

EXPLORING VARIABILITY IN SHAPE MEMORY PROPERTIES OF STEREOLITHOGRAPHY PRINTED PARTS

Y. Y. C. Choong*, M. Saeed†, H. Eng†, P. -C. Su*, and J. Wei†

* Singapore Centre for 3D Printing, School of Mechanical & Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

† Singapore Institute of Manufacturing Technology, 73 Nanyang Drive, Singapore 637662

Abstract

Shape memory polymers (SMPs) are smart materials that can change shape and revert to their permanent shape upon external stimulus. Most fabrications of SMPs are based on conventional methods which limit design freedom, hence additive manufacturing presents an alternative to expanding more possibilities for applications. In this study, curing process parameters were optimized for printing of photopolymerized thermoset SMPs by the stereolithography process. Tert-butyl acrylate (tBA) and di (ethylene glycol) diacrylate (DEGDA) were copolymerized with variations in crosslinkers to create networks with well-separated transition temperatures (T_g) that varied in a range from 43.6 to 74.1°C. A fold-deployable shape memory test was performed and revealed that free-strain recovery and retention deteriorate with increasing T_g . Nevertheless, the SMPs can undergo at least 20 repeated fold-deploy cycles before failure. These results are intended to provide better understandings in processing SMPs via stereolithography, while exploring variability in T_g widens the range of possible applications.

Introduction

Additive Manufacturing (AM) or 3D Printing has attracted significant interest lately due to its great freedom in design in terms of the geometric complexity of the fabricated parts [1]. The development of AM technology over the years has been reviewed intensively, and research interests in this field have been mainly focused on discussing the constraints of AM processes. As this technology advances, it comes to realize that the parts printed are generally static and non-adaptive. But this unique capability can be complementary to shape manipulation via the shape memory programming. Thus, combining smart materials such as shape memory polymers (SMPs) with 3D printing offers great potential in two aspects: producing SMP devices with practically relevant complex geometries that cannot be easily made by traditional processing methods; more shape variants can be realized for a 3D printed SMP part via shape memory programming. The time-dependent SME offers an additional dimension (i.e., time), leading to the so-called fourth-dimensional printing [2]. 4D printing is now primarily based on polymer-based AM processes where these printed SMPs offer greater flexibility with more degree-of-freedom and able to withstand significantly larger recoverable strains for shape transformation as compared to metals or alloys [3]. The combination of functionalities with great flexibility in terms of geometric complexity makes the fabricated SMPs more versatile and effective as an active material.

In principle, 4D printing can be realized in two ways according to whether they can be printed as a single material or a combination of multi-materials [4]. One of the most common single materials with shape memory properties used in 3D printing is polylactide (PLA) which

serves as the most popular filament among other materials used in Fused Deposition Modelling (FDM) [5]. PLA can be recognized as a “4D ready” material due to its thermoplastic nature which displays empirical indication of shape memory functionality such that above its melting temperature, the polymer softens upon heating to enable molding and reshaping, but solidifies back once it is cooled. However, FDM produces parts with lower resolution and poorer surface finish as compared to other 3D printing systems. Their thermoplastic SMP materials also experience creep after prolonged mechanical stress, and hence significantly affecting the long-term performance of the SMPs. On the other hand, 4D printing is widely demonstrated with the use of multi-materials printing since the launch of Stratasys’ Connex multi-material 3D inkjet printing technology. Different material with different properties can be specifically inkjet in different sections of a designed geometry and by utilizing the water-absorbing or thermal-sensitive properties of the materials, the self-assembly process is activated [2]. The thermoset resins from the inkjet printers do not exhibit shape memory properties on its own, but requires a matrix of rigid plastic and elastomeric material in order to demonstrate shape memory properties. Despite the numerous advantages brought about from multi-material printers to enable fabrication of responsive parts, these multi-material printed parts are prone to material degradation after repeated cycles of folding and unfolding. They are more vulnerable to interface or boundary cracks due to dissimilar materials which can give non-uniform properties such as coefficient of thermal expansion. Hence, this results in shorter fatigue life of the parts and reducing the durability of the parts.

