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Contactless Reversible 4D-Printing for 3D-to-3D Shape Morphing

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Abstract

4D printing provides a means to create dynamic structures for self-actuating devices fabricated by additive manufacturing techniques. Most existing 4D printing processes are only capable of one-way shape morphing using a single mechanism for stimulation. In the limited successful reversible 4D-printing studies, most only demonstrate 2D-to-3D shape morphing. This study introduces a contactless shape setting mechanism to empower reversible 4D printing using a combination of stimuli. The forward shape programming is realized by asymmetric swelling with heated ethanol, and the shape recovery is accomplished by dry heating. The shape morphing can be predicted using a simulation model. Several designs are 4D-printed to achieve different forms of morphing to obtain 3D-to-3D shape morphing. The entire shape morphing cycle could be completed within as short as 3 minutes. The capability of 3D-to-3D shape morphing and reversibility of our 4D-printing process promise great potential for different applications such as biomimetics and soft robotics.

Keywords: additive manufacturing, reversible, shape memory polymers, 4D printing, 3D printing

1. Introduction

4D printing is widely known as the extension of additive manufacturing over the fourth dimension, which is time (WuGe, Qi, & Dunn, 2013; Tibbits, 2013, 2014). In a 4D-printing process, the properties of 3D-printed components, such as shape, mechanical strength, and colour, undergo a designed transition over time when stimulated (Chua & Leong, 2017; Gardan, 2019; Lee, An, & Chua, 2017). It provides a means to create dynamic structures for self-actuating devices fabricated using additive manufacturing techniques (Campbell, Bourell, & Gibson, 2012). A variety of materials have been used for 4D printing such as polymers (Cui, Chen, Zhu, & Jiang, 2020; Ge et al., 2016; Teoh, Zhao, An, Chua, & Liu, 2017; Yap & Yeong, 2015; Yu, Ritchie, Mao, Dunn, & Qi, 2015), composites (Yang et al., 2017; F. Zhang, Wang, Zheng, Liu, & Leng, 2019) and metals (Dadbakhsh, Speirs, Kruth, & Van Humbeeck, 2015;

Donoso, Walczak, Moore, & Ramos-Grez, 2017; Haberland, Meier, & Frenzel, 2012; Meier, Haberland, Frenzel, & Zarnetta, 2009). Amongst all materials, shape memory polymers (SMPs) have been widely used in the study of 4D printing as they have high recoverable strains (Ge et al., 2013; Hornat, Yang, & Urban, 2017), tunable properties (Xie, 2010), and high biocompatibility or biodegradability (Mehrpooya, Gisario, Azizi, & Barletta, 2020; Zhao, Zhang, Leng, & Liu, 2019). A wide variety of stimuli, ranging from heat (Tamagawa, 2010; C. C. Wang, Huang, Ding, Zhao, & Purnawali, 2012; Q. Zhang, Yan, Zhang, & Hu, 2015), swelling (Huang, Yang, An, Li, & Chan, 2005; C. C. Wang et al., 2012), pH (Muzaffar et al., 2020), and light (Lendlein, Jiang, Jünger, & Langer, 2005), have been explored to induce the 4D transition. More importantly, they are less expensive than shape memory alloys in terms of both material and printing costs. Since the introduction of 4D polymer printing, its unlimited possibilities have invited much interest from various industries such as soft robotics (Ding et al., 2017; Ge, Dunn, Qi, & Dunn, 2014; Ge et al., 2016; Haberland, Elahinia, Walker, Meier, & Frenzel, 2013; Khoo et al., 2015; Mao et al., 2015; Teoh, An, et al., 2017; Teoh et al., 2018; Teoh, Zhao, et al., 2017; Wu et al., 2016; Yu et al., 2015; Y.-F. Zhang et al., 2019) and biomedical applications (Ashammakhi et al., 2018; Cui et al., 2020; Ding et al., 2017; Du et al., 2019; Su et al., 2018). In medical context, one-way 4D printing is used to fabricate personalized stents (Lin, Zhang, Liu, Liu, & Leng, 2020) small enough for children (de Marco et al., 2019), which minimise the risk from invasive surgery. Also, Leist *et al.* has managed to fabricate smart textile with thermal sensing capability by using 4D printing (Leist, Gao, Chiou, & Zhou, 2017).

Customized designs of intricate architectures that cannot be fabricated by conventional methods is a key advantage of 3D printing, which has been inherited by 4D printing. Additionally, 4D printing adds another layer of intricacy by introducing dynamic structures to the already detailed and complex geometries fabricated by 3D printing, offering a significant

degree of flexibility and freedom in design and functionality. For example, 4D printing is ideal for packaging where it allows a flat sheet to shape change to any shape via designed morphing using an origami concept (Ge et al., 2014; Mehrpouya, Azizi, Janbaz, & Gisario, 2020; Teoh et al., 2018). 4D printing also allows multiple shape-changing by having various active materials with different glass transition temperatures (T_g) in a single print (Mao et al., 2015; Wu et al., 2016). However, most well-developed 4D printing processes are currently confined to one-way shape morphing stimulated by a single mechanism, hence lack reversibility (Ding et al., 2017; Ge et al., 2014; Ge et al., 2013; Pandini et al., 2020; Wu et al., 2016). The one-way shape morphing is viewed as partial or incomplete 4D printing when used in practical applications where reversible operations such as on and off, open and close are ubiquitous. The one-way shape morphing is uni-directional, and a manual re-programming is required to recover the shape in each cycle. Hence, there is a pragmatic need to develop reversible 4D printing.

