction of those points in real time.

3.4.1. Sample

While samples varied in composition, the general size of samples was maintained constant. A typical sample was 8 cm long and placed in the same location for each test. The size and location were chosen in an effort to keep the projected image close to the centers of the cameras to ensure accurate position reconstruction. Voltage was applied through alligator clips held in place by sticky tack and a white sheet of paper was placed over the clips and tacked to prevent confusion between the yellow tack and yellow dots on the sample.
3.4.2. Point tracking

A number of colored dots were painted or placed along the side of the sample with more being placed along the areas of a high curvature as shown in Figure 5. Before applying a voltage, the entire images from both cameras were compared to the specific RGB and range value thresholds for each camera and each dot. If all dots are found in user-accepted
locations, the program stored the points and used a reduced search area centered on the latest known location of each dot for the current search. In the event that a dot is not found in its reduced search area, the program searches the entire frame for the dot which adds roughly 112 ms to run-time for the current system. To reduce background noise, the test bed was covered in white paper before the placement of the sample.

3.4.3. Shape-memory effect of SMPs

Figure 6 demonstrate the macroscopic shape-memory effect of the SMP nanocomposites. The permanent shape is a flat strip, and the temporary shape is an ‘n’ shape. It can be seen that, at the same actuation voltage, the recovery time of four samples is 5123, 582, 110, and 94 s, for samples G1, G2, G3 and G4 respectively. The shape memory effect of the SMP was improved by coating CNFP due to more CNFs involve to the surface conductive network. Meanwhile, blending 1 wt% CNFs into SMP will further facilitate the recovery of SMP which is a result of the increase of bulk thermal and electrical conductivity. As a result of this synergistic effect, we can see that G4 is dramatically faster than 95 s, which is less than 1/10 of the recovery time of G1.

3.5. Control tests of SMP nanocomposites

3.5.1. Control system

As can be seen in Figure 7, pixel coordinates $u$ and $v$ from each camera are obtained using the vision system discussed in the previous section. This camera data is used in

![Figure 6](image)

Figure 6. Series of photographs showing the macroscopic shape-memory effect of SMP composite for G1–G4. The permanent shape is a flat strip of composite material, and the temporary shape is deformed as right-angled shape.
reconstruction to obtain the states $x_i$, $y_i$, and $z_i$ and then calculate $\Theta$. This deflection angle is compared to the desired angle, $\Theta_d$, creating the error signal $e = \Theta_d - \Theta$. As will be explained in a later section, a command voltage $V_c$ is calculated from the proportional-integral-derivative (PID) controller and sent through the voltage regulator in conjunction with the power supply and applied to the sample as $V_{\text{input}}$. This voltage heats the material through resistive heating causing a change in the position as $T_m$ (i.e. the material temperature) approaches and then surpasses $T_g$ (i.e. the glass temperature).

3.5.2. PID control design

Based on the error signal $e(k)$, the following PID controller is designed and three gains are proportional gain ($k_p$), integral gain ($k_i$), and derivative gain ($k_d$). The PID controller is

$$u(k) = k_pe(k) + k_i \int_0^k e(\tau) d\tau + k_d \dot{e}(k)$$

(2)

For the discrete system with a time-step $T_s$, it is useful to define the integral portion $I(k) = \int_0^k e(\tau) d\tau$ using the trapezoidal rule as $I(k) = [e(k) + e(k+1)]T_s/2 + I(k-1)$ and the derivative portion as

$$D(k) = \frac{e(k) - e(k-1)}{T_s}$$

(3)

The proportional value, $P(k)=k_pe(k)$, remains unchanged.

3.5.3. Variation in integral value

In many systems, such a controller would achieve the desired response with the appropriate gains. Since the response of the material is one directional, however, a precaution was taken with the integral controller. To prevent wind-up that could not be compensated by the other gains, a reset function that would set the iterative sum back to zero based on the following:

$$I(k) = P_I \left( k_i T_s \frac{1}{2} [e(k) + e(k-1)] + I(k-1) \right)$$

$$\left( k_i T_s \frac{1}{2} [e(k) + e(k-1)] + I(k-1) \right)$$

(4)
is designed. Ideally, \( I_{\text{max}} \) would be chosen such that

\[
I_{\text{max}} \leq \sqrt{Rh[T_m - T_{\infty}]}
\]

in which \( T_{\infty} \), \( R \) and \( h \) are the ambient temperature, the resistance and the coefficient of convection, respectively. However, it was found that a constant value proved adequate.

### 3.5.4. Results of PID control of SMP nanocomposites

The Figure 8 shows the final results of a PID control after iterative tuning of its parameters \((k_p = 20, k_i = 15, \text{ and } k_d = 4k_d)\). Each sample was first heated with a voltage of 25 V until malleable, deformed under loading to \( \sim 180^\circ \) from the memorized state, and allowed to cool down to room temperature before testing. These had a reasonably fast response of \( \sim 90 \text{ s} \) and could be repeatedly commanded to the desired angle within 5%.