Therefore, to overcome the various issues with current 4D printing, our approach is to develop a single thermoset resin that has intrinsic shape memory properties using stereolithography (SLA) process. In this process, layers of photocurable resin are selectively cured on a platform using a UV laser, layer by layer, to form the 3D object. Material development and fabrication of SMPs using SLA will be more straightforward since SLA has less restriction in material options due to its open build environment and easily accessible resin vat. Inkjet printers are mostly closed systems where they only allow usage of their own proprietary materials, hence materials and parameters cannot be easily changed. Moreover, SLA has been known to produce excellent surface finish which can minimize defect-induced failures, hence enhancing the durability of any printed SMPs during repeated thermomechanical cycles.

Materials and Methods

Preparation of SMP resins: Commercial tert-butyl acrylate (tBA) monomer were synthesized with di(ethylene glycol) diacrylate (DEGDA) crosslinker (10, 20, 30, 40 and 50wt%) and UV photoinitiator Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) (2wt%). The chemicals were all ordered from Sigma Aldrich and used as received conditions without further purification. The DEGDA crosslinker was first added dropwise to the tBA monomer, subsequently with the addition of photoinitiators in continuous mixing of the solution using magnetic stirring, followed by planetary vacuum mixer at 1900 rpm until the photoinitiators completely dissolved. The syntheses of the chemicals were performed in an ultra-violet (UV) proof environment to minimize pre-photopolymerization.

Fabrication of SMPs using SLA: A modified bottom-up scanning SLA (DigitalWax System 029X, Italy) as shown in Figure 1 was utilized and its build platform is immersed into the resin on a transparent base and the resin is cured by laser scanning from below. The bottom-up

configuration also uses fewer amounts of resins, which makes it more economically efficient in developing SMP resins for SLA. Photoinitiation was induced by a UV solid state laser at a fixed wavelength of 405 nm with computer controlled scanning speed. After scanning each layer whereby the polymer hardens onto the platform, the z-positioning elevator rises to detach from the bottom surface and allow liquid resin to flow in and the process repeats until the 3D object is completely built. The temperature of the printing environment was kept at below the transition temperature of the SMP to prevent the printed SMP from being too soft and gel-like since the SMP is thermally sensitive.

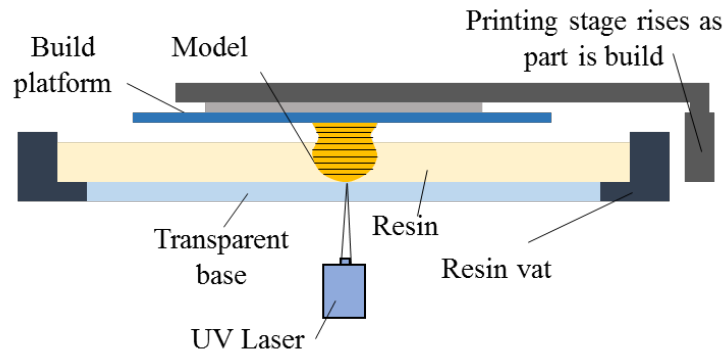


Figure 1. Schematic of bottom-up SLA.

Dynamic Mechanical Analysis: Given that the shape memory effect of thermoset SMPs revolves around a temperature range centered at the glass transition temperature (T_g) in which the material is rigid below the T_g and become rubbery when above it, hence the T_g and viscoelasticity of the SMPs were determined using Dynamic Mechanical Analysis (TA Instruments DMA Q800, USA). Samples printed in the shape of rectangular bars with dimensions of 17.5 mm x 11.9 mm x 1.20 mm were placed onto the DMA single cantilever clamping fixture under a dynamic load of 1 Hz with the amplitude set at 25 μm . The samples were heated from 20°C at a heating rate of 3°C min^{-1} . Glass transition temperature which is defined by the $\tan\delta$ peak and storage modulus in both the glassy and rubbery state can be analyzed from the DMA.

