4D printing of shape memory polymer via liquid crystal display Stereolithography

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Abstract

In this study, we report a new epoxy acrylate based shape memory polymer(SMP) fabricated by Liquid crystal display (LCD) Stereolithographic 3D printing. The printed 3D object has a high resolution and high transparency in visible light region. The uniaxial tensile tests showed enhanced tensile toughness and tunable mechanical properties. The fix-recovery and cycle tests indicated high shape recovery properties including high shape recovery rate and excellent cycling stability. In addition, a smart electrical valve actuator was fabricated that can be used in fast heat or electricity responsive electrical circuits. LCD 3D printing provides a low-cost and high efficient way to fabricate fast responsive SMP, which can be used in wide applications in various fields on aerospace engineering, biomedical devices, soft robots and electronic devices.

Keywords: Shape memory polymer; LCD; Transparency; High shape recovery rate; Fast responsive.

1. Introduction

Shape memory polymer (SMP), also known as smart material, has gained

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increasing research interest and considerable progress in recent years. SMP have the capacity to recover their deformed shape or properties to original state under the external stimuli, such as heat, light, electricity, as well as humidity[1-7]. Heat-activated stimuli for SMP is the most important type due to the intrinsic glass phase transition of polymer[8]. SMP could be easily fixed to temporary shape under a force when temperature is lower than glass transition temperature (T_g), and recover to their original shape after temperature increases over T_g[8-10]. SMP have been widely applied in soft robots, vascular stents, aerospace structures, sensors, as well as electronic devices[2, 4, 11-15]. However, the significant drawback of SMP is that it is difficult to fabricate complex geometries of shape memory structures by conventional molding and machining techniques, which limit the advanced applications in various areas[16, 17].

Three-dimensional (3D) printing, also known as additive manufacturing, has drawn a considerable amount of attention due to its capability for fabrication of complicate structures. 3D printing technology has been widely used in various field, including robots, microfluidics, wearable electronics, as well as biomedical devices[14, 18-22]. There are many different 3D printing technologies have been developed, such as stereolithography (SLA), digital light projection (DLP), photopolymer inkjet (PolyJet), selective laser sintering (SLS), fused deposition modeling (FDM) and LCD 3D printing[23-25]. The 3D printing technology applied to fabricate shape memory polymer, has been termed as 4D printing, which adds a fourth dimension of time to 3D printed structures[8, 26-28]. For instance, Devarshi Kashyap *et al.* demonstrated a radiopaque, porous, and custom 4D printed shaped shape memory polyurethane (SMPU) fabricated

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by fused deposition modeling (FDM) 3D printing technology for its application in endovascular embolization[29]. Tingting Zhao *et al.* synthesized a type of photopolymer to apply through stereolithography (SLA) 3D printing technology to fabricate 4D printed shape memory polymers, which shows high shape memory performance and mechanical properties[30]. Besides, Marta Invernizzi *et al.* demonstrated a 4D printed shape memory polymer with thermally induced healing abilities, which was achieved by digital light projection (DLP) technology[31]. 4D printing opens new opportunities to fabricated SMP with advanced application, yet the resolution and performance of SMP remain the bottleneck, which requests more advanced properties and functions of materials to broaden application of SMP.

LCD 3D printing, one of most commercial used 3D printing technology, is based on the selective photopolymerization reaction of liquid resin[32]. By changing the reactive formulations of liquid resin, various functional materials can be printed using such a technology. In addition，LCD 3D printer has a low cost and high resolution below 50 μm with a 2D screen LED and enable a way to fabricate complex 3D objects. In this study, we prepared a type of liquid resin that was applied to print 3D object with shape memory properties though LCD 3D printing. Compared with previous reported shape memory polymer, the fabrication of shape memory polymer with high resolution and complex structure can be achieved easily. The shape memory polymer shows super transparency in visible light region. Furthermore, the enhanced tensile toughness and tunable mechanical properties of shape memory polymer are studied. The shape memory performance of printed samples is evaluated through fix-recovery and cycle test, which shows high shape recovery properties and cycling stability. Thus, this shape memory polymer is a significant candidate of material for 4D printing. Using these technology and material, a smart electrical valve actuator is fabricated that can be used in heat or electricity responsive electrical circuits. We believe the shape memory polymer based 4D printing has potential for application in various filed including aerospace, biomedical device, soft robots as well as electronic devices.