Reversibility offers materials a “two-way memory” so that the materials can morph between two permanent shapes (Mao et al., 2016; Naficy, Gately, Gorkin, Xin, & Spinks, 2017; Yuan et al., 2017). Introducing reversibility into 4D printing enables repeated self-programming for many prospective applications such as soft robotics (Shiblee, Ahmed, Kawakami, & Furukawa, 2019; W. Wang, Li, Cho, & Ahn, 2018), packaging and logistics (Ge et al., 2014; Khoo et al., 2015), and biomedical applications such as drug delivery (An, Chua, & Mironov, 2016; Z. Zhang, Demir, & Gu, 2019). Reversibility allows precise contactless shape-setting and shape recovery. In one-way 4D printing, the shape usually undergoes shape-setting and is recovered by manual re-programming using mechanical forces. By introducing reversibility, the 4D-printed part can be programmed without physical contact and recover to the original shape consistently given the same stimulation conditions in every cycle. Reversible shape morphing of 4D-printed SMPs is primarily accomplished using conventional processes

established for SMPs. Up to date, there have only been a limited number of demonstrations of reversible 4D-printing (Chen, Hu, Zhuo, & Zhu, 2008; Lee, An, Chua, & Zhang, 2019; Mao et al., 2016). Most works on reversible 4D-printed SMPs only demonstrate the 2D-to-3D shape morphing (origami) (Mao et al., 2016; Naficy et al., 2017; Odent et al., 2019; van Manen, Janbaz, & Zadpoor, 2017; Yuan et al., 2017) or a mere change in size (Pandini et al., 2020). One of the examples is the study done by Naficy *et al.* (Naficy et al., 2017), which focused on achieving reversible shape morphing with a hydrogel composite. They used two stimuli, temperature, and hydration, to achieve reversible shape morphing with contactless programming in 4D-printing for the first time. Another similar study by Odent *et al.* utilized temperature and pH as the stimuli to create a reversible actuator with a hydrogel (Odent et al., 2019). Nevertheless, there are many limitations to hydrogel-based 4D-printed devices (Jang et al., 2018). Firstly, the mechanical strength of hydrogels is deficient for many applications. Much like reversible SMPs fabricated by conventional methods (Cui et al., 2020; Du et al., 2019; Li, Liu, & Leng, 2018), the as-built devices made of hydrogels are mostly 2.5D at best (a vertical projection from 2D) instead of 3D, which limits the structure complexity and functionality. Only upon stimulation could the device be converted to a simple 3D structure. There are two types of 2D-to-3D shape morphing. One type is printed in 3D and then manually programmed into 2D or forced to deformed for later recovery back to 3D upon stimulation (e.g., origami) (van Manen et al., 2017; G. Wang et al., 2018; Zarek et al., 2015). The other type is printed in 2D or 2.5D and then stimulated to morph into 3D (e.g., hydrogel composite). It is rare to find a direct 3D-to-3D shape morphing with true 3D architectures in both permanent shapes. This is because manual recovery is required to reconfigure the printed parts back to its original shape, and it is much easier to flatten a 3D structure compared to crafting it into a complex 3D configuration.

Most demonstrations of reversible 4D printing have a long response time on the scale of hours to days (Lee et al., 2019; Mao et al., 2016; Shiblee et al., 2019). The study by Mao *et al.* used three materials to fabricate a reversible 4D-printed part using Polyjet, and use temperature and hydration as the programming and recovery stimuli, respectively (Mao et al., 2016). However, the reversible shape morphing in this study requires approximately 12 hours for an entire cycle to be completed. Another study by Shiblee *et al.* used a similar mechanism of hydrogel swelling and heating, and it took approximately 40 minutes for the demonstrative flower to fully close. Therefore, reducing the time taken for actuation and recovery using swelling and heating can lead to a more efficient 4D-printing system. In general, swelling and heat-based 4D-printing systems usually have a slow response, but they are easy to operate (Champeau et al., 2020).

Currently, most reversible 4D printing studies focus on qualitative analysis, such as the feasibility of shape programming and reversibility (Mao et al., 2016; Naficy et al., 2017; Yuan et al., 2017). Secondary shapes were usually approximated based on the design without any quantitative study on the final shape. The lack of predictability makes it tough to design any functional 4D-printed devices as the dimensions of the morphed shape is left unknown.

This paper reports a predictable contactless swelling- and heat-driven reversible 4D-printing process. Our study takes advantage of Polyjet 3D-printing Technology to obtain intricate structures in a single print. Contactless shape-setting is introduced to overcome the limitation of manual programming. Thus, it enables the 3D structure to morph into another recoverable 3D configuration directly with high consistency and precision. A simulation model is used to assist the designing and predicting the shape morphing. This 4D-printing process does not rely on complicated structures and fabrication processes, and the shape morphing completes within a matter of minutes under-stimulation. It is realised by programming *via* asymmetric swelling of the bilayer structures in heated ethanol and recovery *via* dry heating to

speed up the actuation processes. The simple and straightforward fabrication process allows easy fabrication of complex 3D structures and enables true 3D-to-3D shape morphing. Additional twisting action is introduced by incorporating alternating stripes printed with different materials to enhance the range of motion. These motions inspire the demonstration of biomimetic functions *via* true 3D-to-3D reverse shape morphing with intricate 3D-printed structures such as flowers and butterflies. Contactless shape-setting and recovery also promise potential applications in soft robotics.