Fold Deployable Test: The shape memory properties of the SLA-printed SMPs were measured based on fold-deploy experiments according to [6]. The specimen (100 mm x 10 mm x 2 mm) was heated to deformation temperature, T_d (10°C above T_g) on a heating plate for 5 minutes, then bent into a ‘U’ shape using a mold with an external diameter of 20mm. The maximum bending angle is measured as θ_{max} which is equal to 180°. The specimen is cooled down before unloading the external force. A slight spring back might be observed, where the bending angle is recorded as θ_{fixed} as shown in Figure 2. Lastly, the specimen was reheated for shape recovery and the final bending angle was recorded as θ_{end} . The shape fixity ratio and shape recovery ratio can be calculated as follows:

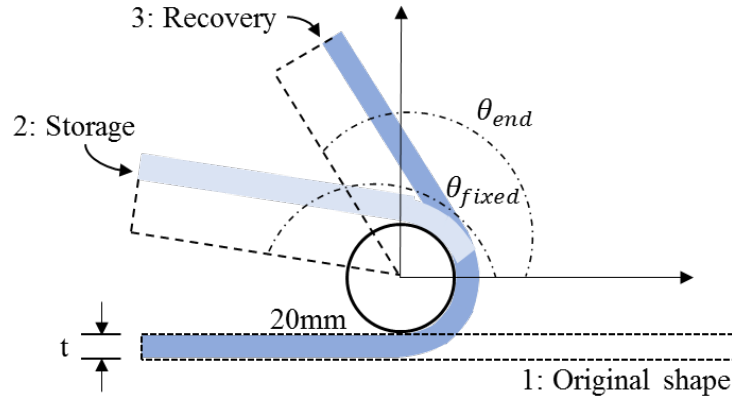


Figure 2. Schematic illustration of the setup for fold-deployable shape memory test.

Shape fixity ratio:
$$R_f (\%) = \frac{\theta_{fixed}}{\theta_{max}} \quad [1]$$

Shape recovery ratio:
$$R_r (\%) = \frac{\theta_{max} - \theta_{end}}{\theta_{max}} \quad [2]$$

Results and Discussion

Synthesis of the SMP resin: The SMP resin was prepared based on thermally induced dual component mechanism, where the thermally induced shape memory behavior is contingent on two components – a soft segment that is responsible for fixing the temporary shape when it is above its glass transition temperature, and a hard segment that is responsible for retaining the original permanent shape. The tBA monomer acts as the soft segment due to its short chain length which allows higher mobility to allow easy deformation to its temporary shape, while the DEGDA forms crosslinkages that remain thermally stable and locked in position even at high temperatures to retain the permanent shape.

Dynamic Mechanical Analysis (DMA): The DMA curves of the SLA-printed SMPs are shown in Figure 3. From Figure 3 **Error! Reference source not found.**, the glass transition temperatures (T_g s) were defined at the peak of the tan delta curve. It can be observed that all samples possess distinctive T_g ranging from 53.9°C to 74.1°C and the T_g values gradually increase as the concentration of the DEGDA crosslinkers increases. The addition of higher amount of crosslinkers results in higher crosslinking density within the structure of the SMP chains. This leads to a closer structure which hinders the movement of the monomers that acts as the soft segment, hence more energy is required in order to change from its original glassy state to a soft rubbery state for shape transformation.

