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4D printing of polyurethane paint-based composites

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ABSTRACT

In recent studies, polyurethane has shown multiple properties that make it an excellent candidate material in 4D printing. In this study, we present a simple and inexpensive additive method to print water-borne polyurethane paint-based composites by adding carboxymethyl cellulose (CMC) and silicon oxide (SiO\textsubscript{2}) nanoparticles to the paint. The first function of CMC and SiO\textsubscript{2} is to improve rheological properties of the polyurethane paint for making a printable precursor, which improves the printing resolution and enhances additive manufacturability. Second, the composite precursors improve the curing rate of the polyurethane paint without changing its inherited shape memory properties. Third, the printed composite parts shown enhanced mechanical strength compared with that of the parts printed with pure polyurethane. Finally, the 3D printed polyurethane-CMC and SiO\textsubscript{2} parts exhibit time-resolved shape transformation upon heat stimulation. To the best of our knowledge, this is the first study of using the polyurethane paint as the precursor for 4D printing, which would open new possibilities in future applications in biomedical engineering, soft robotics and so on.

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Introduction

In the past decade, three-dimensional (3D) printing technology has been developed rapidly and has shown the ability to create the structures with complex topographical features and used for a wide variety of applications ranging from electronics, soft robotics to biomedical implantation [1–10]. However, the current 3D printing method can only create static objects and do not involve any functional variation in either intrinsic or extrinsic properties. For example, the printed structures can only maintain its linear elastic behavior and mechanical properties with a small deformation. Motivated by these needs, four-dimensional (4D) printing has emerged. The definition of 4D printing is using 3D printing technology to fabricate structures with active material, which is capable of altering the functionality of printed 3D shape over the time in response to the external stimuli such as heat[11], magnetic or light [12,13], and others [14]. The 4D printing technology also shows the capability of exhibiting large deformation, which has shown great potentials in various applications such as biomedical[15], electronical[16], and robotic systems[17].

There are mainly two types of polymeric materials used for 4D printing, responsive hydrogel and shape memory polymers (SMPs). In hydrogel-based 4D printing [18–20], the non-swellable medium is anisotropically distributed in swellable polymer network. Despite some advantages, the printed structures have poor mechanical strength and require a long time for shape transformation. In addition, based on current technologies, the shape transformation principle is mainly based on bilayer structures, which consisting of active and passive layers. It unavoidably increases the fabrication processes, limiting its practical applications. In SMP-based 4D printing, the SMPs are able to recover their original shape after being programmed from an original permanent shape to a temporary shape, which can be recovered by an appropriate stimulus such as heat, UV radiation [21], electric [22], or magnetic fields [23]. The advantage is that the printed structures can respond rapidly after applying the external stimuli, leading to potential applications in tissue engineering [20,24,25], soft actuation [26], and biomedical devices [27–29]. Among a variety of SMPs, polyurethane (PU) is a thermoplastic SMP, which is of special interest due to its unique material properties: biocompatibility, biodegradability, shape memory effect, high elasticity, and high tear resistance [18,30–32]. PU can be synthesized in a large scale from various sources. The most abundant one is the petroleum-related source. It can be also synthesized from renewable sources, such as fish oil[33], vegetable oil[34], soybean oil[30], and others. Thus, PU has been explored as one of mainstream SMPs for 4D printing [25,30,35,36]. The past studies have shown that polyurethane composites filled with particles [37], carbon nanotubes [38], and fibers [39] exhibit improved functionalities [37,40,41]. However, none of them reported 4D printing of the commercially available PU paint-based composites with improved properties and functionalities.

Herein, we demonstrate a simple and inexpensive 4D printing of waterborne polyurethane paint (PU) composites that are mixed with micro-size preswollen carboxymethyl cellulose (CMC) and PU mixed with silicon oxide nanoparticle (NPs), respectively. Each composite has shown the improved rheological behavior and printability, which helps the inks flow through a narrow nozzle smoothly without clogging and maintain the geometry without the deformation after printing. Moreover, the mechanical properties of the printed structures are greatly improved. In the work, characterizations of rheology
behaviors were carried out to optimize printing conditions. The mechanical and thermo-
mechanical properties of PU composites were conducted and evaluated by tensile test
and differential scanning calorimetry (DSC). Shape recovery test was also performed and
evaluated. To illustrate the generality of the methodology, more than five different 3D
printed structures were demonstrated and their shape memory performances were tested.
To explore their applications, a griper and an electronic actuator were demonstrated. To
the best of our knowledge, this is the first demonstration of using PU paint based
composites as printing materials for 4D printing, which would pave new route to tailor
composite materials and create new possibility for widespread applications.

