



A facile approach to fabricate shape memory polyvinyl alcohol/short carbon fibre composites with self-folding properties

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Abstract. In this article, electroactive shape memory polyvinyl alcohol (PVA)/short carbon fibres (SCFs) composites were prepared by simple solution casting method. The self-folding properties of PVA/SCF composites were achieved by shape programming procedure and multilayer assembly technology. The design concept was a three-layer self-folding structure, which utilized three easily obtainable materials; namely, PVA/SCF composite films (shape change layer), polyimide tape (structural layer) and copper wire. The reliability of spontaneous shape recovery of self-folding samples was studied by electrical and shape memory performance tests. The results showed that with the appropriate increase of the applied voltage, the deformation time of the samples decreased and shape memory performance improved. A sample completed the entire shape recovery process within 48 s under a low triggered voltage of 35 V, and shape recovery ratio (R_r) reached 95%. In addition, shape memory cycle tests showed that the samples had good cycle stability. After 15 consecutive times of unfolding/self-folding cycles, the R_r and the shape fixity ratio (R_f) of the samples were all greater than 93%. A 2D self-folding component was fabricated by properly assigned PVA/SCF composites in a plane, which could complete shape changing at 35 V. This showed the feasibility of self-folding samples in actuating the conversion of 2D framework to 3D structure. The study provides a unique strategy to expand the application of shape memory PVA/SCF composites in smart 3D structures with self-folding properties.

Keywords. Polyvinyl alcohol (PVA); shape memory properties; self-folding; composites.

1. Introduction

Shape memory polymers (SMPs) are a class of smart materials with the ability to recover from a pre-programmed temporary shape to the permanent shape as required in response to an environmental stimulus [1,2], such as temperature [3], moisture [4], magnetic [5], light [6], etc. In order to expand applications of SMPs to meet the requirements of different occasions, it is necessary to study the performance and structure of the materials. Various composites with enhanced properties can often be obtained by compounding SMPs with other materials. On the other hand, SMPs and its composites are manufactured into different structures. After shape programming, these structures can realize some new functions, such as self-folding and self-unfolding. Self-folding structures manufactured based on SMPs can actuate the conversion of 2D framework to 3D structure, which is achieved by the shape memory effect of SMPs [7,8]. In addition, compared to shape memory alloys (SMAs), SMPs have a series of advantages, such as high strain recovery rate, low density, low cost, simple shape programming procedure and easy control of recovery temperature [9].

Currently, SMPs with self-folding properties have been widely applied in various areas, such as industry, medicine, aerospace, logistics, etc. They include robot actuators and bionic soft structures [10,11], containers for drug delivery and biological devices [12,13], folding satellites and solar arrays [8,14]. In addition, many self-folding structures are not composed of single SMPs, and their application can be expanded when combined with other materials to form composite structures. By combining SMPs with paperboard or flexible circuit boards, a self-folding hinge was formed, which could drive the self-assembly and walking of soft robots in response to an environmental stimulus [15]. The complex and sequential self-folding components could be printed by 3D printing of SMPs [16]. Compared with other polymers, polyvinyl alcohol (PVA) has the advantages of light weight, high mechanical properties and excellent shape memory performance. This makes it have great application potential in structures that require light weight and large deformation, such as robots and folding satellites. PVA is also a polymer with good chemical stability, and its glass transition temperature is easy to adjust. After modification, the mechanical properties and shape memory performance of PVA can be further improved [17–19]. Similar

to polylactic acid (PLA), PVA has good biocompatibility and degradability. However, PVA also has high flexibility and hydrophilicity, which makes it suitable for drug sustained-release carriers, tissue engineering scaffolds and other biomedical fields [20].

However, most of SMPs currently studied are non-conductive, whose self-folding structures are actuated by heating methods such as heating plate, oven and hot water/oil etc. [21,22]. Due to the electrical insulation and spatial distribution of the deformed material, these heating methods have the disadvantages of not being able to heat at a long distance and nonuniform heating. The equipment for applying thermal stimulus are often complex, expensive and space-consuming. Furthermore, for the SMPs with self-folding properties, it is always desirable to achieve minimal human intervention and long-distance rapid deformation.