2. Experiments

2.1 Material

Epoxy acrylate (EA) was purchased from Guangzhou Runao Chemical Co. Ltd. Isobornyl acrylate (IBOA) and trimethylolpropane triacrylate (TMPTA) were purchased from Shanghai Guangyi Chemical Co., Ltd. Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) from Sigma-Aldrich was applied as photoinitiator. All materials were acquired commercially and used as received.

2.2 Preparation of liquid resin

The liquid resin was prepared by mixing epoxy acrylate (EA) with Isobornyl acrylate (IBOA) and trimethylolpropane triacrylate (TMPTA) with different ratios. Then 3 wt% of diphenyl(2,4,6-trimethylbenzoyl)- phosphine oxide (TPO) as photoinitiator was added into the mixture and stirred for 30 min. Once finished, the mixture was degassed in a vacuum oven for 15 min to remove bubbles for following 3D printing.

2.3 3D printing fabrication

The LCD 3D printer (Photon-s, Shenzhen Anycubic Technology Co., Ltd., China) with“bottom-up” approach was used to fabricate shape memory polymer. A designed

3D model was first slice into a series of 2D images. Using the LCD image principle of liquid crystal display, selective transparent areas was modified by these 2D images. The 405nm of light from LED array was irradiated to liquid resin though transparent areas, while the opaque areas of LCD screen block the light. The irradiated liquid resin was solidified to form a layer, and the part of resin that was not irradiated still maintains the liquid. The substrate with fabricated structure was lifted, followed by next exposure and solidification. The process continues until the whole 3D model was fabricated. During the printing, the sliced thickness of each layer was 10 μm, and the exposed time of each layer was 5 s. After printing, the obtained structure was washed by ethanol to remove uncured resin followed by secondary curing in UV oven for 30 min.

2.4 Characterization

The resolution of printed sample was measured by electron microscope (SUPEREYES, China). The transparent spectrum was performed on an UV–vis spectrophotometer (NOVA-EA, China) from 400 to 800 nm. The FTIR spectrum was acquired on a Nicolet 5700 FTIR spectrometer (China). The TG-DSC curves were measured using differential scanning calorimetry analysis (TA Q600, USA).The tensile tests were performed on an electronic universal mechanical testing machine (ZQ-990A, 50 N, China).

3. Results and discussion

3.1 3D printing procedures for shape memory polymer.

The 3D printing procedure for shape memory polymer is schematically in **Figure 1a**. The patterned 405 nm of light though the LCD screen is illuminated onto the liquid resin, then the exposed liquid resin is solidified to form a solid layer, followed by rise of substrate to solidify a new one. Layer by layer solidification proceeds until the whole structure fabricated (details in part of Experiment). As for chemistry of liquid resin, epoxy acrylate (EA) was used as oligomer, and isobornyl acrylate (IBOA) and trimethylolpropane triacrylate (TMPTA) were used as monomer. The resin also contains a photoinitiator to initiate fast co-polymerization of epoxy acrylate (EA), isobornyl acrylate (IBOA) and trimethylolpropane triacrylate (TMPTA). Based on these technique and resin, we printed a series of complex structures (**Figure 1b**).The resolution of LCD screen is 47 μm, we evaluated the printing resolution of liquid resin by printing cylinder with height of 10mm and different diameters (200, 250, 300, 400, 500,600,700 μm). All cylinder can be successfully printed other than the one with width of 200 μm due to the instability of pixel (**Figure 1c**). These results demonstrate the ability of liquid resin to reach a high resolution of 250 μm, and the print resolution can be further improved by employing a higher resolution printer.