2. Materials and Methods

2.1. Materials

All the samples were fabricated using an Objet500 Connex3 Polyjet printer (Stratasys, USA). The materials used in the present research were provided by Stratasys (USA): VeroWhitePlus and TangoBlackPlus (product codes from Stratasys are RGD835 and FLX980). VeroWhitePlus is a hard and rigid material at room temperature with a glass transition temperature of 58 °C, whereas TangoBlackPlus is soft and rubbery at room temperature with a glass transition temperature of –10 °C ("Fullcure Material. Vero Family,"). The TangoBlackPlus liquid resin comprises urethane acrylate oligomer, exo-1,7,7-trimethylbicyclo hept-2-yl acrylate, methacrylate oligomer, polyurethane resin, and a photoinitiator. The VeroWhitePlus liquid resin consists of isobornyl acrylate, acrylic monomer, urethane acrylate, epoxy acrylate, acrylic monomer, acrylic oligomer, and a photoinitiator. The solvent used was 99% ethanol, obtained from A.P.C. Chemical Industries.

2.2. Printing parameters

The materials were printed with an Objet500 Connex3 Polyjet printer (Stratasys, USA) using the Digital Material mode at a resolution of 300 dpi/inch along the *x and y* axes. The Digital Material mode fixed the printing parameters at 100 µm per min with a layer thickness of 30

μm and up to $85\ \mu\text{m}$ for the x and y axes. The resins were cured by ultraviolet (UV) light within the printer.

2.3. Simulation

The strain and stress relationships of TangoBlackPlus (TBP) and VeroWhitePlus (VWP) are non-linear. Ansys 19 was used to obtain these parameters experimentally. The fitted curve is shown in the Supporting Information. The Mooney-Rivlin, a five-parameter model, is widely used for hyperelastic material models. The resulting parameters are listed in **Table 1**. The bulk moduli of TBP and VWP were calculated by the equation: $K = \frac{E}{3(1-2\mu)}$, where E is the Young's Modulus, and μ is the Poisson ratio at 60°C . The results of TangoBlackPlus and VeroWhitePlus are 58.1MPa and 2.09MPa , respectively.

After obtaining all the necessary parameters, the program Solid mechanics module of COMSOL 5.4 was used to conduct the simulation of the shape morphing; the material model was hyperelastic. The model was symmetric, so the fixed constraint boundary condition was set at the midplane of the strip. The meshing method was swept, maximum element size and minimum element size were 1 and 0.1, respectively. The loading was directly defined by the external strain; the stretch rate of TBP at 60°C was measured to be 1.075 when soaked in ethanol for 60 minutes, which was obtained experimentally. After computing, the node displacements of the interface line between two strips would be exported at the y - z plane by the 1D plot group. Subsequently, the final curvature could be computed by the known node displacements. Further details of the simulation are described in section 2 in the Supporting Information.

2.4. Response rate and recovery rate studies

The sample slabs were printed with a dimension of $10 \times 60 \times 1\ \text{mm}$ (overall thickness). The specific dimensions of the samples are described in **Table 2**. The samples were placed in ethanol at 60°C . 60°C was chosen to effectively swell TBP and soften VWP while maintaining

a low temperature to prevent degradation due to overheating in ethanol, and the relatively low temperature also prevents rapid ethanol evaporation. Snapshots of the samples were taken before they were placed in the heated ethanol and every 10s after being soaked in ethanol. A snapshot was also taken 1s after the samples were placed in the heated ethanol to study the initial rate of increase in curvature when the sample was first exposed to heated ethanol. After 60 seconds, the sample was removed, and a snapshot was taken for the final shape (represented by a 61-second mark). The photos were then processed with ImageJ to extract information on curvature. The curvature was calculated as $\kappa = \frac{8c}{d^2+4c^2}$ where c is the chord height, and d is the chord length. The curvature was plotted as a function of time as a scatter graph in Originlab. Each data point was an average of three measurements.

The samples of the same dimension were used to study the recovery rate. Each sample was placed in 60°C ethanol for 60 seconds to undergo the programming process. After programming, it was cooled in ice water at 0°C for 20 seconds. The recovery was carried out in an oven heated to 70°C, above the T_g of VWP. 70°C was used for dry heating during recovery to ensure sufficient and quick uniform heating for 4D morphing. A snapshot was taken every 10 seconds until the sample was fully straightened. The images were also processed with the same method as the response rate.

2.5. Parts with alternating stripes

The samples were designed and printed in three layers. The first layer was a 0.1 mm thick VWP, the middle layer was an alternating layer of TBP and VWP that is 0.4 mm thick, and the last layer is a 0.5-mm TBP. The orientation of stripes was pre-set by design. The TBP sections were 1 mm wide, and VWP sections were 2 mm wide. The last layer was a 0.5 mm thick TBP. The samples slab was $10 \times 60 \times 1$ mm (overall thickness), similar to the test carried out for the response and recovery rate. The samples were placed in ethanol at 60°C for 60 s. They were then removed, and a photo was taken. The photo was then processed with ImageJ to obtain the

helix angle; further details are described in the Supporting Information. An average of three sets of samples was obtained.