Results and discussion
The fabrication process for 4D printing of PU paint-based composites is illustrated in
Figure 1(a). The commercial PU paint was firstly mixed with CMC and SiO$_2$ nanoparticles
with weight ratios of 10:2.5 and 10:8, respectively. As a control experiment a pure PU
paint, which is in liquid form was also printed under the same conditions. According to
the guideline of printability [42], the result shows that it is not printable. To remove the
associated liquid in the PU composite paint precursors for obtaining solid structures,
various heating methods including natural evaporation under ambient conditions, UV
light exposure, and hotplate heating were employed (Figure S1). The result shows that
the hotplate heating results in the highest mass loss of $> 5\%$ in 10 min and 56\% at 24 h.
Thus, all the experiments were conducted by using such a heating method to ensure the
best printing quality. Figure 1(b) shows an example of a shape memory behavior of a
printed PU/SiO$_2$ composite. First, a butterfly structure was printed to make a permanent
shape. Then, the wing of the butterfly was manually deformed by heating above the
glass transition temperature ($T_g$) to a temporary shape, which was then fixed after
cooled down below $T_g$. Once the part is heated above its $T_g$ the deformed butterfly
structure is recover to its original shape.

Figure 1. (a) Schematic of a 3D printing process of PU paint composites. (b) Photographs of a
printed butterfly pattern showing a shape memory effect.
Further study shows that the printing quality highly depends on the viscoelastic characteristics of the PU paint composites. In order to understand their printability, rheological properties were tested and evaluated. Figure 2(a) shows the dependence of elastic modulus ($G'$) and viscoelastic modulus ($G''$) on the shear stress for pure PU ink. The result shows that $G''$ is greater than $G'$ for all strains, which shows an all liquid-like behavior with a viscosity of pure PU paint and it is not suitable for 3D printing because it does not appear a solid-like behavior. A good rheological behavior for inkjet printing method should have a relatively high viscosity which is quickly decreased when a shear force is applied and then recovered to the original one when the shear force is removed. By this way, the ink can easily flow through the fine nozzle and then stack on the substrate or previous layers without spreading or collapsing to form solid-like patterns. When the CMC (12.5 wt%) or SiO$_2$ NPs (8 wt%) were added into the PU paint, the composites show the solid-like behaviors. Dependence of the elastic modulus ($G'$) and viscoelastic modulus ($G''$) on the shear stress for PU/CMC and PU/SiO$_2$ inks were shown in Figures 2(b) and 2(c). The results show that in both samples $G'$ is greater than $G''$ in the low stress range, indicating a high viscosity. When the shear stress increases > 477 Pa for the PU/CMC samples and > 139 Pa for the PU/SiO$_2$ samples, both moduli decreases with increases of the shear stresses with higher $G''$ than $G'$, showing liquid-like behaviors. This solid-like to liquid-like state transition facilitates the inks to flow through

![Figure 2](image_url)

**Figure 2.** Elastic and viscous modulus of (a) pure PU paint, (b) PU/SiO$_2$ composite (8 wt% SiO$_2$), PU/CMC composite (12.5 wt% CMC) (c) as a function of share stress obtained by amplitude sweep at 1 Hz. Viscosity as a function of shear rate at room temperature (c).
the printing nozzles. The viscosity as the function of the shear rate for these three types of samples is shown in Figure 2(d). The viscosity of PU composites increases remarkably comparing to the pure PU in the initial state. And an increased shear rate results in a decreased viscosity of all samples, which is highly thixotropic and can be characterized as a shear thinning behavior. To make the composites have suitable rheological properties we found that the weight ratios of CMC and SiO\textsubscript{2} NPs in the composites are better in a range of 25 wt%–40 wt% and 6 wt%–10 wt%, respectively.