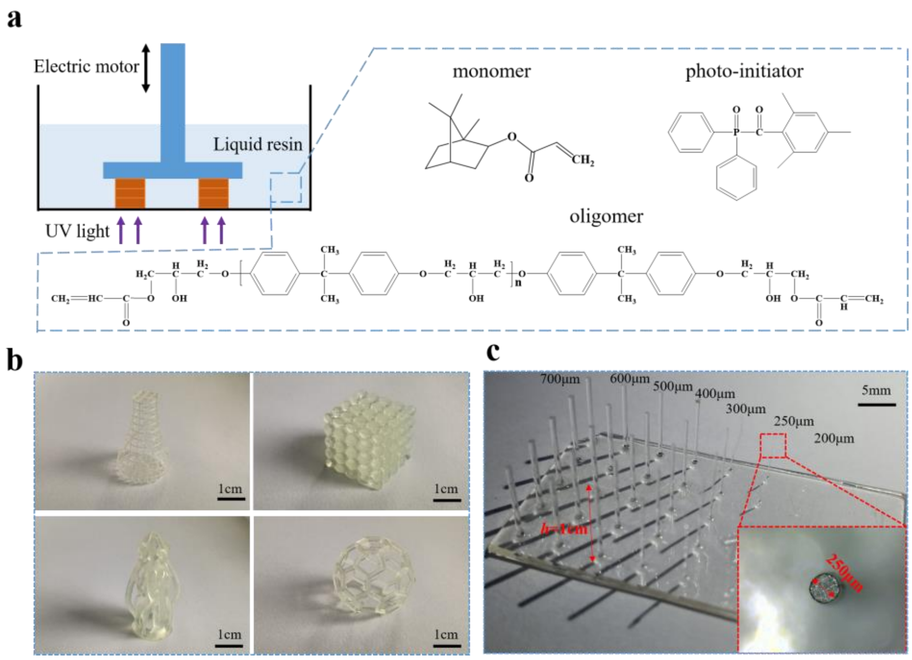

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Figure 1. Fabrication of shape memory polymer by Liquid Crystal Display (LCD) Stereolithography based 3D printer. a) Schematic diagrams of Liquid Crystal Display (LCD) Stereolithography based 3D printer and chemistry of liquid resin for 3D printing. b) Photographs of the printed 3D objects. c) The resolution of liquid resin by printing lines with different width (200, 250, 300, 400, 500, 600, 700 μm).

3.2 Transparency of printed sample.

As shown in **Figure 2**, the printed sample with 0.25mm thickness was completely transparent, and photograph covered by sample still can be observed clearly (inset figure of Figure 2). To further investigate the transmittance in visible range, **Figure 2** shows the transmittance spectra of printed sample in the wavelength range from 400 to 800nm. Remarkably, the printed sample exhibit 95.6% average transmittance in the visible light region.

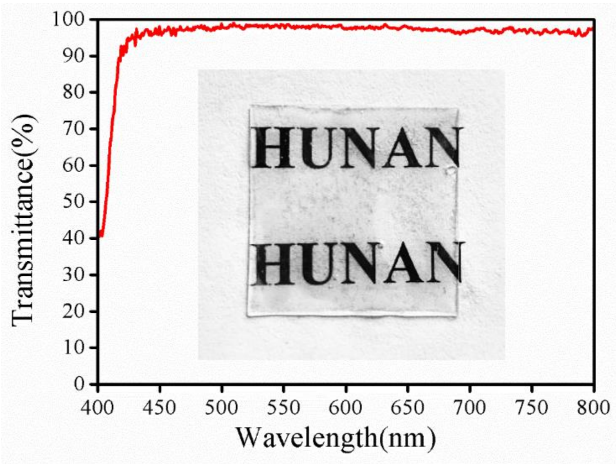

Figure 2. Super transparency of printed shape memory polymer. Transmittance spectra of printed sample with 1mm thickness in the visible light region (wavelength, 400–800 nm). Inset: photograph can be seen clearly through the top of printed sample.

3.3 FTIR analysis

The FTIR spectrum of shape memory polymer with different content of epoxy acrylate (EA) was shown in **Figure 3**. The peaks at 2954 cm^{-1} and 2878 cm^{-1} were assigned to the stretching vibration of $-CH_3$ and $-CH_2$, respectively. The characteristic peak at 1636 cm^{-1} were due to the stretch vibration of C=C double bond. The strong peak at 1735 cm^{-1} was ascribed to the stretching vibration of C=O, which shift from 1735 cm^{-1} to 1724 cm^{-1} with decreasing content of epoxy acrylate (EA) from 60% to 20%. The peak of the stretching vibration of O-H was expressed at 3442 cm^{-1}, changing to 3452 cm^{-1} when the content of epoxy acrylate (EA) decreases to 20%. It is noticed that the intensity of peaks attenuates with the decrease of epoxy acrylate (EA) content.