In this article, a facile approach to fabricate SMPs with self-folding properties is presented. The electroactive shape memory PVA/short carbon fibre (SCF) composites prepared by solution casting were utilized. This was because PVA possessed the advantages of light weight, large deformation, non-toxic, good film-forming property and easy processing. SCF had good conductivity and high specific strength [23]. The PVA/SCF composites showed excellent conductivity when a small amount of SCF was filled. Self-folding structures were fabricated using the prepared PVA/SCF composites, and their self-folding properties were achieved by shape programming procedure and multilayer assembly technology. When the wire was introduced into the conductive PVA/SCF composites, the temperature of samples could be rapidly and uniformly increased at a long distance by using the Joule heating effect. In addition, the electrical and shape memory performance experiments were used to study the reliability of spontaneous shape recovery of the samples. The self-folding samples in this study could actuate the conversion of 2D framework to 3D structure when properly assigned in the plane.

2. Methodology

2.1 Design and fabrication

The electroactive shape memory PVA/SCF composites were prepared by simple solution casting method. The degree of polymerization and alcoholysis of PVA were about 1700 and 50%, respectively. The fibre diameter of SCFs was 7.5 μm . The PVA/SCF composites with a weight ratio of 94:6 were obtained by filling the PVA matrix with SCFs. As shown in figure 1, SCFs were firstly dispersed in deionized water for 0.5 h using the ultrasonic, followed by adding PVA with magnetic stirring (DF-101S, Shanghai Lichen Bangxi Instrument Technology) for 7 h at 95°C. Then, the mixture was put into a vacuum dryer (LGJ-10D, Beijing Science Instrument) to remove air bubbles. After that, the uniformly mixed solution was poured on a smooth glass plate, and the solvent was evaporated in an oven at 70°C. Finally, the PVA/SCF films with uniform thickness were obtained and stored in an electronic dryer. The prepared PVA/SCF composite films with 6 wt% of SCFs were cut into different shapes and sizes with precise cutting tools. Using CAD software and 3D printing technology, we could flexibly design and print the mould with the required shape and size. The cut PVA/SCF composite films were placed in the printed mould to obtain various permanent shapes through plasticity.

After the electroactive shape memory PVA/SCF composites were prepared, a multilayer assembly technology was used to fabricate it into a multilayer self-folding structure. The self-folding structure was designed as a three-layer composite structure, whose shape and dimensions are shown in figure 2. The middle layer was a PVA/SCF composite film with a thickness of 0.2 mm, which was a shape changing layer. The upper and lower layers, made of 0.055 mm-thick polyimide tape (PI) with an adhesive on one side, formed the non-deformable structural layer. These two layers were adhered to the PVA/SCF composite film

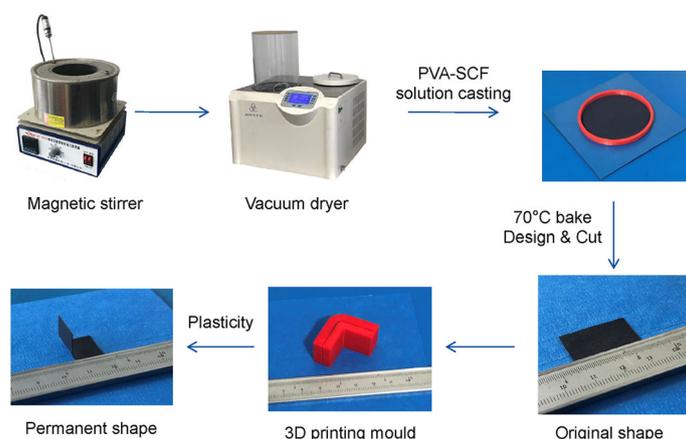


Figure 1. The fabrication of PVA/SCF composite films with a permanent shape.

