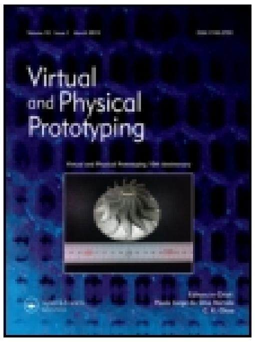

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3D printing of smart materials: A review on recent progresses in 4D printing

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ABSTRACT
Additive manufacturing (AM), commonly known as three-dimensional (3D) printing or rapid prototyping, has been introduced since the late 1980s. Although a considerable amount of progress has been made in this field, there is still a lot of research work to be done in order to overcome the various challenges remained. Recently, one of the actively researched areas lies in the additive manufacturing of smart materials and structures. Smart materials are those materials that have the ability to change their shape or properties under the influence of external stimuli. With the introduction of smart materials, the AM-fabricated components are able to alter their shape or properties over time (the 4th dimension) as a response to the applied external stimuli. Hence, this gives rise to a new term called '4D printing' to include the structural reconfiguration over time. In this paper, recent major progresses in 4D printing are reviewed, including 3D printing of enhanced smart nanocomposites, shape memory alloys, shape memory polymers, actuators for soft robotics, self-evolving structures, anti-counterfeiting system, *active origami* and controlled sequential folding, and some results from our ongoing research. In addition, some research activities on 4D bio-printing are included, followed by discussions on the challenges, applications, research directions and future trends of 4D printing.

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Additive manufacturing; 3D printing; smart materials; 4D printing; 4D bio-printing

1. Introduction

Since the first additive manufacturing system has been introduced in the late 1980s, there have been huge advancements in the area of additive manufacturing (Donnell *et al.* 2014, Pei 2014). Additive manufacturing (AM), commonly known as three-dimensional (3D) printing or rapid prototyping (RP), has many different applications. These applications include the fabrication of physical prototypes such as mock-ups (Tibbits *et al.* 2013, Chua and Leong 2014), functional evaluation of product designs (Chua and Leong 2014, Pei 2014), healthcare products and living biological structures (Seliktar *et al.* 2013, Huang *et al.* 2013, Murphy and Atala 2014, Chua and Yeong 2015). Moreover, 3D printing has been used to manufacture end-use products as well such as the replication of components or objects (Chua and Leong 2014, Frazier 2014), 3D printed electronics (Donnell *et al.* 2014), fashion and jewellery products (Yap and Yeong 2014) and advanced multifunctional honeycomb structures (Yap and Yeong 2015). In addition to these applications, 3D printing also provides a new manufacturing route that can overcome the various limitations in processing materials by conventional methods. One such example is the processing of ceramics using 3D printing to eliminate the problem of high tool wear and size shrinkage associated with the conventional processing methods (Yeong *et al.* 2014).

Besides, over the past few years, the number of materials manufactured by 3D printing has increased by a large extent. One category of materials that has been in the spotlight recently is the smart materials. Although smart materials are widely researched and used in practice, there is still disagreement on the definition of what smart materials are (Bogue 2014). One of the definitions is that smart materials are materials that demonstrate coupling or conversion of energy between various physical domains such as the conversion of thermal energy into mechanical work (Leo 2007). Others define smart materials as materials that can sense fluctuations in its external environment and generate a useful response to the fluctuations by either changing their material properties or geometries (Varadan *et al.* 1992). Thus, in the context of this paper, we shall consider both definitions and define smart materials as materials that would either change their shape or properties between different physical domains in a useful manner under the influence of certain stimuli from the environment.

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Due to the ability of smart materials, the 3D fabricated components consisting of such materials would be able to evolve in a predefined manner over time. Hence, this gives rise to a new term called '4D printing' (Tibbits *et al.* 2013). However, not all 3D printing processes that produce animate components such as printed living hinges are categorised as 4D printing since they do not demonstrate 'smart' behaviour such as self-sensing, self-actuating and shape changing (Bogue 2014, Pei 2014). Additionally, the developments in 4D printing are largely made possible due to the recent advancements in multi-material printing by using the PolyJet technology (Stratasys Ltd) and the fabrication of metallic components by using the Selective Laser Melting (SLM) technology (SLM Solutions).

PolyJet 3D printing is a technology that is similar to inkjet printing. However, instead of jetting inks on to the paper, PolyJet printers deposit curable liquid photopolymer layer-by-layer on top of the building platforms to create 3D components. Furthermore, with the recent improvement in PolyJet technology, PolyJet printers can now deposit multiple materials concurrently to fabricate components that are made up of several materials (Vaezi *et al.* 2013). Thus, this improvement in PolyJet technology has been utilised in 4D printing to create multi-material components that consist of smart materials and conventional materials.

On the contrary, SLM technology is a powder-based 3D printing method that uses a high energy density laser to melt layers of metallic powder in order to create a dense and homogenous 3D metallic structure without any binder and the need for supports (Loh *et al.* 2015). Similarly, SLM technology has been utilised in 4D printing to create components that are made up of single metallic smart materials.

Hence, in order to differentiate 3D printing from 4D printing, the definition of 4D printing needs to be properly defined. According to Pei (2014), 4D printing is 'the process of building a physical object using appropriate additive manufacturing technology, laying down successive layers of stimuli-responsive composite or multi-material with varying properties. After being built, the object reacts to stimuli from the natural environment or through human intervention, resulting in a physical or chemical change of state through time'.

On the other hand, Tibbits *et al.* (2013) stated 4D printing as a new process that 'entails multi-material prints with the capability to transform over time, or a customised material system that can change from one shape to another, directly off the print bed' with 'the fourth dimension described here as the transformation over time, emphasising that printed structures are no longer static, dead objects; rather, they are programmably active and can transform independently'.

Thus, according to these two definitions, the main difference between them is that Pei considered 4D printing to incorporate either a physical or chemical change of state while Tibbits *et al.* only considered shape changes.

In this paper we shall consider 4D printing to incorporate the different characteristics and differences in definitions. We shall define 4D printing as an additive manufacturing process that integrates smart materials into the starting form of the printing material for 3D printed structures/components. After fabrication, the 3D object would respond in an intended manner to external stimuli from the environment or through human interference, resulting in a change in shape or physical properties over time. Hence, based on this definition, the present paper will review some examples of 3D printed smart materials/structures that are regarded as 4D printing. These examples are categorised according to whether the printed components consist of a single material or multiple materials. Furthermore, the challenges, applications, research directions and future trends of 4D printing will be discussed. In addition, some results on 4D bio-printing are also explained in this paper.