In a typical response, the proportional gain (Figure 9) drove the response of the sample in each test for around 50 s. Saturation control and resetting function in the iterative gain kept this initial input acting as the standard step input seen in most SMP testing. With time, however, the error signal becomes small enough to almost negate the proportional gain and the integral gain (Figure 10) and becomes the dominant driver of the voltage. It was found that in the pursuit of a fast response, a small derivative gain was desirable thus making its contribution to the voltage input minimal. Larger values increased the response time by up to 40 s, while only decreasing the overshoot 2\(^\circ\).

![PID control response for varying values of \( k_p \) and \( k_i \).](image1)

![Typical proportional gain input.](image2)
4. Conclusion

In this study, the electrical conductivity of the SMPs was significantly enhanced by incorporating CNF and CNFP into them, and a vision-based control system was developed to achieve flexible shape changes of the material. Specifically, experiments were conducted to examine the synergistic effects of CNF and CNFP on the shape recovery. The electrical conductivity of the SMP nanocomposites was increased by incorporating CNFP onto the SMP resin and further reduced by blending CNFs into the SMP resin matrix. The shape-memory response was significantly accelerated. Meanwhile, a vision-based control system was developed, which offered a noninvasive approach to measure and precisely control the shape of the SMP nanocomposites. The actuation test results show that the responses of the SMP nanocomposites under this controller were fast and accurate, and the performance was repeatable.

4. References

[1] A. Lendlein, H. Jiang, O. Junger, and R. Langer, Light-induced shape-memory polymers, Nature (London). 434 (2005), pp. 879–882.
[2] A. Lendlein and S. Kelch, Shape-memory polymers, Angew. Chem. Int. Ed. 41 (2002), pp. 2034–2057.
[3] J.S. Leng, H.B. Lu, Y.J. Liu, W.M. Huang, and S.Y. Du, Shape-memory polymers: A class of novel smart material, MRS Bull. 34 (2009), pp. 848–855.
[4] X. Lan, Y.J. Liu, H.B. Lv, X.H. Wang, J.S. Leng, and S.Y. Du, Fiber reinforced shape-memory polymer composite and its application in a deployable hinge, Smart Mater. Struct. 18 (2009), pp. 024002–024010.
[5] A.L. Browne and N.L. Johnson, Method for controlling airflow. United States Patent 7178859, 2007.
[6] I. Bellin, S. Kelch, R. Langer, and A. Lendlein, Polymeric triple shape materials, Proc. Natl Acad. Sci. USA. 103 (2006), pp. 18043–18047.
[7] C.H. Zhang, H.G. Wei, Y.Y. Liu, H.F. Tan, and Z.H. Guo, Enhanced toughness and shape memory behaviors of toughed epoxy resin, High Perform. Polymers. 24 (2012), 702–709.
[8] R. Vaia, Nanocomposites-remote-controlled actuators, Nat. Mater. 4 (2005), pp. 429–430.
[9] D.J. Maitland, M.F. Metzger, D. Schumann, A. Lee, and T.S. Wilson, Laser activated shape memory polymer microactuator for treating ischemic stroke, Lasers Surg Med. 30 (2002), pp. 1–11.
[10] H.B. Lu, F. Liang, and J. Gou, Nanopaper enabled shape-memory nanocomposite with vertically aligned nickel nanostrand: Controlled synthesis and electrical actuation, Soft Matter. 7 (2011), pp. 7416–7423.
[11] H.B. Lu, P.P. Bai, W.L. Yin, F. Liang, and J. Gou, Magnetically aligned carbon nanotubes in nanopaper for electro-activated shape-memory nanocomposites, Nanosci. Nanotechnol. Lett. 5 (2013), pp. 732–736.
[12] A.M. Schmidt, Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles, Macromol. Rapid Commun. 27 (2006), pp. 1168–1172.
[13] M.Y. Razzaq, M. Anhalt, L. Frommann, and B. Weidenfeller, Mechanical spectroscopy of magnetite filled polyurethane shape memory polymers, Mater. Sci. Eng. A 471 (2007), pp. 57–62.

[14] J.S. Leng, H.B. Lv, Y.J. Liu, and S.Y. Du, Comment on “water-driven programmable polyurethane shape memory polymer: Demonstration and mechanism” [Appl. Phys. Lett. 86, 114105, (2005)], Appl. Phys. Lett. 92 (2008), pp. 206105.

[15] H.B. Lv, J.S. Leng, Y.J. Liu, and S.Y. Du, Shape-memory polymer in response to solution, Adv. Eng. Mater. 10 (2008), pp. 592–595.

[16] H.B. Lu, Y.J. Liu, J.S. Leng, and S.Y. Du, Qualitative separation of the effect of solubility parameter on the recovery behavior of shape-memory polymer, Smart Mater. Struct. 18 (2009), pp. 085003.

[17] J. Gou, S.O. Braint, H. Gu, and G. Song, Damping augmentation of composites using carbon nanofiber paper, J. Nanomater. 2006 (2006), pp. 1–7.

[18] J. Gou, Single-walled nanotube bucky paper and composites, Polym Int. 55 (2006), pp. 1283–1288.