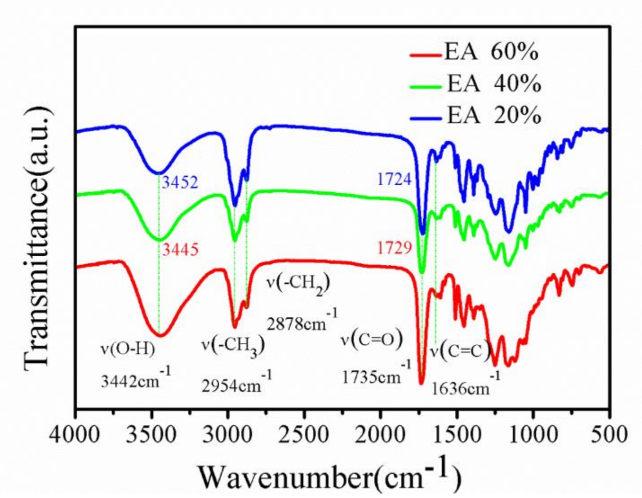

Figure 3. FTIR spectrum of printed shape memory polymer. FTIR spectrum of shape memory polymer with different content of epoxy acrylate (EA).

3.4 Thermal properties

TG analysis was used to study the thermal properties of shape memory polymer. As shown in **Figure 4a,** the initial decomposition temperature decreased with decreasing of content of epoxy acrylate (EA). This might attribute to improvement of thermal stability of polymer with higher epoxy acrylate (EA) concentration. To further

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determine the thermal properties of shape memory polymer affect by weight content of epoxy acrylate (EA), the DSC curves of printed samples with different weight content of epoxy acrylate (EA) were shown in **Figure 4b**. It can be seen that the epoxy acrylate (EA) concentrations decreased from 60 to 20 wt%, and the melting temperature (T_m) improved from 299.27 to 305.65 °C, indicating the potential applications including stents and soft robotics without thermal decomposition in low temperature.

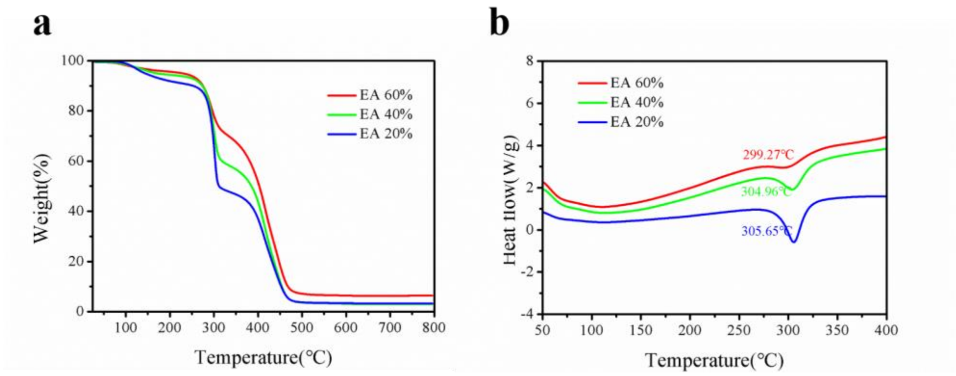

Figure 4. Thermal properties of shape memory polymer. a) TG analysis of shape memory polymer with different content of epoxy acrylate (EA). b) DSC curves of shape memory polymer with different content of epoxy acrylate (EA).

3.5 Mechanical properties

The mechanical properties of shape memory polymer were evaluated by the uniaxial tensile tests. These tests were conducted on an electronic mechanical testing machine with an extension rate of 1 mm min^{-1}. All tensile strength measurements were carried out at 25 °C (room temperature), which is below the glass transition temperature of shape memory polymer. Stress−strain curves was generated as shown in **Figure 5**. It illustrates that the modulus of shape memory polymer with 60 wt% of epoxy acrylate (EA) was around 26.4 MPa; and the ultimate strains was about 12.6 %. With decreasing of content of epoxy acrylate (EA), the ultimate strains decreased, while the modulus increased, indicating tunable mechanical properties of shape memory polymer.

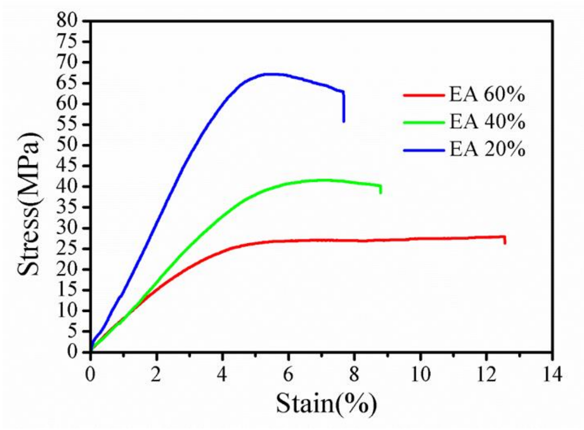

Figure 5. Mechanical properties of shape memory polymer. Stress−strain curves of printed samples with different weight content of epoxy acrylate (EA).