In the simulation for this study, a constant stretch rate of 1.05 was used instead due to a shorter duration for the swelling which was tested and obtained experimentally.

2.6. 2D and 3D demonstrations

The samples were printed according to the schematics that were described in each of the studies. Prior to the cycle, they were preheated to achieve an initial shape that could differ slightly from the printed shape due to gravitational pull. They were placed in ethanol at 60°C for various durations. In the same tank, the ethanol was drained and heated using RS Pro Heat Gun at strength I which produces an airflow of 250L/min at 350°C.

3. Results and Discussion

3.1. 4D-Printing Mechanism and Validation

The reversible 4D-printing cycle comprises programming and recovery stages with two steps in each stage, as shown in **Figure 1a**. In the programming stage, the printed part with a bilayer structure is programmed into the second shape in heated ethanol that acts as the first stimulus for rapid contactless shape-setting. The elastomer (TangoBlackPlus (TBP)) is swelled via the diffusion of ethanol. The ethanol is heated to speed up the rate of diffusion. The high temperature also heats the transition material (VeroWhitePlus (VWP)) above its glass transition temperature (T_g) to reduce its stiffness for easy reshaping. When soaked in ethanol, only the elastomer is swelled. This asymmetric swelling results in a difference in strain between the elastomer and the transition material. The induced strain exerts a force on the transition material. As the entire printed part is heated above T_g , the transition material becomes rubbery and morphs into a different shape under the exerted strain. The pre-stress incurred by the difference in strain causes the printed bilayer to curl, as shown in Figure 1a. The part is then quenched in cold water by cooling the transition material below its T_g to restore its stiffness and fix the

shape. In the recovery stage, the printed part is dry heated using an air gun or in a convection oven to recover its original shape. Dry heating is used to speed up the evaporation of ethanol from the elastomer and to heat the transition material above its T_g for easy reshaping. The volume of the elastomer decreases as the ethanol evaporates and diffuses out of the elastomer. In consequence, the elastomer acts as a spring pulling the component back into its original shape. Heating while drying allows the transition material to soften and decreases in mechanical strength. The elastic energy of the elastomer pulls it back into its original shape after ethanol evaporation. In the end, the printed part is allowed to cool down to room temperature to fix the shape. In the study by Mao *et al.* (Mao et al., 2016), the hydrogel was swelled for 12 hours and then placed in hot water for 10 seconds to program the shape. The entire reversible cycle took ~10 – 20 hours. In our previous study (Lee et al., 2019), the time used for programming was 1 hour, and the entire reversible cycle took around 4 hours. While it was significantly shorter than the programming mechanism used by Mao *et al.*, it was still too long for real-world actuation applications. The original reversible 4D-printing cycle comprised a total of five steps from programming and recovery, of which three belonged to the programming stage, and the rest two belonged to the recovery stage. In this study, faster programming is achieved with a combination of stimuli (*i.e.*, ethanol and heat) acting on the materials concurrently. The combination of stimuli in each step helps to reduce the number of steps in the entire cycle, and, in turn, minimizes the duration required for programming and recovery. With the new process, the entire reversible cycle only takes minutes to complete, which is one of the fastest amongst reversible 4D-printing processes enabled by contactless stimulation.

In our earlier study, the shape morphing was only analysed with a simple analytical model that predicted the bending angle of a bilayer slab printed with a transition material and an elastomer. However, that model had several limitations. It was only able to predict the bending

angle within a very narrow range, probably due to the assumption that the behaviour of the materials was elastic instead of being hyperelastic. The architecture of the bilayer slab was not optimised, leading to very thick constructs and long response time.

We have developed a model to simulate the shape morphing in the current 4D-printing process. The curvature induced at the programming stage was validated with experimental and simulation results. The material used to validate the elastomer was TBP, and the transition material used was VWP. The simulated result of a TBP and VWP bilayer sample with a thickness of 1.5-mm shows the shape and stress distribution (Figure 1b). As the sample is heated above T_g for stress relaxation, the simulation shows that there is close to no stress along the TBP section. The stress along the VWP section reduces to less than 1 MPa due to the low modulus when heated above T_g . However, two regions have higher stresses of 1-2 MPa. The stress is slightly higher along the boundary of the two materials as the boundary stress prevents the materials from delamination; TBP exerts compressive stress on VWP. Also, at a distance of 20 mm along the y-axis (midpoint of the long axis), there is a sharp increase in stress, as shown in Figure 1b. The bending stress exerted on the VWP creates a high-stress concentration in the middle region. Figure 1b and c are representative simulation and experiment results that characterized the 4D-printing process by the bending curvature of the bilayer slab. The experimental results agree well with the simulation, with less than 10% difference, as shown in Figures 1d and 1e. The curvature is calculated based on measure chord length and height. A light difference in measured values, either due to actual variability or measurement error, may lead to a large difference in calculated curvature. Overall, the small differences suggest that the simulation model can predict the structure accurately. This simulation model overcomes the limitations of the previous study and provides a better prediction of the bending curvature of a thin slab at a high temperature as the simulation model is dependent on stretch rates at respective temperatures that are determined experimentally. The relationship between the

thickness of VWP and the final curvature is established. For a fixed thickness of TBP, the bilayer part with a thinner VWP layer would be able to attain a more significant curvature due to the lower overall stiffness of the slab, as shown in Figure 1d. Likewise, given a fixed thickness of VWP, thinner TBP results in a more significant curvature as the slab has a lower overall stiffness. As the increase in stiffness due to increasing TBP was not as significant as the effect due to increasing VWP, the decrease in curvature was less drastic with increasing TBP compared to increasing VWP, as shown in Figure 1e.