2. Developments in 4D printing

In this section, some developments of 4D printing that exhibit physical changes of the printed components/structures are illustrated. They are classified according to whether they are printed with a combination of multiple materials or with a single material. In particular, research activities on enhanced smart nanocomposites (Kim *et al.* 2014), shape memory alloys (SMAs) (Meier *et al.* 2009, Meier *et al.* 2012, Dadbakhsh *et al.* 2014), 3D printing of shape memory polymers (SMPs), actuators for soft robotics (Rossiter *et al.* 2009), self-evolving structures (Raviv *et al.* 2014), anti-counterfeiting system (Ivanova *et al.* 2014), *active origami* and controlled sequential folding (Ge *et al.* 2013, 2014, Yu *et al.* 2015) will be summarised and discussed. Meanwhile, some results from our ongoing research will also be illustrated.

2.1. *4D printing with single material*

In this section, we include 4D printing of either a single smart material or a mixture of smart material and conventional material as the starting form for printing. For the printed components that consist of a single smart material or a mixture of smart and conventional materials, the smartness of the materials plays a more important role in achieving the intended response than in the case of a multi-material component. The smartness of the smart materials or mixtures describes the self-adaptability, self-sensing, shape memory, decision making and multiple functionalities of the materials or mixtures (Varadan *et al.* 2006, Kamila 2013). It is these characteristics that determine how the printed components change their properties in response to the external stimulus and they provide various promising applications of these materials. In the following, recent developments of 4D printing that consist of either a single smart material or a mixture of materials as the starting form will be highlighted, including enhanced smart nanocomposites (Kim *et al.* 2014), SMAs (Meier *et al.* 2009, Meier *et al.* 2012, Dadbakhsh *et al.* 2014) and 3D printing of SMPs.

2.1.1. *Enhanced smart nanocomposites*

One important type of smart material that has been used widely is the piezoelectric material that is able to produce electrical charge or voltage when experiencing an externally applied stress and vice versa (Uchino 2010, Kim *et al.* 2014, Lin *et al.* 2014). The applications of piezoelectric material can be found in loud speakers (Lang and Muensit 2006, Kim *et al.* 2014), acoustic imaging (Vijaya 2013, Kim *et al.* 2014), energy harvesting (Lang and Muensit 2006, Vijaya 2013, Kim *et al.* 2014, Wong *et al.* 2015), actuators (Lang and Muensit 2006, Uchino 2010, Vijaya 2013, Kim *et al.* 2014, Rajabi *et al.* 2015), transducers (Lang and Muensit 2006, Uchino 2010, Rajabi *et al.* 2015) and tissue regeneration (Rajabi *et al.* 2015).

Different categories of piezoelectric materials offer different capabilities. Piezoelectric polymeric materials have some unique characteristics as compared to other piezoelectric materials. These materials are suitable for systems that require mechanical flexibility, small active elements, biocompatibility and solution-based processability. However, it is still a difficult task to fabricate piezoelectric polymeric materials into complex 3D structures or small active elements. Thus, further improvement in the manufacturability of piezoelectric polymers will definitely have a huge contribution to the development of various applications which require micro-scale and nano-scale piezoelectric polymers, such as biodiagnostic devices, micro-scale and nano-scale electromechanical systems, imaging systems, compact sensor designs and electronics (Kim *et al.* 2014).

Although there are many different techniques available for microfabrication and nanofabrication of piezoelectric materials, they are not easy to adopt. Kim *et al.* (2014) have presented a new nanofabrication method that produces 2D and 3D piezoelectric nanoparticle-polymer composite structures by using digital projection printing (DPP). The main advantage of DPP is that its resolution can be as small as 1 μm and it can be carried out over a large area with high reproducibility and precision (Kim *et al.* 2014). Moreover, the equipment is less complex and the fabrication time is much shorter as compared to some other techniques (Melchels *et al.* 2010, Vaezi *et al.* 2013, Kim *et al.* 2014).

The starting form of the material was created by embedding barium titanate ($BaTiO_3$, BTO) nanoparticles into a polyethylene glycol diacrylate (PEGDA) matrix and the material was sonicated for more than 24 hours before printing (Kim *et al.* 2014). However, other piezoelectric materials and photoliable polymers can be utilised as well in the same manner. In addition, the BTO nanoparticle's surfaces were modified chemically with linker molecules that are photosensitive before adding into the PEGDA photoliable polymer solution. Hence, under the influence of light, the polymer would form cross-linking and direct covalent bonding with the chemical groups of the smart nanoparticles and this grafts the nanoparticles to the backbones of the polymer.

By using the DPP to photopolymerise the piezoelectric nanocomposite, some 2D and 3D samples have been fabricated by Kim *et al.* (2014) and the 2D samples are shown in Figure 1. These 2D samples

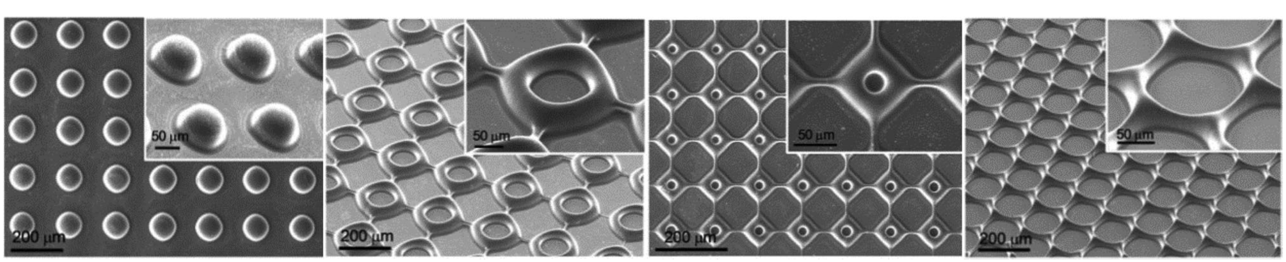

Figure 1. 2D nanocomposite samples including (a) dot array, (b, c) square arrays with different sizing and (d) honeycomb array (see (Kim *et al.* 2014) for details). Reprinted (adapted) with permission from ACS Nano, vol. 8 (10), pp. 9799–9806. Copyright (2014) American Chemical Society.

include a dot array, square arrays with different sizing and a honeycomb array. One of the 3D samples fabricated was a microtubule structure. The microtubule structure was made by first projecting a honeycomb image onto the nanocomposite solution. Once the solution has been polymerised, the 2D honeycomb array was removed and it rolled up into the tubule shape automatically. The diameter of the tube and the extent of the rolling can be controlled by printing the layers with different thermal expansion coefficients, densities or lattice parameters.