3.6 Shape memory effect

To demonstrate the excellent shape memory effect of printed sample, the test was carried out as follows: Firstly, the printed sample was heat to temperature above T_g and then bend into shape of "U", then the printed sample was cooled down to 25°C(below T_g) to fix the shape of "U" and the angle was measured as θ_f. Lastly, the printed sample was reheat to temperature above T_g to recover its original shape and the angle was measured as θ_r. The shape recovery ratio (R_r) is determined using equation:

$$R_r = \frac{(\theta_r - \theta_f)}{(180° - \theta_f)} \times 100\%$$

Where θ_r is the recovery angle, θ_f is the fixed angle.

Figure 6a shows the change of shape recovery ratios of printed 0.2mm of thickness with 40 wt% of epoxy acrylate (EA) at different temperature, it can be seen that the sample recovered to its original shape within 6s at higher temperature, which was faster than one at lower temperature. This phenomenon is because that greater mobility of polymer chains in higher temperature, which lead to excellent shape memory effect. The images of recovery progress of printed sample were shown in **Figure 6d**, the printed sample rapidly recovered to its original shape within 21 s at temperature of 80°C. Similarly, the printed sample with different content of epoxy acrylate (EA) also has effect on shape recovery ratio and recovery speed (**Figure 6b**). With decreasing of content of epoxy acrylate (EA), the recovery ratio and speed decreased. We further studied the repeated shape memory properties of printed sample. **Figure 6c** shows the value of shape recovery ratio (R_r) during 15 cycles. It can be seen that shape recovery ratio (R_r) was 97.8% for repeated shape memory process, which was nearly the same with the original one, indicating stability of shape memory effect.

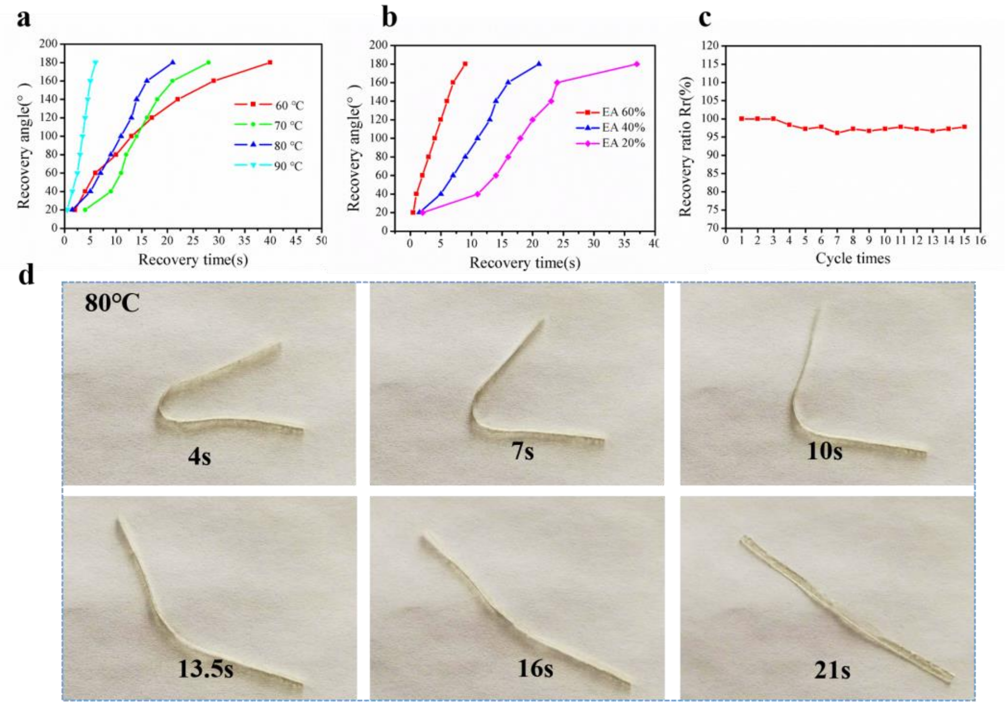

Figure 6. Shape memory properties of polymer. a) The change of shape recovery ratios of printed samples 0.2mm of thickness with 40 wt % of epoxy acrylate (EA) at different temperature. b) The

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change of shape recovery ratios of printed samples with different content of epoxy acrylate (EA) at temperature of 80 °C. c) Shape recovery ratio during 15 cycles. d) The images of recovery progress of printed sample at temperature of 80 °C.