3.2. Faster response and control of the bending angle

The response rates of two parts with different overall thickness are shown in **Figure 2a**. Both samples had a 1:1 ratio of VWP to TBP. The curvatures were measured every 10 seconds and plotted against time. It was evident that by limiting the overall thickness to 1mm, there was a significant increase in curvature at any point in time compared to the other one with an overall thickness of 3 mm. Also, curvature increased more rapidly at the initial stage for the specimen of small thickness, likely to be due to the increase in surface area to volume ratio and the reduction in overall stiffness. This phenomenon is also described by Fick's law of diffusion,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(\frac{\partial c}{\partial x} \right),$$

where c is the concentration of the solvent, t is the time taken, and x is the distance.

The rate of diffusion is faster when the distance travelled by the solvent is shorter. This contributes to a reduction in time taken to achieve a force required to cause bending. Therefore, the speed of the reversible cycle can be increased by reducing the overall thickness. There are other benefits to using a thinner layer. A thinner layer implies an overall decrease in stiffness, which means a smaller amount of induced stress is needed to cause bending. A thinner layer would also ensure uniform heating during recovery; A thin layer would also lead to a quicker transition of mechanical properties, such as stiffness, of the transition material (VWP).

A reduction in thickness and the combined use of stimuli bring about relatively fast programming amongst contactless stimulated 4D-printing processes. The thin bilayer slab

comprising VWP and TBP was able to achieve a considerably large curvature within a much shorter time. The sample was first placed in heated ethanol of 60°C for 60 seconds. After 60 seconds, the entire sample became rubbery. Subsequently, it was placed into ice water at 0°C for 30 seconds to fix its shape, during which VWP became stiff. The sample was then heated with the RS Pro Heat Gun with an airflow of 250L/min at 350°C until it was straightened, which took 90 seconds. The entire reversible 4D-printing process took approximately 3 minutes to complete. Following this result, the overall swelling time was reduced to 60 seconds for the remaining study. To our best knowledge, this process is the fastest among all swelling and heat-driven contactless reversible 4D-printing processes.

A repeatability test was also carried out to ensure that the thin bilayer slab is able to achieve the same curvature during actuation and the same flat shape during recovery after multiple uses. The results were shown in Figure 2b. The sample was able to achieve a curvature of $\sim 30 \text{ m}^{-1}$ consistently in its fifth cycles. It was also capable of returning back to the flat shape when heated with the RS Pro Heat Gun for approximately 90 seconds. This shows that the shape morphing of this 4D printing process is both reversible and repeatable. However, it is important to note that extensive heating and swelling in ethanol might degrade the material. This was studied in an earlier study (Lee et al., 2019).

Although the overall thickness of the bilayer slab was kept the same, the relative thickness of each layer would result in different maximum curvature. In this section, parts were printed with different ratios of VWP to TBP while the overall thickness was maintained at 1 mm, according to **Table 3**. Table 3 shows that the maximum curvature (after being swelled in heated ethanol for 60 s) increased as the ratio of TBP to VWP increased. However, the trend plateaued at around 1:3 of VWP to TBP, as seen in samples 3 to 5, which showed similar maximum curvature. The response rate and recovery rate of the five samples in Table 3 were studied further, and the results are shown in Figures 2c and 2d, respectively.

Figure 2c depicts the response rate of all five samples. Except for sample 1, all other four samples had a sharp initial increase in curvature once they were placed in ethanol at 60°C. The rate of change in curvature, or the response rate, was calculated using the first derivative of the curvature with respect to time. The initial response rate for sample 1 was calculated to be 1.82 m⁻¹s⁻¹ in the first second, drastically lower than the other four samples which had the initial response rate in the range of 14 to 19 m⁻¹s⁻¹ in the first second. In sample 1, the modulus of VWP was still high at the early stage as it might not have been uniformly and sufficiently heated due to the thicker VWP layer, which resulted in a low curvature. As the sample progressively being heated up, the amount of ethanol that diffused into the sample increased, too. The average rate of increase in curvature for sample 1 was 1.56 m⁻¹s⁻¹ for the first 10s, with the rate from 2-10 seconds being 1.53 m⁻¹s⁻¹. While the other four samples showed a high response rate for the first 10s, and most of the increase in curvature happened within the first second with a response rate of up to 19 m⁻¹s⁻¹. The average rate from 2-10 seconds was approximately 0.6 to 1.2 m⁻¹s⁻¹. These results suggested that the VWP section in samples 2-5 were uniformly and rapidly heated above T_g within a second, which reduced the material stiffness. Sample 2 then had a slower overall response rate compared to the remaining samples 3-5. Samples 3-5 had a similar response rate throughout the entire programming process. However, once removed from ethanol, sample 5 had the largest reduction in curvature of 36.75% with respect to the maximum curvature obtained before being subjected to stimulated recovery, whereas the rest only had less than a 10% decrease in curvature. This indicates that having a 1:9 ratio of VWP to TBP might not have much functional usage as the shape cannot be retained outside the ethanol environment. When the sample is in the heated ethanol, the osmotic pressure is balanced, and the TBP is saturated with ethanol. Once taken out from the ethanol bath, the imbalanced osmotic pressure causes ethanol to diffuse out of the elastomer before the structure is quenched. The reduction in sample 5 is relatively large as the low

stiffness of the extremely thin VWP makes it difficult to retain the shape as the ethanol evaporate. The other four samples, on the other hand, have relatively good shape retention abilities.