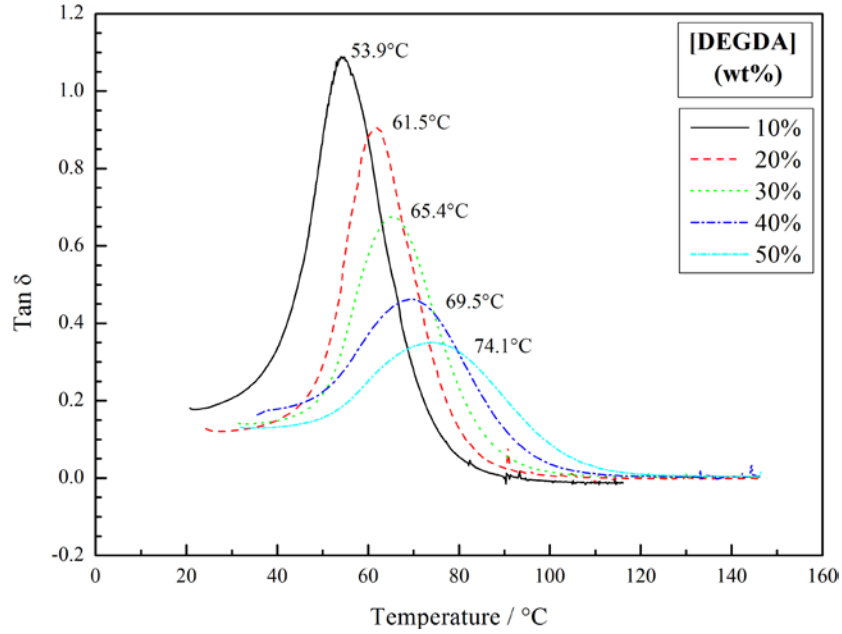


Figure 3. DMA curves of SLA-printed SMPs with $\tan \delta$ as a function of temperature.

The DMA curves also illustrate the storage moduli of the SLA-printed SMPs being dependent on temperature as shown in Figure 4. When the temperatures are below the T_g s of the specimens, the storage moduli remain high, denoting that the SMPs are in the rigid glassy state where the movement of the segments is heavily hindered. The storage modulus of an SMP is also a measure of elasticity of the material, hence with increasing content of crosslinkers, there is an observable decline in the storage moduli of the SMPs. Nevertheless, all specimens showed a difference of at least 2 orders of magnitude drop in E' upon reaching its T_g , which is evident of its shape memory properties since a large and sharp drop in storage modulus in the glass-to-rubber transition zone is necessary for a favorable SMP [7].

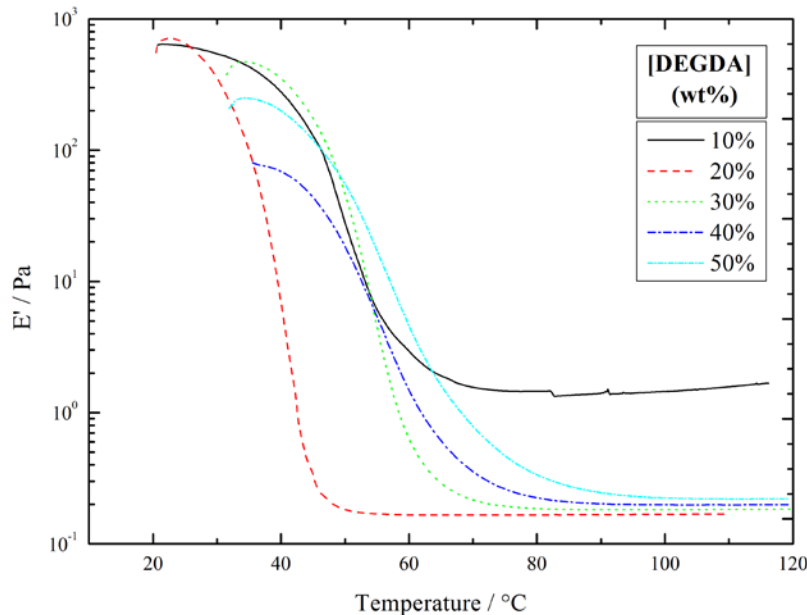


Figure 4. DMA curves of SLA-printed SMPs with storage modulus as a function of temperature.