3.7 3D printed structures and devices

Using LCD 3D printing technique, we printed a series of structures including logo "SMP", vascular stents, and robot arm to exhibit shape memory behavior. **Figure 7a** shows shape recovery process of the printed logo "SMP", which could rapidly recover back to its original shape within 13s. In addition, vascular stents with high complexity and resolution are a challenge to fabricate by traditional manufacturing approaches. **Figure 7b** shows that the 3D-printed vascular stents with high transparency, the stents was programmed to shape with small diameter and recovered to its original shape with a larger diameter within 16s. This phenomenon indicate that such responsive objects could be used in fabrication of soft robotics, minimal invasive surgery.

By integrating the printed sample with conductive materials such as paste with silver nanoparticle, the shape memory polymer could be applied in electrical devices. We fabricated a smart electrical valve actuator. This device was composed of printed sample with conductive silver paste, this silver paste acts as electrical contacts could print on shape memory polymer due to its solidify at room temperature, and two individual copper electrode was attached to device. As shown in **Figure 7c**, the original shape was an open electrical circuit, the programed shape was a closed electrical circuit with LED bulb lighted. When the temperature was above the glass transition temperature (T_g), The temperature enables recovery of shape memory polymer and

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change of electrical circuit from a closed state into the original open state, and LED bulb lighted does not work. The results indicate the device has great potential application for fire alarm and monitor systems and enables complex structure which are not easily accessible by other fabrication techniques.

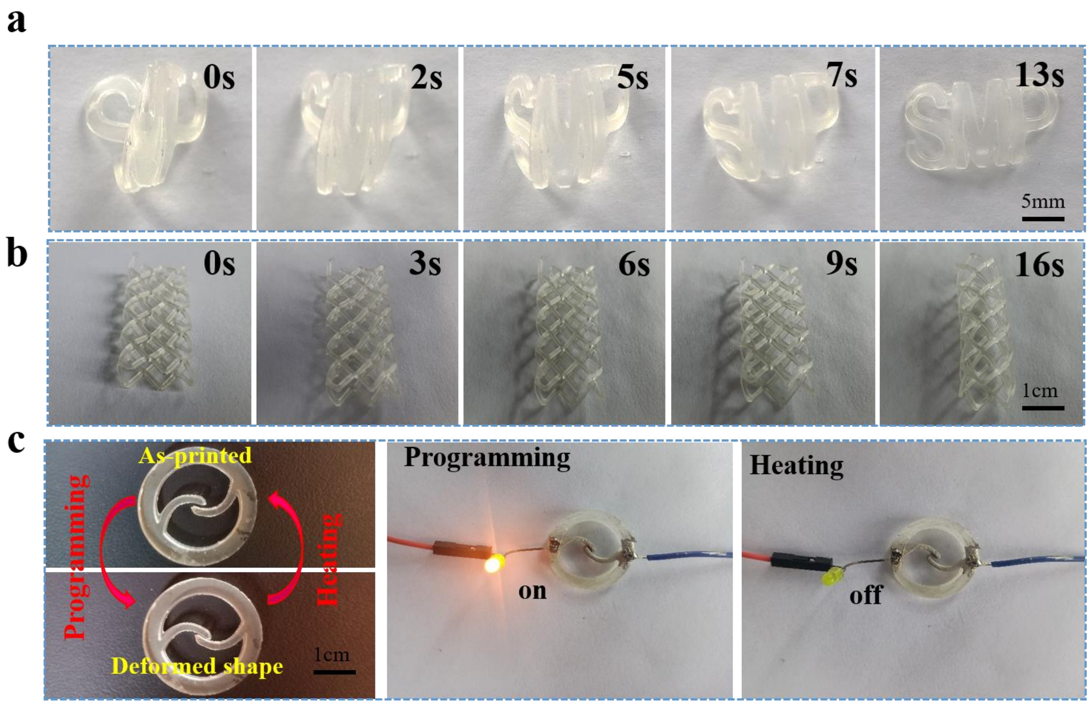

Figure 7. 3D printed structures to exhibit shape memory behavior. a) Shape recovery process of the printed logo "SMP". b) Shape recovery process of 3D-printed vascular stents. c) Shape programming and recovery process of smart electrical valve actuator

4. Conclusion

In summary, we fabricate a shape memory polymer LCD 3D printing, which shows high resolution and high transparency (95.6 %). The uniaxial tensile tests show enhanced tensile toughness and tunable mechanical properties of shape memory polymer. The shape memory properties have been proven through fix-recovery and cycle tests. The deformed sample could recover to its original shape at temperature of

90 °C within 6 s. The recovery ratio (R_r) was more than 97.8 % even after 15 cycles, indicating high shape recovery properties and cycling stability. Moreover, a smart electrical valve actuator is fabricated that can be used in heat or electricity responsive electrical circuits.