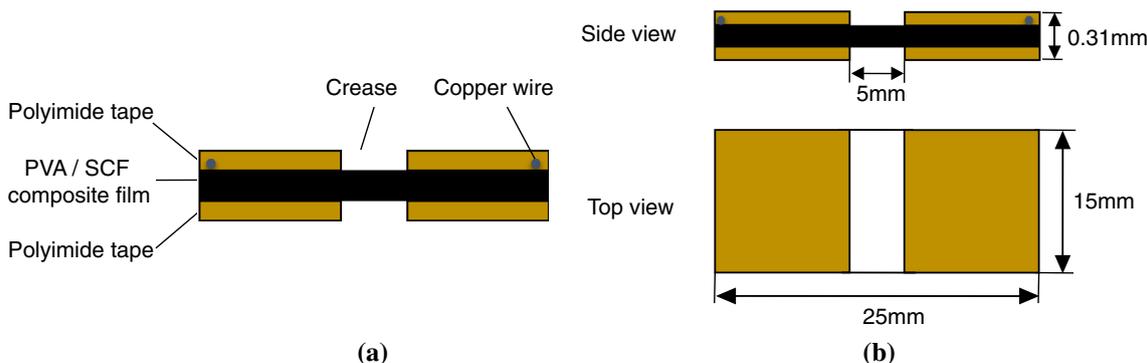


Figure 2. The fabrication of multilayer self-folding structure. (a) Three-layer assembly of polyimide tape (structural layer) and PVA/SCF composite film (shape change layer) and (b) the dimensions of the sample (dimensions are not to scale).

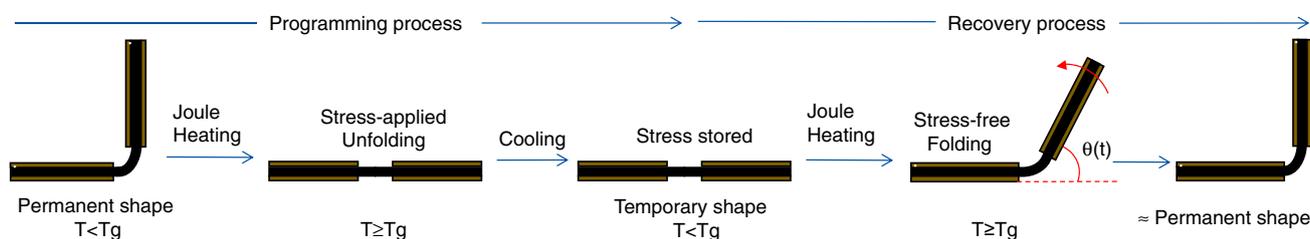


Figure 3. Diagram of the experiment performed to evaluate the shape memory response of sample.

using precise cutting tools. Polyimide possessed the advantages of high temperature resistance and high insulation, which could well preserve the heat generated inside the material during ohmic heating. At the same time, it was a highly flexible elastic material suitable for making 3D structure hinge. Since the PVA/SCF composites were electrically conductive, copper wires (0.1 mm thick) were introduced on both sides of the middle layer so that electrical stimulation could be transmitted at a distance. This contributed to achieve minimal human intervention and long-distance rapid deformation of the self-folding structure. In order to prevent the bending of the PVA/SCF layer from being affected, 5 mm gap widths were reserved on the two polyimide layers.

The shape memory effect of electroactive PVA/SCF composites enabled the self-folding samples to produce spontaneous shape changing. Figure 3 shows a shape memory cycle of the self-folding sample, including shape programming process and shape recovery process. In the shape programming process, the electrical stimulation was transmitted to PVA/SCF layer through wire when a proper voltage was applied, and the temperature of samples was increased by generated Joule heat. When the temperature reached above the glass transition temperature (T_g) of the PVA/SCF composites section, an external force was applied to deform the sample into a straight shape. Then the constraint of the external force was maintained and the stimulus was removed. When the temperature was cooled below T_g , the sample was held for a time sufficient to equilibrate the

strain (~ 15 min). After that, the external force was released and the temporary programming shape was fixed. In the shape recovery process, when the stimulus was applied again under the same conditions, the free shape recovery of the sample was activated with the increase of temperature. Finally, the sample recovered from temporary programming shape to permanent shape.