The recovery rate of the five samples has also been studied at a constant temperature of 60°C, as shown in Figure 2d. In general, the smaller the ratio of VWP to TBP for a given overall thickness, the quicker the specimen fully recovers. The recovery rate was also calculated using the first derivative of curvature with respect to time. Sample 1 recovered at an almost constant rate. Sample 2 and 3 showed two distinctive response rates. Up to 60 seconds, both samples were recovering at an average rate of $\sim 0.55 - 0.58 \text{ m}^{-1}\text{s}^{-1}$ before it slowed down and recovered at a slower average rate of $\sim 0.23 - 0.33 \text{ m}^{-1}\text{s}^{-1}$. Both samples 4 and 5 showed a similar pattern as 2-3, but the transition in response rate occurred at around 40 seconds with an average rate of $\sim 0.93 - 1.1 \text{ m}^{-1}\text{s}^{-1}$ in the first phase and $\sim 0.14 - 0.17 \text{ m}^{-1}\text{s}^{-1}$ in the second phase. Sample 2 – 5 likely underwent two distinct recovery stages. The fast-initial recovery rate was primarily due to the sudden release of pre-stored stress when the transition material was heated above its T_g . The stress was pre-stored in VWP when the specimen was quenched in ice water at 0°C. In addition, the elastomeric recovery also took effect as the ethanol evaporated. After the pre-stored stress was released, the recovery rate reduced as only the elastomeric recovery mechanism was in place. Sample 1 did not display two phases as it may not have as much pre-stored stress as the other samples due to the thin TBP layer. The ability to recover was largely due to the residual stress formed as the ethanol evaporated. Hence, it had a more uniform but slower recovery rate.

3.3. Control of twisting angles

The twisting action was enabled by introducing alternating stripes to achieve more versatile 3D transformation during programming. To further elaborate on the twisting function, the samples were printed with a middle layer that is shown in **Figure 3a**. A thin layer of VWP was

printed as a top layer to prevent one side of the TBP from being directly exposed to ethanol, as shown in the cross-sectional view of the 0° sample, which helped to maintain the asymmetric swelling for shape morphing. This layer was intended to be as thin as possible to achieve substantial curling and twisting. The middle layer with alternating stripes, along with the top layer of VWP and a bottom layer of TBP, allowed the two materials to interlock, as displayed in the cross-section of the 0° sample. This arrangement allowed anisotropic expansion when the sample was swelled in ethanol. As a result, the slab would curl about an axis parallel to the orientation of the alternating stripes in the middle layer. For example, for the sample whose middle layer contains alternating stripes oriented at 45° , the TBP in the middle layer was not able to expand isotropically. The preferential expansion forced the slab to curl about a 45° axis (Figure 3b). Figure 3c shows a good agreement between the orientation of the stripes and the helix angle formed with a maximum standard deviation of 5° . This result suggests that parts with controlled twisting can be incorporated in our 4D-printing process by introducing carefully designed helical structures. The simulated models of the twisting action are shown in Figure 3d. The simulated results were in agreement with the experimental results in terms of the twisting angles. The middle plane for all the five simulation models shows a high-stress distribution as the midplane of the alternating layers was set to be the fixed constraints. Unlike the VWP on the surface, the middle VWP experienced stress from the surrounding swollen TBP.

3.4. 3D shape morphing

One of the various prospects of reversible 4D printing is soft robotics. Various structures were designed and used to establish the 3D shape morphing to demonstrate such applications. First, a 2.5D flower whose petals contained alternating stripes of different angles was printed to demonstrate the widely popular 2.5D to 3D shape morphing. Next, two 3D structures were designed to mimic the actions that occurred in nature with the 3D-to-3D shape morphing; they

were meant to mimic a butterfly flapping its wings and the flower blooming. The 2.5D flower and butterfly showed how the alternating stripes would induce desired twisting in different designs. The 3D flower demonstrated how the structures could be used to mimic nature reversibly. As the current 4D-printing process had a faster response, a possible load-bearing application was demonstrated with a 4D-printed soft robotic gripper.

3.4.1. Biomimetic shape morphing

In the 2.5D six-petal flower, each petal was printed with a middle layer of alternating stripes oriented in a distinct angle ranging from 0° and 90° about the long axis of the petal as shown in **Figure 4a**. Two were printed 30° to the axis of the petal, two were 60° , one was 0° , and the last was 90° . The 2.5D flower was printed with a 0.2 mm of VWP as the top layer, with the other two layers being 0.4 mm to maintain an overall thickness of 1 mm. The VWP layer was designed to be 0.2 mm for optimised bending curvature and response rate. Out of all five samples, the sample with a VWP to TBP ratio of 1:4 was able to achieve one of the highest curvatures, and it was also one of the fastest in terms of recovery rate. It has decent initial shape retention, losing only 3.36% of curvature when being removed from ethanol bath. Figure 4d illustrates how the 2.5D flower morphs into the 3D shape over time (Supplementary Video 1). The curled flower was heated to full recovery using the RS Pro Heat Gun, as shown in Supplementary Video 2.