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Data Availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Reference

1. Chen, K.; Kuang, X.; Li, V.; Kang, G.; Qi, H. J., Fabrication of tough epoxy with shape memory effects by UV-assisted direct-ink write printing. *Soft Matter* **2018,** *14* (10), 1879-1886.
2. Ge, Q.; Sakhaei, A. H.; Lee, H.; Dunn, C. K.; Fang, N. X.; Dunn, M. L., Multimaterial 4D Printing with Tailorable Shape Memory Polymers. *Scientific Reports* **2016,** *6*, 31110.
3. Wang, J.; Xue, Z.; Li, G.; Wang, Y.; Fu, X.; Zhong, W.-H.; Yang, X., A UV-curable epoxy with "soft" segments for 3D-printable shape-memory materials. *J Mater Sci* **2018,** *53* (17), 12650-12661.
4. Zarek, M.; Layani, M.; Cooperstein, I.; Sachyani, E.; Cohn, D.; Magdassi, S. J. A. M., 3D printing of shape memory polymers for flexible electronic devices. *Advanced Materials* **2016,** *28* (22), 4449-4454.
5. Garcia Rosales, C. A.; Garcia Duarte, M. F.; Kim, H.; Chavez, L.; Hodges, D.; Mandal, P.; Lin, Y.; Tseng, T.-L., 3D printing of shape memory polymer (SMP)/carbon black (CB) nanocomposites with electro-responsive toughness enhancement. *Mater Res Express* **2018,** *5* (6).
6. Wang, W.; Liu, X.; Xu, W.; Wei, H.; Liu, Y.; Han, Y.; Jin, P.; Du, H.; Leng, J., Light-induced microfluidic chip based on shape memory gold nanoparticles/poly (vinyl alcohol) nanocomposites. *Smart Materials and Structures* **2018,** *27* (10).
7. Huang, W. M.; Yang, B.; Zhao, Y.; Ding, Z., Thermo-moisture responsive polyurethane shape-