3. Results and discussion

3.1 Characterization

The free shape recovery of PVA/SCF polymers could be effectively activated when the temperature was above the glass transition temperature (T_g). In our previous work, it was found that the PVA composites with 6 wt% of SCFs had better conductive network and mechanical property, and its T_g value was measured to be 56.5°C [18]. In the following, we performed microscopic morphology analysis, electrical and shape memory performance characterization tests on self-folding samples fabricated above.

The microscopic morphology of the samples was examined by using a scanning electron microscopy (SEM, HITACHI SU-1500). The SEM analysis was performed in order to evaluate the distribution of SCFs in the PVA matrix. Figure 4 shows SEM images of PVA/SCF composite film with 6 wt% of SCFs. It could be observed that SCFs were well dispersed in the PVA matrix, the

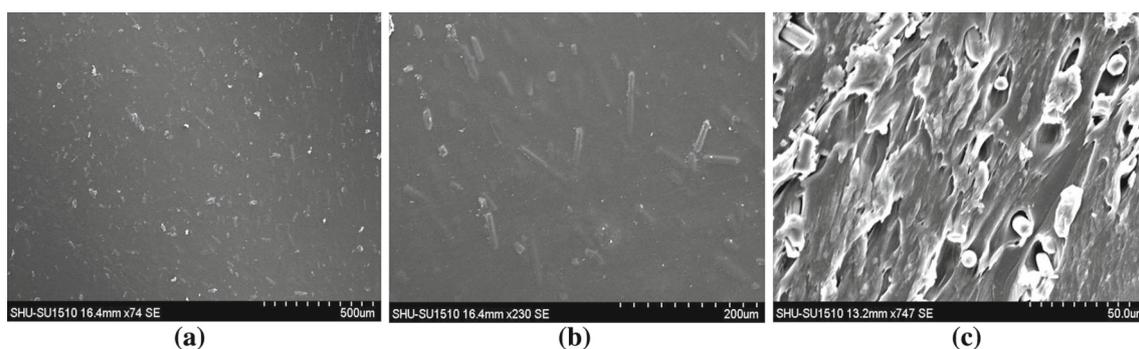


Figure 4. SEM images of PVA/SCF composite film with 6 wt% of SCFs. (a and b) The surface morphology and (c) the cross-sectional morphology.

compatibility between SCFs and PVA was good, and there was no obvious agglomeration formed by SCFs. In addition, the SCFs connected to each other and formed a continuous conductive network in PVA matrix, which made the PVA/SCF composites have electroactive shape memory capability.

For the self-folding samples fabricated based on PVA/SCF composites, its deformation speed and degree of deformation were two important factors to evaluate the ability of spontaneous shape changing. The samples in this study were deformed by electric actuation, and their deformation speed was mainly affected by the electrical properties of PVA/SCF composites. When a proper voltage was applied, the Joule heat generated inside the PVA/SCF layer could be determined by the formula: $Q = U^2T/R$, where U , T and R represented the average voltage, time and resistance, respectively. For the samples of a specific size, their resistance was a stable value, the resistance of samples in this study was 1015Ω . However, the increase of U and T would increase the material temperature. The spontaneous shape changing of the samples was completed at a lower trigger voltage, which was often desirable. However, when the applied voltage was too small, it was necessary to extend the time to reach the deformation temperature, which increased the deformation time. Therefore, a proper voltage needed to be selected to ensure that the deformations of the samples were completed in a short time.