The rolling up of the honeycomb array was due to the presence of stress gradients within the array. One possible reason for the formation of the stress gradients might be due to the discrepancy in the thermal expansion between the top layer and the bottom layer of the honeycomb structure as a result of the curing process. In other words, the different layers might be experiencing different magnitudes of expansion and/or contraction during the curing process, which eventually leads to the formation of stress gradients within the array.

Overall, the research by Kim *et al.* has shown positive results in fabricating enhanced smart nanocomposites (2014). These results include a higher stress transfer efficiency to the BTO nanoparticles due to covalent bonding between the nanoparticles and polymer, and a significantly higher piezoelectric coefficient for chemically modified BTO nanoparticles embedded into the PEGDA matrix as compared to the other composites. However, there are still some areas to work on including doing more work to minimise the DPP fabrication time by tuning the irradiation power, photoinitiator concentration, monomer concentration, nanoparticle loading and the addition of a quencher (Kim *et al.* 2014). Moreover, the resolution limits of both 2D and 3D samples fabricated are about 5 μm, which can be further reduced by using a more focused light source and adjusting its wavelength such that the adsorption of the light source can be maximised (Kim *et al.* 2014). Smaller photopolymerisation spots can be obtained as well by using non-linear optical process such as two-photon absorption (Kim *et al.* 2014). Nonetheless, multiphoton process requires higher laser power and the fabrication time will be much longer.

Another potential research area is to determine the upper limits of the piezoelectric coefficient of nanocomposites and investigate their relationship with other parameters such as nanoparticle composition, polymer matrix, size of the nanoparticle, linker molecule used, grafting density and linker length (Kim *et al.* 2014). In addition, the size of the nanoparticle has the potential to be further reduced to achieve a better optical transparency (Kim *et al.* 2014).

Overall, the results obtained from the above research have shown the possibility of fabricating piezoelectric nanocomposites by using DPP and a new method to improve the piezoelectric coefficient. These results might have important impact on various research fields such as bioengineering, materials science, physics and chemistry (Kim *et al.* 2014).

2.1.2. *Shape memory alloys*

SMA is a type of smart materials which can directly convert thermal energy into mechanical work that is known as the shape memory effect (SME) (Fremond and Miyazaki 1996). SME is a result of the transformation between two different crystalline phases in the SMAs, namely the low temperature phase (martensite) and the high temperature phase (austenite). It can be observed that when the SMA is deformed in the martensitic phase, followed by heating the alloy above a critical temperature, a reverse phase transformation can be induced (Trasher *et al.* 1992, Fremond and Miyazaki 1996, Leo 2007). The initial shape of the deformed alloy will be restored as the crystalline structure transforms from martensite back to austenite.

Another property of the SMA is the superelasticity, whereby the alloy demonstrates a large recoverable strain upon loading and unloading. Unlike the case of SME where the reversible martensitic phase transformation is due to temperature change, the phase transformation in superelasticity is a result of mechanical actions (Fremond and Miyazaki 1996). One example of SMA that can exhibit both SME (thermal memory) and superelasticity (mechanical memory) is the nickel-titanium (NiTi) SMA (Meier *et al.* 2012, Dadbakhsh *et al.* 2014). The SME and superelasticity effect of NiTi are characterised by its transformation temperatures. However, the transformation temperatures are very sensitive to the variation in the Ni/Ti ratio. A slight drop in the Ni content can lead to a huge increase in the transformation temperatures (Frenzel *et al.* 2010, Meier *et al.* 2012, Bormann *et al.* 2012, Elahinia *et al.* 2012).

NiTi SMAs are often used in engineering applications due to their outstanding functional properties (Elahinia *et al.* 2012, Meier *et al.* 2012, Dadbakhsh *et al.* 2014). Examples of applications of NiTi can be found in biomedical implants (Bormann *et al.* 2012, Elahinia *et al.* 2012), smart composite materials (Sanusi *et al.* 2014), actuators (Sharma *et al.* 2015), micro-electromechanical systems (MEMS) (Sharma *et al.* 2015) and electrical devices (Sharma *et al.* 2015) etc. In addition, NiTi exhibits the best shape memory behaviour such as high percentage of shape recovery, large superelastic strain and recovery stress among all the different types of SMAs (Van Humbeeck 2008).

However, NiTi SMAs are not easy to process by conventional methods (Meier *et al.* 2009, Elahinia *et al.* 2012). First, the NiTi alloys are extremely compositional sensitive. Impurity elements can be easily picked up during high temperature processing and cause problems such as oxidation and microstructural defects. These problems can then lead to a shift in the transformation temperatures. Second, NiTi SMA has a poor machinability. The shape memory properties of NiTi alloy are known to make it difficult for precise machining and it causes a significant amount of tool wear (Meier *et al.* 2009, Meier *et al.* 2012, Elahinia *et al.* 2012, Weinert and Petzoldt 2004). Furthermore, thermomechanical treatments, annealing treatments and shape setting treatments can affect the phase transformation behaviour of NiTi significantly (Meier *et al.* 2009).

Therefore, one potential solution is to fabricate NiTi parts by additive manufacturing processes such as SLM (Meier *et al.* 2009, Bormann *et al.* 2012, Meier *et al.* 2012, Shishkovsky *et al.* 2012, Zhang *et al.* 2013, Shishkovsky *et al.* 2013, Dadbakhsh *et al.* 2014). In one of the research done by Meier *et al.* (2009), NiTi parts have been produced by SLM (SLM NiTi).

The advantages of using SLM include cutting down on the number of manufacturing cycles as the extent of machining and thermomechanical treatments can be minimised (Meier *et al.* 2009, Zhang *et al.* 2013). In addition, NiTi alloys with small and complex structures that cannot be manufactured by conventional methods can now be fabricated (Meier *et al.* 2009, Bormann *et al.* 2012, Shishkovsky *et al.* 2012). However, one of the problems found in the SLM processed NiTi was the lower content of Ni due to evaporation (Meier *et al.* 2009). This is because Ni has a lower evaporation temperature (evaporation temperature of Ni = 3186.15 K (Yaws 2011a) and evaporation temperature of Ti = 3560.15 K (Yaws 2011b)) and hence it has a higher tendency to evaporate. Another explanation is that the heat transfer during the melting process was not uniform due to the geometric conditions. Therefore, areas that were typically characterised with reduced heat transfer such as the bottom regions and edges were subjected to high temperature for a longer period of time. This resulted in more Ni evaporation and thus leading to the formation of Ti_2Ni precipitates during solidification. Moreover, due to the decrease in the content of Ni, the phase transformation temperatures of SLM NiTi were found to have increased by 30 K (Meier *et al.* 2009).