We then investigated the mechanical and thermomechanical properties for the printed structures. First, we performed uniaxial tensile testing and the geometry of the samples were designed and molded according to the ASTM standard. The stress-strain curves are shown in Figure 3(a). The pure PU has a fracture strain of 110%, and ultimate tensile strength (UTS) of 0.5 MPa. After forming composites with additives of CMC and SiO\textsubscript{2}, the fracture strains decrease to 11% and 19%, respectively. But their tensile strength is greatly increased. The PU/CMC composite with 40 wt% of CMC and PU/SiO\textsubscript{2} with 8 wt% of SiO\textsubscript{2} NPs show UTSs of 1.01 MPa and 1.89 MPa, respectively. The standard derivation of UTSs of the PU/CMC and PU/SiO\textsubscript{2} composites are 46 kPa and 52 kPa, showing consistent mechanical properties of PU composites (Figure S2). The UTSs of the PU/CMC composites can be improved by increasing the weight ratio of CMC additive from 30 wt% to 40% wt% (Figure S3). The result shows that PU/SiO\textsubscript{2} has higher strength and toughness than the PU/CMC composites. We believe that such tradeoffs could arise from their modified material structures after two nanomaterials are added. Such modification and their impact on the shape memory performance of the PU are worth future investigation. The glass transition temperature (T\textsubscript{g}) of the pure PU and PU composites were determined by DSC (Figure 3(b)). The results show that even though additives are added into the composites, their T\textsubscript{g} are close to ~121°C, showing that external fillers (CMC and SiO\textsubscript{2} NPs) in the PU matrix barely alter its inherited thermal properties [39,43].

To further understand the shape memory behaviors of resulting structures, the shape recovery testing was performed. The initial angle of the strip is 180° and the programmed U-shape has angle of 0° (Figure S4). A recovery angle is defined the difference between the final angle and the angle of the programmed U-shape. The evolved recovery angles versus time are shown in Figure 3(c). It takes ~15 s for PU/CMC composites with a CMC weight ratio of 25% and 20 s for PU/SiO\textsubscript{2} with a SiO\textsubscript{2} weight ratio of 8% to reach stable geometries. We found that the PU/CMC samples have a better shape recovery behavior, showing almost complete recovery (recovery angle of ~160°), while the PU/SiO\textsubscript{2} can only recover ~102°. This could be due to higher residue strains in the structures printed from the PU/SiO\textsubscript{2} than that from PU/CMC. To evaluate the cyclability of the printed samples, we further tested the residual angles of the PU/SiO\textsubscript{2} samples (Fig. S5). It shows that the residual angle is well maintained below 47° after 25 cycles, which indicates the robustness of the 3D printed PU/SiO\textsubscript{2} composites.

After the shape memory behaviors are tested, a variety of geometries of printed patterns including circle lattice, star, MU logo, square, and three petal flower from these composites were realized (Figure 4(a)). The Circle lattice and MU logo were printed with 8-layer PU/CMC composites with a CMC weight ratio of 25 wt%. The star pattern was printed with 27-layer PU/CMC composites with a CMC weight ratio of 37.5 wt%. The 10-layer square and the three-petal flower pattern were developed using PU/SiO\textsubscript{2} composites with a SiO\textsubscript{2} weight ratio of 8%. The purpose of printing contrasting patterns is to
Figure 3. Stress-strain curves (a) and DSC curves for PU, PU/CMC composite (30 wt% CMC), and PU/SiO$_2$ composite (8 wt% SiO$_2$) composites (b). (c) Recovery angle versus time during the shape recovery process.
confirm the reliability of both PU/CMC and PU/SiO$_2$ composites in printing any particular shapes. Then the shape memory behaviors of these printed structures were evaluated. The circle lattice was first programmed to a cylinder shape which recovers back to its original form after reheating above $T_g$. The star pattern, which was programmed to a compressed star shape, returned to its authentic form as well when recovered. Similar consummations were captured for the rest of the patterns. Moreover, we printed and programmed PU/SiO$_2$ composite patterns around a PI (Polyimide) box for achieving the purpose of holding and capturing (Figure 4(b)). The printed strips can function as a gripper by programming it into a temporary shape, which can hold or capture an object. The enveloped object can be then transported to a desire place and be released by reheating it above $T_g$ to recover it to the original and permanent shape. The attached PI area can be also integrated with sensor or electronics, opening potential applications in tissue engineering, 4D electronics device and others.