The electrical properties of the samples were tested, and the relationships among surface temperature, applied voltage and time were obtained. The constant voltage was provided by a DC power supply (MP1005D, China) and the temperature was monitored by a digital thermocouple (VC890C, China). As shown in figure 5, when the voltage was the same, the sample temperature increased with time. When the voltage was 15 V, the temperature of the samples increased slowly and reached only 38°C in 70 s. This temperature was much lower than the T_g (56.5°C) of the PVA/SCF composites, resulting in that the free shape recovery could not be activated. However, within 70 s, the temperatures of the samples at 25, 35 and 40 V reached 65, 97 and 118°C , respectively, which were higher than the T_g

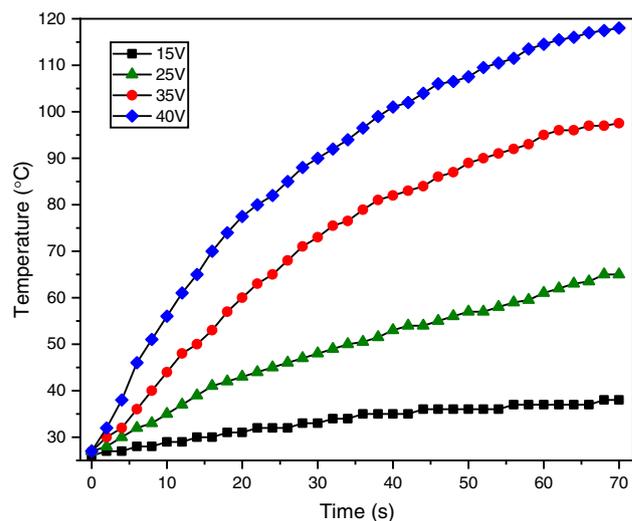


Figure 5. Temperature evolution of the samples as a function of time at various triggering voltage.

of the PVA/SCF composites. In addition, when the time was the same, the rate of temperature rise increased with increasing voltage. The temperature of the samples reached only 50°C in 35 s at 25 V voltage. However, within 35 s, the temperatures of the samples at 35 and 40 V quickly rose to 77 and 95°C , respectively. Therefore, in order to achieve the spontaneous shape recovery of self-folding samples and shorten their deformation time, the applied voltage could be appropriately increased.

The deformation degree of the samples consisted of programming of the temporary shape and recovery of the permanent shape. The shape fixity ratio (R_f) and shape recovery ratio (R_r) were determined by using the following formulas:

$$R_f(\theta)\% = \frac{\theta_f}{90} \times 100\% \quad (1)$$

$$R_r(\theta)\% = \frac{\theta_t - \theta_0}{90 - \theta_0} \times 100\% \quad (2)$$

where θ_f was the folding angle of the samples after removal of the load in the shape programming process, θ_t the time

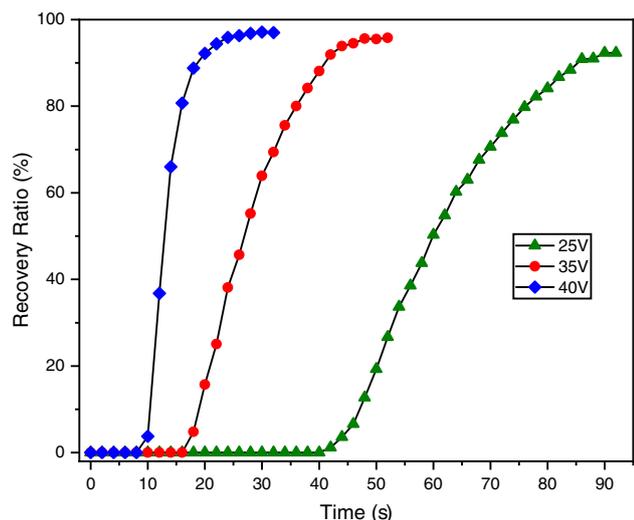


Figure 6. Shape recovery ratio of the samples as a function of time under three constant voltages.

Table 1. Shape memory properties of the samples at different voltages.