Nonetheless, the research did show some positive results (Meier *et al.* 2009). One unexpected observation was that the SLM process did not result in an increase in the impurity level. Moreover, NiTi spring actuators were fabricated and tested through deformation and reheating and they were found to return to their original shape. This observation demonstrates that the SLM NiTi part is able to possess SME that is comparable to the conventionally fabricated NiTi (Meier *et al.* 2009).

In another research conducted by the same authors, compression tests were performed on SLM NiTi to study their mechanical and functional properties (Meier *et al.* 2012). The obtained results were then compared to the results of conventional NiTi parts which were hot worked and straight annealed. According to the results obtained (Meier *et al.* 2012), the main issue faced for the SLM NiTi was their lower fracture strains and stresses as compared to that of the conventional NiTi parts. Under the compression mode, the stress–strain curves of SLM NiTi samples are similar to the stress–strain curves of conventional NiTi parts during the early deformation stage, and the SLM NiTi fractured at a lower stress level than the stress level at which the first cracking was observed in conventional NiTi. However, since SMAs are usually not exposed to such high loads during the operations, this issue may not be a big concern. Nevertheless, with further research to improve the quality of the SLM NiTi parts through fundamental understanding of the relation between microstructures and SLM processing parameters, such problem can be minimised. Conversely, one interesting result was that SLM NiTi had shown good functional stability. According to Meier *et al.* (2012), they exhibited higher reversible strains and less irreversible strains than the conventional NiTi. Nonetheless, such observations need further confirmation and understanding. Since in both cases the samples were tested under compression mode, the effect of microstructural defects such as micro-voids formed as a result of SLM processing on the mechanical property is insignificant. Whether the porosity plays a role in the result is yet to be revealed. On the other hand, tensile test of the SLM sample and its comparison with conventionally produced NiTi is to be conducted to provide further information on the capability of SLM process.

Overall, the above results demonstrated to some extent that good quality NiTi components can be fabricated by SLM with minimum machining and thermomechanical treatments. As for the future work, more research that are related to the evaporation, precipitations or residual stresses of the SLM NiTi can be conducted for the purpose of more complex applications (Meier *et al.* 2009). Furthermore, porosity of the SLM NiTi parts should be studied as well and tension test should be performed on the produced parts since microcracks that might have formed in the SLM parts are more sensitive to the tensile stress.

In a separate research conducted by Dadbakhsh et al. on the SLM fabrication of NiTi, various NiTi parts were fabricated with different SLM parameters (2014). The objective was to determine how the SLM parameters affect the transformation temperatures and the mechanical performance of the fabricated parts. The SLM processes performed on the NiTi powder were categorised as low laser parameters (LP) and high laser parameters (HP). The LP corresponded to low laser power, low scanning speed, slower heating and cooling rates while HP corresponded to high laser power, high scanning speed, higher heating and cooling rates. Both set of parameters were found to be able to produce parts with density of approximately 99%.

From the differential scanning calorimetry (DSC) results, SLM NiTi samples were found to be more homogenous than NiTi powder. The SLM-LP and SLM-HP products only exhibited a single stage transformation (single peak) while the NiTi powder exhibited multistage transformation (multiple peaks). The multistage transformation can be a result of inhomogeneity of the powder such as local change in chemical composition and crystalline size.

Another interesting observation was that before annealing, both the powder and SLM-HP parts were austenitic while the SLM-LP parts were martensitic at room temperature. However, after annealing, their transformation temperatures shifted to the same range. This result indicates that the SLM process has not significantly altered the composition of the powder. Moreover, the annealing process only increased the transformation temperatures of the NiTi powder and SLM-HP parts. It did not have any significant impact on the transformation temperatures of the SLM-LP parts. These results suggest that through proper selection of the SLM parameters, the transformation characteristics of the NiTi powder can be retained in the SLM NiTi parts. The reason for the difference in the transformation temperatures of the parts produced by LP and HP needs to be further understood.

Recently, we have also conducted research on SLM processing of NiTi SMA and have explored the various parameters to fabricate NiTi parts. One of the NiTi samples produced with a laser power of 20 W, scanning speed of 700 mm/s and a pitch distance of 5 µm is shown in Figure 2. DSC was used to determine the transformation temperatures which are presented in Figure 3. These transformation temperatures are martensitic transformation start (M_s) and finish (M_f) temperatures, and austenitic transformation start (A_s) and finish (A_f) temperatures. The transformation characteristics indicate the presence of the phase transformations in the SLM fabricated NiTi samples and it provides the important condition for obtaining SME.

According to the transformation temperatures, the sample is in martensitic state at room temperature. In order to evaluate the SME of this sample, a tensile load was applied on the sample which has a gauge length of 23.41 mm and was pre-strained to about 3.1%. Upon releasing the load, a residual strain of approximately 2.1% remained. Next, the sample was heated up from room temperature to about 140 °C to allow shape recovery under a stress-free condition. The strain–temperature curve of the sample is presented in Figure 4.

As shown in Figure 4, the SME of the sample was about 0.5% (sample recovered from about 2.2% strain to roughly 1.7% strain) and the reverse transformation temperatures of the sample differs from the temperatures derived in Figure 3. One of the possible reason for the difference in the reverse transformation temperatures can be attributed to the effect of martensite stabilisation (Liu *et al.* 1999, Tong and Liu 2010). Martensite stabilisation is a one-time effect where the reverse transformation temperatures are higher in the first heating than the second heating as the martensite state has not been stabilised by deformation in the first cycle. Since the fabricated sample only undergoes one cycle of heating, the higher reverse transformation temperatures shown in Figure 4 could be due to the effect of martensite stabilisation.

Figure 2. Fabricated 2D NiTi sample (5 mm × 60 mm) with a laser power of 20 W, scanning speed of 700 mm/s and a pitch distance of 5 µm.