Conclusions

In the present work, we demonstrated 4D printing of PU paint based composites. The additions of CMC and SiO$_2$ into the PU paint improve the rheological properties of the composites, making the composites more suitable for 3D printing. Tensile tests show that the strength of the composites are greatly enhanced. Thermomechanical tests indicate that the added fillers barely modify their shape memory behaviors. Finally, complex 3D structures were printed and show impressive shape memory behaviors.
Furthermore, an integration of PU composite SPM with other functional materials can create an actuation function, and the success of the work would provide a new avenue to fabricating complex smart structures, leading to potential applications in tissue engineering, biomedical device, soft robotics and beyond.

**Experimental section**

**Printing of PU/CMC and SiO\(_2\) composites**

The 3D printer (Prusa i3) that was used for printing was modified by replacing the original extrusion nozzle with a digital air syringe dispenser (Loctite 883,976). Depending on the CMC concentration, the pump pressure was varied from 3 to 50 psi. The preparation of the printing material started from mixing CMC (Whatman CMC pre-swollen microgranular cation exchanger CM52) or SiO\(_2\) polyurethane paint (RUST-OLEUM triple thick polyurethane clear matte). After being vigorously stirred for 5 min the PU composites became viscoelastic paste. These PU composites were then loaded into a syringe with a nozzle of 600 µm in diameter. The patterns were designed by CAD software (SOLIDWORKS).

Then the prepared ink was poured into the syringe of the 3D printer 3D printing patterns were designed by stacking the same 2D pattern multiple times by raising 0.5–0.7 mm for each additional layer in the z-axis. The substrates that the ink was printed on were a glass plate coated with candle wax which can help to help remove the patterns from the substrates. This specific substrate was chosen due to its rigidity and resistance to deformation (polyurethane paint with CMC will bend upward as it dries). During the injection process, the substrates were heated to 50°C with the built-in heating bed. The printing process required a 1–2 min delay between each layer. The printing patterns were left on the glass substrate for 30 min for them to be dried followed by removing from the glass substrates. To program the shape of a printed object, the printed object was placed on a hotplate above \(T_g\) (121°C) and was deformed to a new shape and immediately removed from the hotplate. To recover the object to its original shape, the printed object was placed on a hotplate above its \(T_g\). All experiments were performed under ambient conditions. All videos and images were captured by Samsung S8.

**Rheological evaluation**

The rheological properties of PU composites were measured at 25°C by a rotational rheometer (Malvern Kinexus Pro) fitted with a cone-plate geometry (diameter of 40 mm, and gap of 0.05 mm). The viscosity of the representative PU/CMC and PU/SiO\(_2\) composites with a PU-CMC weight ratio of 10:2.5 and a PU-SiO\(_2\) weight ratio of 10:8 were measured as a function of shear rates (\(\gamma\)) from 0.01 to 100 s\(^{-1}\). The shear elastic modulus (\(G'\)) and viscoelastic modulus (\(G''\)) of these representative PU/CMC and PU/SiO\(_2\) composites were measured using amplitude sweeping at the frequency of 1 Hz.

**Material characterization**

A mechanical tensile tester (MARK-10) was used to measure the stress-strain curves. We prepared three samples for each PU/CMC (30 wt% and 40 wt%) and PU/SiO2 wt% and the geometry of test sample was designed according the ASTM D638 type.
Thermal characterization

A differential scanning calorimetry (DSC) (Perkin-Elmer DSC 8500) was used to measure the glass transition temperature. In the test, 5.43–9.26 mg of the samples were encapsulated in an aluminum pan and tested in a temperature range from 0 to 160°C. The heat flow (W) was recorded as a function of sample temperature.

Recover angle analysis

The PU/CMC (25 wt%) and PU/SiO$_2$ (8 wt%) composites were prepared. We printed strips with length of 28 mm and let them be dried completely for 24 h in a vacuum oven. The samples were then programmed to a U-shape with a radius of 2 mm at T$_g$ for 3 min and then removed from the heat source and cooled down for 3 min. After that, we heated up the samples to slightly above T$_g$ and measured the recovery angles$^{[44]}$.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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