The alternating stripes were also included in the butterfly, as illustrated in Figure 4b. The hinge was designed with just a simple bilayer structure with a ratio of 1:4 of VWP to TBP. This is created to have the most substantial amount of curl for an apparent flapping motion of the wings. The tips of the wings incorporated the design of alternating VWP and TBP to allow the wings to twist slightly. The butterfly was designed in a way that, during programming, the wings would reach the top of its flight, and after recovery, the wings would drop. Repeated reversible programming and recovery mimicked the butterfly flapping its wings. Figure 4c

shows that butterfly before programming, after programming and after recovery. The recovered structure was also similar to that of the initial shape. The contactless programming and recovery were also displayed in Supplementary Video 3. However, as it was recovered using the RS Pro Heat Gun at 350°C, the temperature might be too high and resulted in a significant difference in heat expansion of the two materials. This was deduced based on the observation that the tips of the wings remained slightly curled despite ethanol being removed entirely.

Figure 4d shows that a true 3D flower that was designed to be closed as-printed. During programming, it was projected to open, like a flower blooming. The outer petals were designed to have a ratio of 1:4 VWP to TBP, while the inner petals had a ratio of 1:2. The outer petals would then unveil to a greater extent than the inner petals. Before programming, the structure was relaxed by being heated above its T_g . This preheating step is necessary because the recovery mechanism restores the part to a shape in which VWP is in its rubbery state. Due to the gravitational pull, the petals of the original 3D flower opened a little. Unlike the butterfly, the shape change of the 3D flower during the preheating is more significant due to the large petal and weak linkage between the petal and the stem. The butterfly has a relatively larger hinge to support its wings, whereas the flower has weak linkages between the large petals and stem. The relaxed shape was set to be the initial shape before the programming. The 3D flower was then swelled in ethanol at 60°C for 2 minutes. A slightly longer time was used for this experiment to ensure full swelling due to its large size and steric hindrance. The flower was then quenched to fix its shape before it was heated using the RS Pro Heat Gun until it fully recovered. This process is depicted in Supplementary Video 4. Figure 4e illustrates that the 3D flower has a similar shape before programming and after recovery.

3.4.2. Soft robotic gripper

The higher mechanical strength of TBP and VWP compared to hydrogels makes our 4D-printing parts well-suited for load-bearing applications. A gripper with claws was designed and

printed with alternating stripes in the middle layer, as shown in **Figure 5a**. Not only were the alternating stripes capable of giving directional twist and curl, but it was also able to induce considerable curvature without losing too much stiffness.

The payload was a 1-cm³ VWP block. The gripper was first relaxed by being heated above its T_g before programming. **Akin to the 3D flower**, the shape of the gripper would change slightly after relaxation **due to gravitational pull and its weak linkage between the arms and stem**. Differing from the other two 3D structures, the gripper was soaked in ethanol for 5 minutes instead to ensure that the gripper fully enveloped the block so that it would not slip out, as shown in Figure 5b and Supplementary Video 5. The gripper first approached and grabbed the payload during the programming. The gripper was then transported by removing it from the tank of ethanol and moving it to the desired drop-off location. It was then unloaded by heating the gripper with the RS Pro Heat Gun. As the gripper was slowly heated up, ethanol was lost, and the gripper opened up slightly, allowing the block of VWP to slip out. The reversible 4D-printing process allows this gripper to pick up and drop the object without any manual intervention. When attached to an x-y translation stage, it has the potential to transport payload between any designated locations.

The designed gripper can be used in situations where a piece of equipment needs to be sterilised in alcohol before usage, such as small medical tools. A similar concept can be used with other biocompatible PolyJet materials such as MED610 which has been used in bioprinting studies (Chan, Fang, Shie, & Shen, 2019).

The current technique is demonstrated with the PolyJet printer, which only prints proprietary materials due to the use of multi-material printing. The contactless programming method is also restricted to the use of ethanol, which presents many challenges for industrial adoption. **Also, heating with alcohol extensively and repeatedly might degrade the materials by transesterification as the proprietary materials used are acrylate-based.** The next step is to

overcome the challenges of materials by having more printable shape-memory materials and stimulation mechanisms. By having more available stimulation mechanisms in disposal, a new reversible 4D-printing process enabled by different stimuli can be developed to suit in the desired operating conditions.

4. Conclusion

Several drawbacks limit the real-world applications of previously reported SMP-based reversible 4D-printing processes, such as slow response, complicated fabrication, and confinement to 2.5D-to-3D shape morphing. Although not all reversible 4D printing techniques induce slow response like the study by Yuan *et al.* where they incorporated the use of liquid crystal elastomer (LCE) into producing a 4D printed part (Yuan et al., 2017), they usually require a complicated multi-technique and multi-platform 4D printing process. Multi-technique and multi-platform are likely to incur more fabrication time and cost as a trade-off for the desired properties. To overcome such limitations, we have introduced a 4D-printing process with a faster contactless shape-setting to achieve reversible shape morphing by using a combination of stimuli. The final shape by contactless shape-setting could be predicted using a simulation model. This study has demonstrated reversible 2D-to-3D and 3D-to-3D shape morphing of parts fabricated in a single print, suggesting that more functional structures can be developed as a result of better prediction of shapes and short programming time. Our study suggests that having a combination of stimuli for programming and recovery is beneficial. Biomimetic reversible morphing was demonstrated with flowers and a butterfly. Also, our study indicates that reversible 4D-printing can be very useful in soft robotics **in sterilised conditions** with the demonstration of a gripper **in alcohol**. **This process can be used in combination of biocompatible materials, in future, to pack and unpack medical tools or products in a sterilised environment.** While all these processes and techniques are still

insufficient to achieve truly functional 4D reversible structures that can be used in industries, it is an advancement to achieving practical 4D reversible printing.