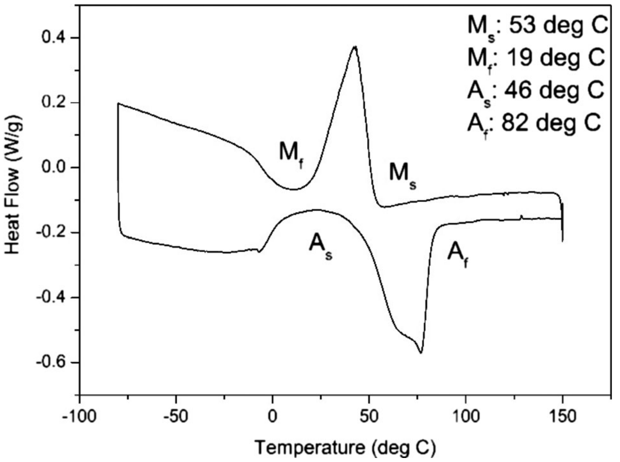

Figure 3. Transformation temperatures of fabricated sample in Figure 2.

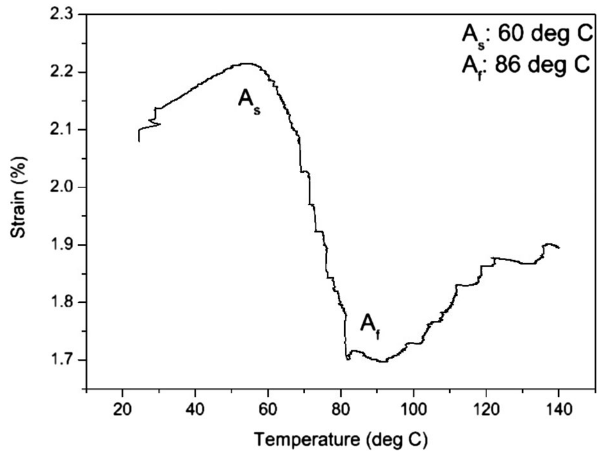

Figure 4. Stress-free recovery of fabricated sample in Figure 2.

Even though the SME measured was only about 0.5%, its presence under tension suggested the possibility of directly fabricating good NiTi parts by using SLM. Further research on the improvement of both the mechanical properties and the SME is on the way through revealing the relation between SLM parameters and resulted microstructures of the fabricated parts. More studies can be done as well to better understand how to optimise the shape memory properties through adjusting the SLM parameters. On the other hand, good controllability of the transformation characteristics through controlling the SLM parameters would be another important research direction. Good understanding on this aspect could allow direct fabrication of NiTi part with different transformation characteristics and thermomechanical properties at different locations of the part conveniently.

2.1.3. *3D printing of SMPs*

SMPs are stimuli-responsive materials that have the designed properties to enable return from a deformed temporary shape to an original permanent shape via application of external stimulus such as temperature, magnetic fields, light and moisture (Lendlein and Kelch 2002, Yu *et al.* 2015). SMPs have some advantages and drawbacks as compared to the SMAs and ceramics (Yu *et al.* 2015). These advantages include high strain recovery, lower density, lower cost, simple procedure for programming of shapes and good controllability over the recovery temperature. Moreover, SMPs can be modified chemically to achieve biocompatibility and biodegradability. As a result, they have gained many research interests in various applications. However, their major drawbacks are their low strength, low modulus and low operating temperatures.

In AM, the permanent shape of SMP components can be set by 3D printing while its temporary shape can be set by deformation at above the T_g temperature followed by cooling. The temporary shape of SMPs is generally maintained until being activated by external stimulus. One example of a 3D printed SMP structure using the PolyJet printer is presented in Figure 5. This SMP structure consists of three connected letters 'NTU' in the as printed form. It was then heated to above its T_g-temperature and straightened at high temperature and cooled to room temperature while maintaining the pulling force. Once the sample has reached room temperature, the pulling force was removed and it took the shape in Figure 5(a). When being heated to above the T_g temperature, the sample returned to the as printed form shown in Figure 5(b), demonstrating a full shape recovery.

2.2. *4D printing of multiple materials*

One important factor to consider when designing a component with multiple materials is the availability of the 3D printing technology. At the current status, PolyJet technology is the most established technology in performing multi-material printing. Thus, most of the developments in 4D printing utilise PolyJet printers in their research to fabricate multi-material components that consist of smart materials and conventional materials.

Moreover, in the developments of 4D printing of multiple materials, the design of the components plays a critical role as the conventional materials do not react to the external stimulus. Hence, the degree of the

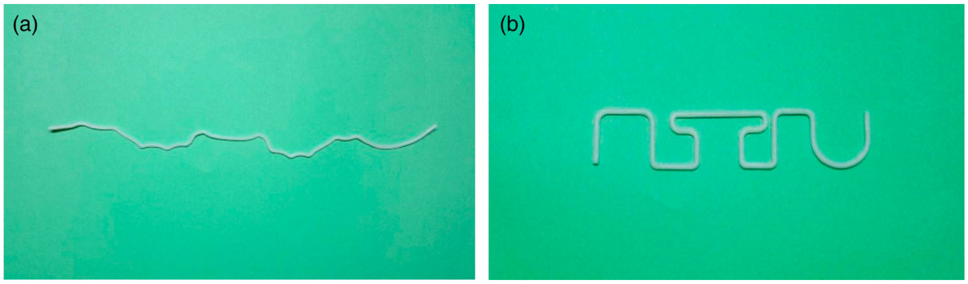

Figure 5. Printed sample of 'NTU' before heating (a) and after heating (b).

change in the printed components upon activation is usually determined by the design of the components. In order to illustrate this point, some examples of the developments in 4D printing of multiple materials are discussed. These examples include printed actuators for soft robotics (Rossiter *et al.* 2009), self-evolving structures (Raviv *et al.* 2014), anti-counterfeiting system (Ivanova *et al.* 2014), *active origami* and controlled sequential folding (Ge *et al.* 2013, 2014, Yu *et al.* 2015) together with some of the results from our ongoing research.

2.2.1. *Actuators for soft robotics*

The development and applications of traditional robotics have involved robots created from hard materials such as metals, ceramics and hard plastics (Rossiter *et al.* 2009, Bauer *et al.* 2014). Although these robots are designed for specific applications, they are not suitable for all applications and environments. For instance, a traditional robot that was built using hard materials could not possibly achieve large structural deformation and mimic a soft-bodied animal such as an octopus (Rossiter *et al.* 2009, Ahn *et al.* 2012). As a result, the gap in this area gives rise to soft robotics. Soft robotics is a popular and emerging field that tries to capture some of the traits of natural organisms by using mainly soft materials, especially soft-smart materials (Rossiter *et al.* 2009, Raviv *et al.* 2014). These soft-smart materials such as electroactive polymers (EAPs) can sense, actuate and vary their stiffness (Rossiter *et al.* 2009, Bauer *et al.* 2014).