Shape memory properties: The average shape fixity ratios for the SLA-printed SMPs with different concentrations of DEGDA crosslinkers is shown in Table 1. The fixity ratio relates to the ability of the SMPs in fixing its temporary shape upon releasing of the external force and Table 1 displays that the fixity ratio decreases with increase in crosslinker concentration. Theoretically, the cooling before the release of the external force serves as a kinetic trap to store all strain energy imposed on the permanent shape that changes the conformation of the polymer chains and maintains the system in a high energy state [4]. However, there exists heavy friction among the molecules that resist the deformation and with higher crosslinking density within the SMP structure, the restrictive force becomes much higher which result in loss of some stored energy, hence generating spring back that reduces its fixity capability.

Table 1. Measurements of fixity and recovery ratio of SLA-printed SMPs.

DEGDA [wt%]	θ_{fixed} [°]	R_f [%]	θ_{end} [°]	R_r [%]
10	169	93.9	180	100
20	167	92.8	157	87.2
30	164	91.1	176	97.8
40	161	89.4	162	90
50	154	85.6	162	90

Figure 5 shows the shape recovery ratio based on the bending angles measured as a function of time. It can be seen that only the SMPs with 10wt% DEGDA concentration achieves 100% shape recovery as compared to the rest of the SMPs. This can be correlated to the loss of strain energy due to the large spring back with increasing crosslinking density. Since the kinetic trap did not completely store all the energy during the cooling stage, the entropic energy released upon reheating becomes insufficient to fully drive the molecular chains back to their lowest energy state, returning to its original shape. Hence, full shape recovery can only be observed in the printed SMP with lowest crosslinker concentration.

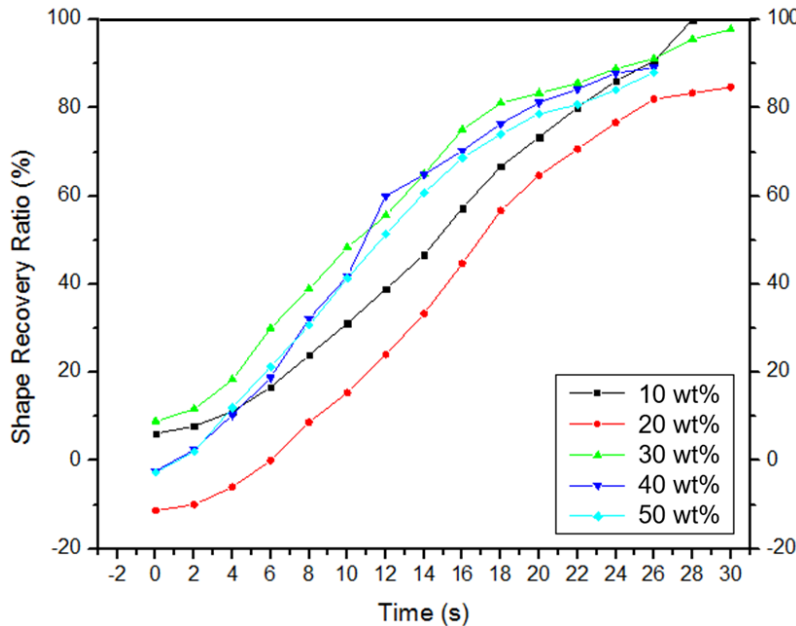


Figure 5. Shape recovery of SLA-printed SMPs.

A series of shape memory cyclic tests was performed on the SMP with 10wt% DEGDA crosslinker to determine the number of folding and unfolding cycles the SMP can withstand before failure by fracture. A 3D graph in terms of stress, strain and temperature is plotted in Figure 6 to illustrate the cycle steps and the shape memory behavior of the SMP. The SLA-printed SMP on average can withstand up to at least 20 repeated cycles with a maximum of 22 cycles recorded, which is comparable with some commercial thermoset SMPs [8].