Voltage (V)	Shape recovery ratio (%)	Shape fixity ratio (%)	Time (s)
25	92.2	93.1	90
35	95	95.7	48
40	97.1	98.4	29

dependent the folding angle in the shape recovery process and θ_0 the folding angle at 0 s.

The shape recovery property of the samples under different voltage was obtained by shape memory test, as shown in figure 6. The experiment process was monitored by a camera. Photographs acquired were processed by image analysis software (Meazure, the USA) to measure the exact value of the folding angle. As shown in the figure, when different voltages were applied, the temperature of the samples was rapidly increased by Joule heat, and the free shape recovery was activated. It was observed that the R_r of the samples firstly increased at a faster rate, and then slowly increased until it finally reached a stable value. When 35 V voltage was applied, the R_r of the samples started to increase at ~16 s, then rapidly reached recovery ratio of 64.3% within 14 s, and finally reached a stable value of 95% at 48 s. In addition, as the applied voltage increased, the final R_r of the samples increased, and the time to complete shape recovery decreased. The detailed data of R_r and R_f of the samples at different voltages are shown in table 1.

Shape memory cycle tests were performed at 35 V to evaluate the cycle stability of the self-folding sample. Figure 7 shows the R_r and R_f values for different shape memory cycles of the sample. In the first cycle, the R_r and R_f values of the sample were 95 and 95.7%, respectively. After 15 consecutive times of unfolding/self-folding cycles,

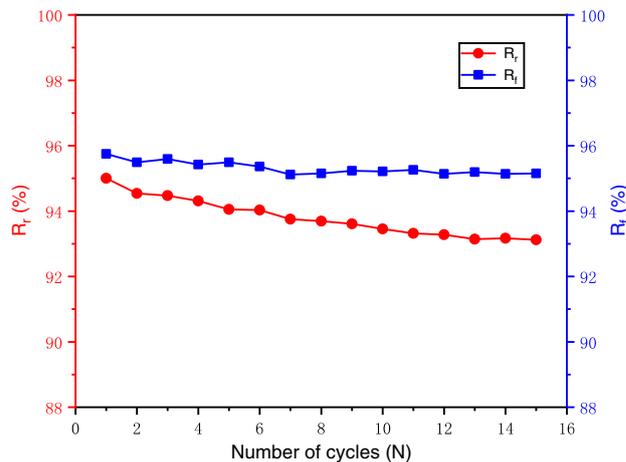


Figure 7. R_r and R_f values for different shape memory cycles of the sample at 35 V.

the R_f of the sample did not change significantly (95.2%), while the R_r decreased slightly (93.1%). Both of them reached a stable value above 93%, which indicated that the sample had good cycle stability.

The visual shape recovery process of a self-folding sample at 35 V is shown in figure 8. The permanent shape of the sample was an ‘L’ configuration, which was then manually unfolded into a straight configuration during the programming process of the shape memory cycle. In the free shape recovery process, the sample recovered rapidly from 16 to 37 s, and recovered slowly from 37 to 48 s. Finally, it spontaneously folded into the permanent shape within 48 s.

3.2 A self-folding component

In order to demonstrate the feasibility of self-folding samples in actuating the conversion of 2D framework to 3D structure, a cubic self-folding component was developed with the 2D multilayer assembly principle. A 0.1 mm-thick paperboard was firstly cut into a 2D plane with precise cutting tools. Since the shape changing process of the self-folding component required that its six surfaces could be folded 90°, six self-folding samples were selected and pre-programmed. All the six samples were firstly unfolded into a straight shape when the temperature reached 60°C ($> T_g$) at 35 V. Then, after removal of the voltage, they were cooled back to room temperature and maintained at the external load for 15 min. Finally, after removal of the load, the temporary straight shape was fixed.