In 2009, Rossiter et al. presented a new way to fabricate dielectric elastomer actuators (DEAs) for soft robotics through a 3D printing process. This new fabrication method helps to address the issues faced in manufacturing DEAs by the conventional methods as they are often difficult and labour-intensive (Bar-Cohen *et al.* 2004).

The dielectric elastomer is basically a soft-smart material that belongs to the group of EAP materials and they are controllable by electrical means (O'Halloran *et al.* 2008). Upon supplying electricity to a DEA, the structure of the actuator will deform and it can generate a significant amount of strain that is more than 100% (Rossiter *et al.* 2009, Bar-Cohen 2010). As a result, the electrical energy inputted into the DEA is transformed into mechanical work.

Furthermore, in their research, the researchers have manufactured a complex prototype of an antagonistic actuator. The actuator components were printed and the two fabricated membranes were forced into a pre-strain state during the assembly process with the electrodes attached on both sides of each membrane. When voltage was applied to the upper membrane, the actuator will move upwards and it will move downwards when the voltage was applied to the lower membrane.

Although having proved the workability of the 3D printed DEA, one of the limitations faced in this research is that a functioning fully assembled DEA cannot be printed in one go (Rossiter *et al.* 2009). This is because currently there is still no solution to the fabrication of a pre-strained membrane by a 3D printer. In addition, the future work for this research will be either to fabricate multi-layered membranes, to produce soft structures that do not require pre-straining or to manufacture uni-morph and bi-morph actuators (Rossiter *et al.* 2009).

Overall, Rossiter *et al.* have successfully proved the idea of fabricating the DEA by 3D printing. It provided a new method to produce DEAs in an easier and less labour-intensive manner and this new technology could be useful to the development of soft robotics.

2.2.2. *Self-evolving structures*

In one of the developments in 4D printing, Raviv et al. printed various multi-material components that would transform into their designed shapes when exposed to water (2014). The authors called this concept self-evolving structure. The self-evolving components were basically made up of an extremely hydrophilic polymer material and a rigid plastic material. When this hydrophilic material is exposed to water, it will absorb the water and results in an increase in its volume up to two times.

During the initial stage of this research, three different components that displayed different types of deformations when exposed to water were fabricated. The three types of deformations are illustrated in Figure 6, where the top and middle components exhibit the stretching deformations while the bottom component exhibits the folding deformation.

The top component in Figure 6 exhibits linear stretching. When this component was exposed to water, its length changes with respect to time and by varying the ratio of hydrophilic material to the rigid material, different percentage of linear expansion can be achieved.

As for the middle component shown in Figure 6, it demonstrates ring stretching. The component was formed by many ring-like shapes and each ring was printed with two different layers of materials. When this component was exposed to water, the inner layer expands and causes deformation of the ring. The overall linear expansion of this component can be controlled by varying the radius or diameter of the rings.

The bottom component in Figure 6 exhibits folding phenomenon. This is done by printing a layer of hydrophilic material over a layer of rigid material. To achieve the desired angle of folding, rigid plates of different

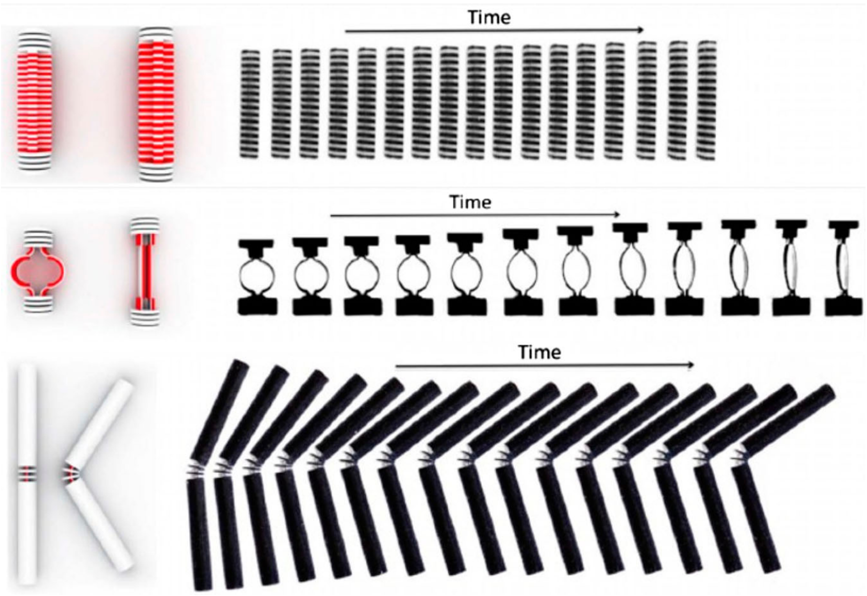

Figure 6. Self-evolving components that exhibited (top) linear stretching, (middle) ring stretching and (bottom) folding over time from left to right (see (Raviv *et al.* 2014) for details). Adapted by permission from Macmillan Publishers Ltd: [Scientific Reports] (4: 7422), copyright (2014).

spacing and diameters were inserted between the bars so as to stop the folding process when the plates interfered physically with each other.

A variety of more complex multi-material components were fabricated based on the results obtained from the stretching and folding deformations. These complex components have demonstrated 1D folding, 2D folding and 2D folding with stretching. The multi-material component that displayed 2D folding with stretching is shown in Figure 7. This component deforms into convex and concave surfaces via the folding deformation and ring stretching deformation.

Nevertheless, according to the results obtained, mechanical degradation was encountered when the components undergo the transformation cycle of folding and unfolding (wetting/drying) repeatedly (Raviv *et al.* 2014). Moreover, degradation of the hydrophilic material can be observed as well when the material was repeatedly wetted and dried. Furthermore, the transformation between the different shapes is not