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Declaration of Interest

The authors declare no competing interest.

Supporting Information

Supplementary Video 1 shows the top view of the contactless programming of the 2D flower using heated ethanol in 60 seconds.

Supplementary Video 2 demonstrates the contactless programming and recovery of the 2D flower using heated ethanol and air gun, respectively.

Supplementary Video 3 demonstrates the movement of the wings of a butterfly during programming and recovery.

Supplementary Video 4 demonstrates the opening and closing of a 3D flower during programming and recovery.

Supplementary Video 5 demonstrates the operations of the 3D gripper by carrying a payload and releasing it.

Supporting Information covers the determining of the material model, the simulation model and the measurement of the helix angle.

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Table 1 *Material constants in Mooney-Rivlin, five parameters*

<i>Parameter</i>	<i>C_{10} (Pa)</i>	<i>C_{01} (Pa)</i>	<i>C_{20} (Pa)</i>	<i>C_{02} (Pa)</i>	<i>C_{11} (Pa)</i>
<i>TBP</i>	1.8015×10^5	-21567	-1.4005×10^5	-3.566×10^5	4.479×10^5
<i>VWP</i>	-1.8408×10^8	2.0045×10^8	6.5254×10^8	1.3749×10^9	-1.8208×10^9

Table 2 Dimensions of the test samples for response and recovery rate

<i>Test samples</i>	<i>Dimensions (mm)</i>		
	<i>VeroWhitePlus</i>	<i>TangoBlackPlus</i>	<i>Overall</i>
1	$10 \times 60 \times 0.50$	$10 \times 60 \times 0.50$	$10 \times 60 \times 1$
2	$10 \times 60 \times 0.33$	$10 \times 60 \times 0.67$	
3	$10 \times 60 \times 0.25$	$10 \times 60 \times 0.75$	
4	$10 \times 60 \times 0.20$	$10 \times 60 \times 0.80$	
5	$10 \times 60 \times 0.10$	$10 \times 60 \times 0.90$	

Table 3 Geometrical size effect on the curvatures

<i>Sample</i>	<i>The thickness of VWP (mm)</i>	<i>The thickness of TBP (mm)</i>	<i>The ratio of VWP To TBP</i>	<i>Peaked curvature (m^{-1})</i>
1	0.5	0.5	1:1	28.26
2	0.33	0.67	1:2	59.65
3	0.25	0.75	1:3	72.87
4	0.2	0.8	1:4	73.60
5	0.1	0.9	1:9	73.26

a

Rapid contactless shape setting (Programming stage)

Step 1: Expose to ethanol at high temperature

Step 2: Cool in ice water

Recovery StageStep 3: Heat above T_g

Step 4: Natural Cooling

b

Stress plot of TBP (Top) and VWP (bottom)

c

d

e

Figure 1 a: Reversible 4D-printing cycle stimulated with heated ethanol and heat. b: Simulated model with 1.5mm of TangoBlackPlus (TBP) and 1.5mm of VeroWhitePlus (VWP) after swelling in ethanol for 60 minutes and heated above T_g c: Snapshot of a sample with 1.5mm of TBP and 1.5mm of VWP after swelling in ethanol for 60 minutes d: curvature of samples against the thickness of VWP for a fixed 1.5mm of TBP e: Curvature of samples against the thickness of TBP for a fixed 1.5mm of VWP

Figure 2 a: Response rate of dual-layered samples, overall 1mm (0.5 of TBP and 0.5mm of VWP) and overall 3mm (1.5mm of TBP and 1.5mm of VWP) b: Repeatability study of a dual-layer sample (0.5 of TBP and 0.5mm of VWP) in 5 cycle c: response rates of the samples listed in Table 2 when soaked in ethanol at 60°C d: recovery rate of the samples when heated at 60°C.

Figure 3 a: Top view of the schematic of the various printing angles and the cross-section of 0° sample. b: Result of samples with different print angle after being soaked in ethanol at 60°C for 60 s. c: Graph of helix angle against the orientation of the stripes d: Stress plots of the simulated and experimental samples of the five different print angles

Figure 4 Demonstration of 3D structures. a: a time-lapse of a flower printed with a different print angle on each petal during swelling b: Top view and front view of the butterfly. c: Experimental demonstration of the butterfly: initial, swell, recover. d: Front and top view of the 3D flower e: Experimental demonstration of the 3D flower: initial, swell, recover.

Figure 5 Demonstration of the gripper. a: Top view, front view and tilted view of the gripper. b: Experimental demonstration of the gripper. During programming, the gripper grabs the payload as it swells up. The gripper transports the payload to another location. During recovery, the payload unloads upon heating.

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