Then the six straight-shaped samples were carefully placed on the 2D plane. The non-bending part of the samples were firmly combined with the paperboard using polyimide tape, resulting in a multilayer assembly. In order to reduce the number of wires, one side of each sample used a single wire, and the other side shared a wire by using conductive copper foil tape. In addition, the copper foil tape

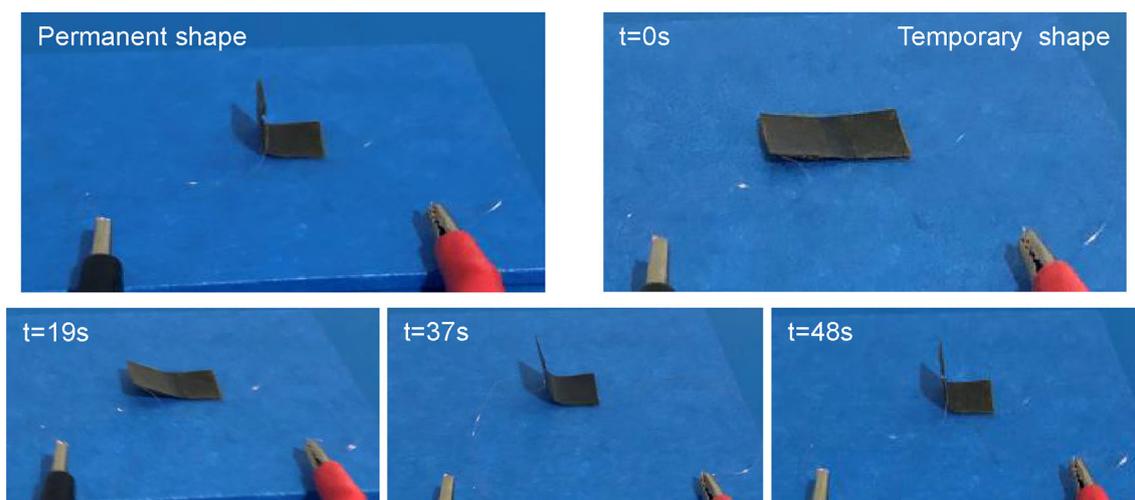


Figure 8. Spontaneous shape recovery process of the sample at 35 V.

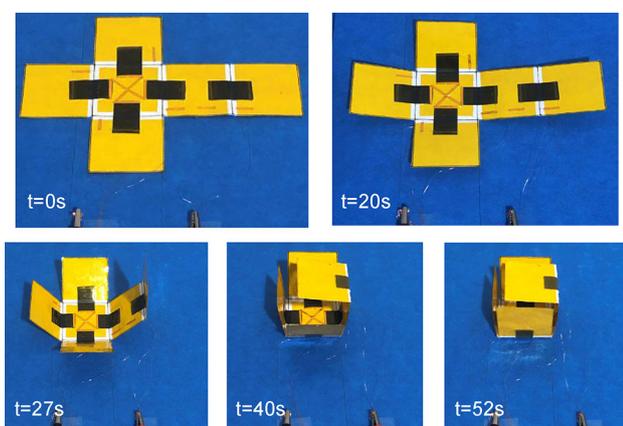


Figure 9. Spontaneous shape recovery process of the cubic self-folding component at 35 V.

could orderly attach the wires to the paperboard, which simplified its wiring scheme. All the wires of the samples were led from small holes on the plane, and were connected to the two poles of the power supply respectively.

To actuate the deformation of the cubic self-folding component from 2D framework to 3D structure, a voltage of 35 V was applied again. The temperature of six samples increased rapidly to above T_g due to the Joule heating effect. As shown in figure 9, the six faces of the cubic component started to actuate at 20 s, and self-folded to an angle of about 75° at 40 s. As the samples gradually recovered from the temporary straight shape to the permanent 'L' shape, the cubic component finally deformed from a 2D plane into a nearly closed 3D cubic structure within 52 s. Compared with the shape recovery process of a single sample, the cubic component took more time. This was because paperboard increases the load of the overall structure. In addition, the defect caused by poor adhesion

between different materials also affected the final deformation effect.