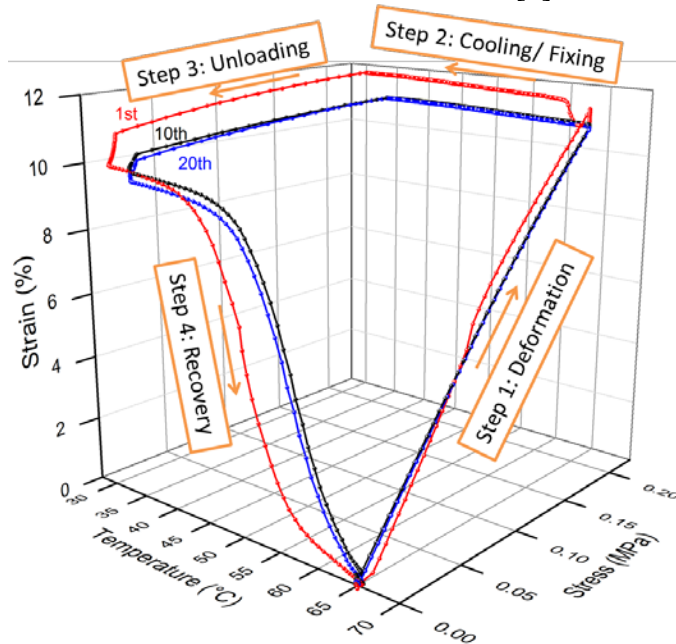


Figure 6. Shape memory cyclic tests of SLA-printed SMPs with 10wt% DEGDA concentration.

Conclusions

In this paper, single thermoset SMP resins with different concentration of crosslinkers were fabricated using a bottom-up SLA process. Some of the findings have been listed below:

1. Distinctive T_g s ranging from 53.9°C to 74.1°C are obtained with increasing concentrations of crosslinkers, showing potential for tuneable properties for a wider range of 4D printing materials.
2. Decline in storage moduli of SLA printed SMPs with an increase in crosslinker concentrations due to reduced elasticity, but all specimens exhibit shape memory properties with at least 2 orders of magnitude drop in storage modulus above its T_g .
3. Decrease in shape fixity and recovery ratio with higher crosslinker concentrations due to loss in strain energy.

Acknowledgement

This project is funded by the Science and Engineering Research Council of Singapore Agency of Science Technology and Research (A*STAR)-IAP (NTU Grant No. M4070219).

References

1. ASTM, S., *F2792. 2012. Standard Terminology for Additive Manufacturing Technologies*. ASTM F2792-10e1, 2012.
2. Tibbits, S., *4D Printing: Multi-Material Shape Change*. *Architectural Design*, 2014. 84(1): p. 116-121.
3. Liu, C., et al., *Review of progress in shape-memory polymers*. *Journal of Materials Chemistry*, 2007. 17(16): p. 1543-1558.
4. Zhao, Q., et al., *Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding*. *Progress in Polymer Science*, 2015.
5. Hwang, S., *Study of materials and machines for 3D printed large-scale, flexible electronic structures using fused deposition modeling*. 2015.
6. Liu, Y., et al., *Thermal, mechanical and shape memory properties of shape memory epoxy resin*. *Materials Science and Engineering: A*, 2010. 527(10): p. 2510-2514.
7. Fan, M., et al., *Thermomechanical and shape-memory properties of epoxy-based shape-memory polymer using diglycidyl ether of ethoxylated bisphenol-A*. *Smart Materials and Structures*, 2013. 22(5): p. 055034.
8. Xie, F., et al., *Thermoset shape memory polymers and their composites*. *Journal of Intelligent Material Systems and Structures*, 2016: p. 1045389X16634211.