# 4D PRINTING OF POLY(LACTIC ACID)-BASED SHAPE MEMORY POLYMERS AND SHAPE MEMORY NANOCOMPOSITES

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## EXTENDED ABSTRACT

## 1 INTRODUCTION

Shape memory polymers (SMPs) and shape memory nanocomposites (SMNCs) are capable of recovering their original shapes from temporary shapes when they are triggered by heat, water, PH value, electrical and magnetic fields, etc [1, 2]. Such unique features enable SMPs and SMNCs extremely suitable for application as shape-changing structures in the areas varing from aerospace to biomedicine [3, 4]. However, conventional processing methods limit the design space of such smart structures [5]. It severely restricts the further developments of SMPs and SMNCs in advanced technologies, such as 4D printing, flexible electronics, and soft robotics, etc.

3D printing technique may be one of the best choices to overcome this challenge. This advanced processing approach can produce materials into custom-defined and complex geometries [6, 7]. By combination of 3D printing technique, some 4D structures based on SMPs have been developed. Their potential applications in flexible electronics and sequential self-folding structures have also been demonstrated [8-10]. However, the printing materials focus on pure SMPs. Meanwhile, the actuation methods of those 4D structures are mainly based on heat. It is not really useful in practical applications. SMNCs with iron oxide ($Fe_3O_4$) has much merit, since $Fe_3O_4$ could be used as inner heating source in the presence of alternating magnetic fields to achieve remote actuation [11, 12]. However, most of the commercially available 3D printers are designed to print specific or pure polymers. It is still hard to achieve the printing of SMNCs.

Direct-write assembly is an open printing method that can be adjusted for processing various materials [13, 14]. In this study, we achieved 4D printing of both SMPs and SMNCs by combination of direct-write assembly with UV Light-emitting diodes (LED). The printing material was based on Poly(lactic acid) (PLA), because it was widely used in not only 3D printing area but also shape memory field. Benzophenone (BP) was chosen as cross-linking agent for excellent shape memory properties. $Fe_3O_4$ was used as functional nanofillers to trigger the remotely actuated shape-changing behavior. Dichloromethane (DCM) was utilized as solvent for its low boiling point.

## 2. RESULTS AND DISCUSSIONS

We first fabricated a serizes of UV cross-linked PLA-based SMPs with the weight ratio of BP/PLA ranging from 0.4/10 to 1.2/10. Their macroscopic capabilities, including thermal properties, mechanical properties, thermal-mechanical properties and shape memory behavior were disscussed. Results revealed that sample (c-PLA-10) with BP/PLA weight ratio of 1/10 showed desired properties. Tensial tests demonstrated that c-PLA-10 presented good mechanical properties with Young's Modulus higher than 1 GPa, maxium stress above 36 MPa, and elongation at break higher than 30%. DMA tests revealed that glass transition temperagture ($T_g$) of c-PLA-10 was 66.0 $^oC$. Meanwhile, storage modulus of c-PLA-10 sharply dropped during the the glass transion process, indicating the potential shape memory behavior of such material. Shape memory cycle showed that c-PLA-10 possessed excellent shape memory behavior with shape fixed ratio higher than 90 % and shape recovery ratio above 99 %. Such properties are important for achieving 4D printing.

To achieve printable property, BP and PLA were dissolved into DCM with weight ratio of 0.1: 1: 3 to prepare the PLA-based SMP ink. After thoroughly mixing, the ink was put into a 3 ml syringe with a suitable nozzle which was then placed into a high pressure dispensing adaptor connecting to a pressure supply. Such apparatus was mounted into the head of the robot. By applying pressure, ink could be extruded from the nozzle. UV LEDs were used to trigger the cross-linking reaction after ink extrusion. The rheological properties of the ink were investigated by depositing filaments onto a glass substrate for 60 s at a speed of 1 mm/s under ten different pressure in the range of 0.35~3.5 MPa using a nozzle of 200 um, followed by drying in a vaccum oven at 50 ºC for 12 h and weighted. The obtained mass was transferred to volumetric flow rate by empolying the density of each ink. With the consideration of Rabinowitch correction, the rheological properties of our designed ink could be obtained [15]. We found that the process-related viscosity of the designed PLA-based SMP ink decreased as the increase of the process-related shear rate. Such phenomenon indicated the ink presented shear-thining behavior, which enabled the extrusion of the ink from needles under high shear rates. The solvent evaporation behavior of DCM was then investigated to evaluate the retention of the printed structures by monitoring the mass change of a 5 mm filament extruded from a nozzle of 510 um for 6 h. Results showed that most of DCM could evaporate in the first 5 min. The fast evaporation behavior of DCM was necessary for maintaining the printed structures. By adjusting the pressure (1.4~1.75 MPa), moving speed (0.1~1 mm/s) and direction ($x$, $y$, $z$) of robot suitabley, structures including 1D filament, 2D mesh, 2.5D tube, 3D layer-by-layer flower and waviness, and 3D freeform sprial could be successfully achieved by using our PLA-based SMP ink. The printed sprial, waviness and flower structures were choosen for the investigation of 4D behavior. Results showed that the configration of those structures could achieve 3D-1D-3D, 3D-2D-3D and 3D-3D-3D changes under heat stimuli (80 ºC), demonstrating the achievement of 4D printing.

In the following study, $Fe_3O_4$ nanoparticles were introduced to the ink for tailoring the actuated method of the 4D structures. The weight ratio of $Fe_3O_4$/BP/PLA/DCM was 0.25/0.1/1/3. Such $Fe_3O_4$/PLA-based SMNC ink presented similar shear-thinning and fast solvent evaporation properties with PLA-based SMP ink, indicating the ink was 3D printable. By controll the printing parameters accurately, a 4D nanocomposite scaffold was successfully printed using $Fe_3O_4$/PLA-based SMNC ink. The scaffold could be remotely-actuated and presented self-expandable behavior after placing the scaffold in an alternating magnetic field. Such 4D scaffold showed great possiblity to be used as self-expandable stent in minimally invasive medicine.

## 3 CONCLUSIONS

In summary, we presented a flexible method for achieving SMP- and SMNC-based 4D printing by combination of DW assembly and PLA-based UV cross-linked inks. This method enabled unique and complex 4D active shape-changing architectures in either macro- or micro-scale with various geometries. More importantly, the actuated methods of the printed structures could be designed by adding different nanoparticles. We believe that this research is important for the further development of 4D printing, soft robotics, micro-systems, and biomedical devices and beyond.

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