4. Conclusions

In this article, a facile approach for fabricating shape memory PVA/SCF composites with self-folding properties is presented. Several easily obtainable materials were utilized, and the manufacturing route could be easily implemented. The design concept was a 2D multilayer assembly with a shape change layer (PVA/SCF composite film), a structural layer (polyimide tape) and copper wire. Self-folding samples were manufactured based on electroactive PVA/SCF composites recovered from temporary programming shape to permanent shape at external electrical stimulus. This free shape recovery was achieved by shape programming procedure and shape memory effect of PVA/SCF composites. The samples showed good shape recovery and cycle stability at 35 V low trigger voltage. Its proper distribution on the 2D plane achieved the 3D transformation of a cubic self-folding component from a 2D framework. In addition, the Joule heating method for the electroactive PVA/SCF composites enabled them to achieve rapid and uniform heating from a long distance, and thus shortened the deformation time of the samples. The findings from this study contribute to expand the application of shape memory PVA/SCF composites in smart 3D structures with self-folding properties.

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References

- [1] Behl M and Lendlein A 2007 *Mater. Today* **10** 20
- [2] Luo X F and Mather P T 2010 *Adv. Funct. Mater.* **20** 2649
- [3] Calvo-Correas T, Shirole A, Crippa F, Fink A, Weder C, Corcuera M A *et al* 2019 *Mater. Sci. Eng. C* **97** 658
- [4] Guo Y F, Lv Z Y, Huo Y R, Sun L J, Chen S, Liu Z H *et al* 2019 *J. Mater. Chem. B* **7** 123
- [5] Razzaq M Y, Behl M, Nochel U and Lendlein A 2014 *Polymer* **55** 5953
- [6] Li T, Li Y, Wang X H, Li X and Sun J Q 2019 *ACS Appl. Mater. Inter.* **11** 9470
- [7] Gomez A and Shin M 2018 *J. Mech. Sci. Technol.* **32** 3107
- [8] Chen T, Bilal O R, Lang R, Daraio C and Shea K 2019 *Phys. Rev. Appl.* **11** 064069
- [9] Xin X Z, Liu L W, Liu Y J and Leng J S 2019 *Acta Mech. Solida Sin.* **32** 535
- [10] Martella D, Nocentini S, Antonioli D, Laus M, Wiersma D S and Parmeggiani C 2019 *Polymers* **11** 1644
- [11] Kobayashi K, Oh S H, Yoon C and Gracias D H 2018 *Macromol. Rapid. Commun.* **39** 1700692
- [12] Fernandes R and Gracias D H 2012 *Adv. Drug. Deliver. Rev.* **64** 1579
- [13] Randall C L, Gultepe E and Gracias D H 2012 *Trends Biotechnol.* **30** 138
- [14] Hu W, He Q, Sun X Q, Yang Y K and Yang B T 2018 *Sens. Actuators A* **281** 196
- [15] Felton S, Tolley M, Demaine E, Rus D and Wood R 2014 *Science* **345** 644
- [16] Mao Y Q, Yu K, Isakov M S, Wu J T, Dunn M L and Qi H J 2015 *Sci. Rep.* **5** 13616
- [17] Shaffer M S P and Windle A H 1999 *Adv. Mater.* **11** 937
- [18] Lin L L, Zhou Q and Li M J 2019 *Polym. Sci. Ser. A* **61** 913
- [19] Liang J J, Huang Y, Zhang L, Wang Y, Ma Y F, Guo T Y *et al* 2009 *Adv. Funct. Mater.* **19** 2297
- [20] Chiellini E, Corti A, D'Antone S and Solaro R 2003 *Prog. Polym. Sci.* **28** 963
- [21] Ding Z J, Yuan L, Liang G Z and Gu A J 2019 *J. Mater. Chem. A* **7** 9736
- [22] Wang D H and Tan L S 2019 *ACS Macro. Lett.* **8** 546
- [23] Leng J S, Lv H B, Liu Y J and Du S Y 2008 *J. Appl. Phys.* **104** 104917