memory polymer and composites: a review. *Journal of Materials Chemistry* **2010,** *20* (17).
8. Lee, A. Y.; An, J.; Chua, C. K., Two-Way 4D Printing: A Review on the Reversibility of 3D-Printed Shape Memory Materials. *Engineering* **2017,** *3* (5), 663-674.
9. Bi, H.; Xu, M.; Ye, G.; Guo, R.; Cai, L.; Ren, Z., Mechanical, Thermal, and Shape Memory Properties of Three-Dimensional Printing Biomass Composites. *Polymers (Basel)* **2018,** *10* (11).
10. Layani, M.; Wang, X.; Magdassi, S. J. A. M., Novel materials for 3D printing by photopolymerization. *Advanced Materials* **2018,** *30* (41), 1706344.
11. Mao, Y.; Yu, K.; Isakov, M. S.; Wu, J.; Dunn, M. L.; Jerry Qi, H., Sequential Self-Folding Structures by 3D Printed Digital Shape Memory Polymers. *Scientific Reports* **2015,** *5* (1).
12. Biswas, A.; Singh, A. P.; Rana, D.; Aswal, V. K.; Maiti, P., Biodegradable toughened nanohybrid shape memory polymer for smart biomedical applications. *Nanoscale* **2018,** *10* (21), 9917-9934.
13. Gao, H.; Li, J.; Zhang, F.; Liu, Y.; Leng, J., The research status and challenges of shape memory polymer-based flexible electronics. *Materials Horizons* **2019,** *6* (5), 931-944.
14. Zolfagharian, A.; Kouzani, A. Z.; Khoo, S. Y.; Moghadam, A. A. A.; Gibson, I.; Kaynak, A. J. S.; Physical, A. A., Evolution of 3D printed soft actuators. *Sensors and Actuators A: Physical* **2016,** *250*, 258-272.
15. Takashima, K.; Kamizono, H.; Takenaka, M.; Mukai, T., Force sensor utilizing stiffness change of shape-memory polymer based on temperature. *ROBOMECH Journal* **2017,** *4* (1).
16. Quadrini, F.; Bellisario, D.; Iorio, L.; Santo, L., Shape memory polymer composites by molding aeronautical prepregs with shape memory polymer interlayers. *Mater Res Express* **2019,** *6* (11).
17. Yuan, C.; Ding, Z.; Wang, T. J.; Dunn, M. L.; Qi, H. J., Shape forming by thermal expansion mismatch and shape memory locking in polymer/elastomer laminates. *Smart Materials and Structures* **2017,** *26* (10).
18. Kang, H.-W.; Lee, S. J.; Ko, I. K.; Kengla, C.; Yoo, J. J.; Atala, A. J. N. b., A 3D bioprinting system to produce human-scale tissue constructs with structural integrity. *Nature Biotechnology* **2016,** *34* (3), 312.
19. Gong, H.; Bickham, B. P.; Woolley, A. T.; Nordin, G. P. J. L. o. a. C., Custom 3D printer and resin for 18 μm× 20 μm microfluidic flow channels. *Lab Chip* **2017,** *17* (17), 2899-2909.
20. Yin, X.-Y.; Zhang, Y.; Cai, X.; Guo, Q.; Yang, J.; Wang, Z. L., 3D printing of ionic conductors for high-sensitivity wearable sensors. *Materials Horizons* **2019**.
21. Lee, A.; Hudson, A.; Shiwarski, D.; Tashman, J.; Hinton, T.; Yerneni, S.; Bliley, J.; Campbell, P.; Feinberg, A. J. S., 3D bioprinting of collagen to rebuild components of the human heart. *Science* **2019,** *365* (6452), 482-487.
22. Amin, R.; Knowlton, S.; Hart, A.; Yenilmez, B.; Ghaderinezhad, F.; Katebifar, S.; Messina, M.; Khademhosseini, A.; Tasoglu, S., 3D-printed microfluidic devices. *Biofabrication* **2016,** *8* (2), 022001.
23. Ambrosi, A.; Pumera, M. J. C. S. R., 3D-printing technologies for electrochemical applications. *Chemical Society Reviews* **2016,** *45* (10), 2740-2755.
24. Ligon, S. C.; Liska, R.; Stampfl, J. r.; Gurr, M.; Mülhaupt, R. J. C. r., Polymers for 3D printing and customized additive manufacturing. *Chemical Reviews* **2017,** *117* (15), 10212-10290.
25. Zhang, Y.; Zhang, F.; Yan, Z.; Ma, Q.; Li, X.; Huang, Y.; Rogers, J. A., Printing, folding and assembly methods for forming 3D mesostructures in advanced materials. *Nature Reviews Materials* **2017,** *2* (4).

26. Peng, B.; Yang, Y.; Gu, K.; Amis, E. J.; Cavicchi, K. A. J. A. M. L., Digital Light Processing 3D Printing of Triple Shape Memory Polymer for Sequential Shape Shifting. *ACS Materials Lett.* **2019,** *1* (4), 410-417.
27. Li, Y. C.; Zhang, Y. S.; Akpek, A.; Shin, S. R.; Khademhosseini, A., 4D bioprinting: the next-generation technology for biofabrication enabled by stimuli-responsive materials. *Biofabrication* **2016,** *9* (1), 012001.
28. Choong, Y. Y. C.; Maleksaeedi, S.; Eng, H.; Wei, J.; Su, P.-C., 4D printing of high performance shape memory polymer using stereolithography. *Mater Design* **2017,** *126*, 219-225.
29. Kashyap, D.; Kishore Kumar, P.; Kanagaraj, S., 4D printed porous radiopaque shape memory polyurethane for endovascular embolization. *Additive Manufacturing* **2018,** *24*, 687-695.
30. Zhao, T.; Yu, R.; Li, X.; Cheng, B.; Zhang, Y.; Yang, X.; Zhao, X.; Zhao, Y.; Huang, W., 4D printing of shape memory polyurethane via stereolithography. *European Polymer Journal* **2018,** *101*, 120-126.
31. Invernizzi, M.; Turri, S.; Levi, M.; Suriano, R. J. E. P. J., 4D printed thermally activated self-healing and shape memory polycaprolactone-based polymers. *European Polymer Journal* **2018,** *101*, 169-176.
32. Mohamed, M.; Kumar, H.; Wang, Z.; Martin, N.; Mills, B.; Kim, K., Rapid and Inexpensive Fabrication of Multi-Depth Microfluidic Device using High-Resolution LCD Stereolithographic 3D Printing. *Journal of Manufacturing and Materials Processing* **2019,** *3* (1).