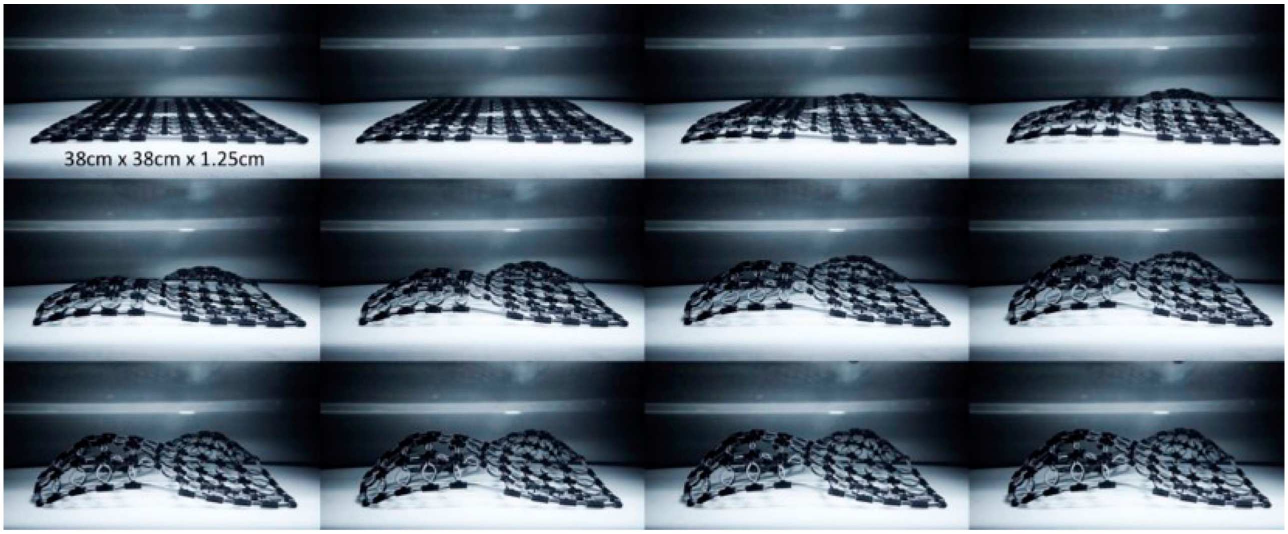

Figure 7. Complex 2D multi-material component exhibiting stretching and folding from left to right, and top to bottom (see (Raviv *et al.* 2014) for details). Adapted by permission from Macmillan Publishers Ltd: [Scientific Reports] (4: 7422), copyright (2014).

permanent. Thus, depending on the applications, this reversible transformation can either be an advantage or disadvantage. Another problem encountered is that the top component in Figure 6 is fragile and the expansion is limited to only 30% (Raviv *et al.* 2014). Nonetheless, this problem might be solvable by exploring new materials in the future research (Raviv *et al.* 2014).

Overall, there are a lot of possible future improvements to be done (Raviv *et al.* 2014). In the research done by Raviv *et al.* (2014), only hydrophilic materials that react to water have been explored. Other activating mechanisms such as temperature change and exposure to UV light can also be explored. In addition, the physical properties of the hydrophilic material and their behaviour can be predicted by simulating on a molecular level instead of using the spring-mass model in this research.

Lastly, this novel design of self-evolving structure could be applicable in many fields. For instance, a structure could be readily assembled under the deep water which would be difficult for humans to do otherwise.

2.2.3. *Anti-counterfeiting system*

As AM advances over the years, it gains more and more popularity among the users in the fabrication of end-use products (Ivanova *et al.* 2014). However, along with the advancement in AM, the potential in manufacturing counterfeiting products is unavoidable. Counterfeiting versions of critical products with lower quality could have adverse effect during the application phases. Thus, it might be worthwhile to physically mark fabricated products with special security features to distinguish them with counterfeiting products.

The current security systems adopted such as RFID tags utilise the secret binary keys or numbers that is only known between the legitimate parties (The Government of the Hong Kong Special Administrative Region 2008). However, this does not stop the binary keys from being copied, extracted or transferred from the security systems. This existing problem in the current security systems will only lead to the compromise of the authenticity of the genuine products.

Hence, a new anti-counterfeiting system for 3D printed products is needed and has been proposed by Ivanova et al. (2014). In their research, an optical Physical Unclonable Functions (PUFs) with quantum dots (QDs) was created. PUFs are functions that describe the relationship between the input and output via a physical system. A typical optical PUF is composed of small reflective particles that are embedded in a transparent medium. The main characteristics of PUFs are that the outputs of the system depend on the randomness of the particles arrangement and it cannot be cloned even by the original manufacturer.

In determining the authenticity of the printed part, the signature of the optical PUF is captured by a camera and its speckle arrangement is analysed by a computer algorithm. The speckle pattern will then act as a security key and that will determine whether the pattern will be accepted or rejected (Ivanova *et al.* 2014).

In choosing the particles for the optical PUFs, the main considerations are the particle size and optical properties. One of the most suitable candidates for the particles will be the QDs as it is a type of photonic nanoparticles that absorbs UV light and emits visible lights. Hence, the difference between the input (UV light) and output (visible light) of QDs makes it an attractive choice for the construction of PUFs.

Before the printing process starts, QDs were mixed into the photopolymer resin. The ability of PolyJet printer to deposit different materials in a single part allows the PUFs to be selectively placed. Moreover, the embedding of PUFs within a printed product would ensure that it is not possible to tamper the security feature without destroying or damaging the exterior geometry of the product (Ivanova *et al.* 2014).

Moreover, in their prior research, the authors have evaluated the printability by analysing the surface tension, the viscosity of the QD suspensions and the size of the jetting nozzle (Elliott 2014). However, due to the risk of agglomeration and subsiding of QDs in the print head, manual deposition approach was adopted instead to embed QD suspensions of different concentrations and void geometry into the printed part in this research. After embedding the QD suspensions, they were cured by using a handheld UV lamp and the printing process was continued to cover up the suspensions within the printed part.

According to the results obtained from Ivanova *et al.* (2014), it was shown that PUFs with visible QDs can be embedded into PolyJet parts. Moreover, by adjusting the void geometry and concentration of the QDs, the PUFs produced could be made non-visible to the naked eyes but yet still visible under the fluorescence microscope.

Although optical PUFs were not printed in one go at this moment, this problem might be solvable in the near future. The reasons for this prediction are because of the potential in reducing the particle size of QDs and the printing machine can be improvised to deposit the QD suspensions. For instance, the filters in the printing fluid lines may prevent agglomerates from being deposited (Ivanova *et al.* 2014). Thus, one of the future works will be to evaluate the compatibility of the PolyJet system printhead with the QD suspensions.

Performing an experiment can be an efficient method to determine whether the QD suspensions are printable, but there is risk of damaging the 3D printer. In addition, another possible future approach will be to understand how the QDs affect the parameters of the photopolymerisation process (Ivanova *et al.* 2014). Overall, if QDs are readily printable then an anti-counterfeiting system for 3D printed products can be fabricated concurrently by 3D printing.

2.2.4. Active origami *and controlled sequential folding*

Although origami is a type of traditional art where a piece of flat paper is being folded into a 3D object, the notion of origami has been widely explored nowadays to provide innovative solutions to the problems of compacting large objects into a small volume of space. For instance, the applications of origami can be found on the airbags for automobiles, cartons, shopping bags and photovoltaic solar cells with shape changing ability. However, the packing process is often challenging and may lead to an increase in the infrastructure cost since new equipment may be required should there be any changes in the folding design. Therefore, the idea of *active origami* is intriguing as it can help to reduce the investment needed for the folding equipment.

Active origami is defined as a design to create an origami object that has the ability to self-fold or self-unfold (Ge *et al.* 2014). In order to do that, smart materials are required. For example, there are researches being performed on the design of origami by using SMPs, light activated polymers and SMAs recently.

Therefore, one of the developments in 4D printing of *active origami* is to make use of multi-material printing technology to print and investigate the performance of printed active composites (PACs) (Ge *et al.* 2013). Examples of PACs are soft composites made up of glassy SMP fibres that reinforce the elastomeric matrix. By adjusting the volume fraction and orientation of the SMP fibres and the stacking order of the laminas, different laminates can be fabricated. These laminates will then undergo thermomechanical programming so as to adopt complex 3D configurations such as bending, coiling, twisting and folding as shown in Figure 8. The original flat plate shape of the laminates can be recovered by heating the deformed laminates. In addition, a self-folding box was designed and printed with PACs as the hinges that connect to the inactive plates made from the stiff plastics (Ge *et al.* 2013).

Following the first part of the research, the second part of the research was conducted by applying the concept of 4D printing to the design and fabrication of *active origami* (Ge *et al.* 2014). The research focuses mainly on the understanding of the thermomechanics of the structures of the PACs hinges (Ge *et al.* 2014). Experiments were performed to determine the relationship between the hinge folding angle and the microstructural parameters. Moreover, theory that describes the observed phenomena was developed as well. The design and fabrication of the *active origami* consists of printing flat polymer sheets that consist of the PACs hinges (Ge *et al.* 2014). These PACs hinges were fabricated in the same manner as the first part of the research conducted. However, the PACs hinges fabricated here have only two layers of PACs laminates. One layer contains only elastomeric matrix material while the other layer contains a pre-determined fibre size and spacing.

Using a theoretical model developed to provide direction in choosing the design parameters, several *active origami* components were designed and fabricated to demonstrate the prescribed folding angles. These components self-folded from flat polymer sheets and they include a box consisting of six sides and a five-sided pyramid as presented in Figure 9, and two origami airplanes. Additionally, directly printing a 3D object was proved to be feasible as well. However, doing so would require more materials due to the need for support structures and longer fabrication time as the removal of these supports would increase the post-processing time.

In summary, the concept of PACs was demonstrated and they were shown to be able to integrate with other printed parts to form a 3D component that can

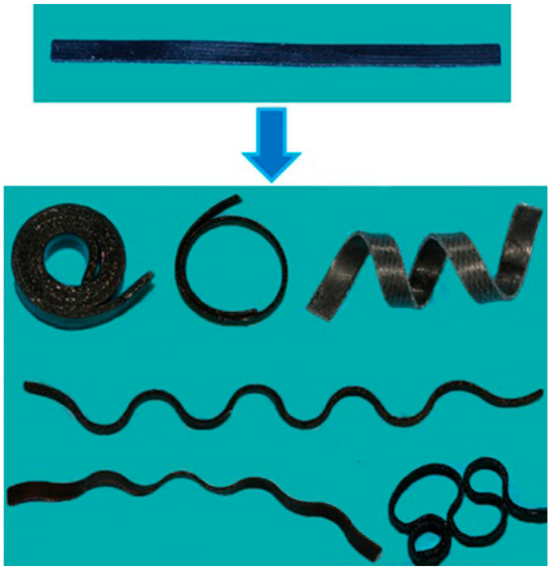

Figure 8. Laminates adopting complex 3D configurations including bending, coiling, twisting and folding (see (Ge *et al.* 2013) for details). Reproduced with permission from *Appl. Phys. Lett.* 103, 131901 (2013). Copyright 2013, AIP Publishing LLC.

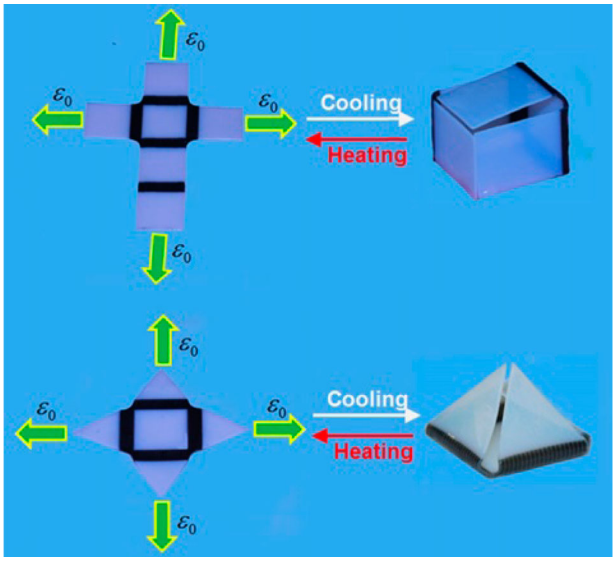

Figure 9. Before self-folding and after self-folding of active origami box and pyramid (see (Ge *et al.* 2014) for details).

transform over time. Moreover, the concept of 4D printing was applied and *active origami* was created. As for the potential and challenges of this research, the most extreme case will be to fabricate a component with continuous and spatially varying material properties (Ge *et al.* 2013). Furthermore, this idea of 4D printing can be further developed by making use of other smart materials and computational design tools such as shape and topology optimisation to come out with the layout of the materials within the composites (Ge *et al.* 2013). In this case, it will be possible to achieve larger changes in the configuration of the components.

Another research area to concentrate on will be to understand and achieve controlled sequential folding or shape recovery of the *active origami*. As the design of the origami gets more complex, folding of the *active origami* parts at the same instant might just cause the different folding parts to interfere with each other before the folding process is complete. Moreover, very few researches have been done on the study of controlled sequential shape recovery of SMPs or *active origami*.

Recently, Yu et al. have performed research on the fabrication of SMPs with spontaneous and controlled sequential shape recovery properties (2015). In their research, the material used is an epoxy-based UV curable SMP with SME that is activated by temperature. Since the SMP is sensitive to thermal changes, controlled sequential shape recovery can be achieved by implementing a customised distribution of the SMP thermomechanical properties to the specified sections. This would allow the different sections to activate their shape recovery at different T_g temperatures and thus achieve sequential folding of the printed components.

In the research done by Yu *et al.* (2015), experiments on helical components and interlocking components were demonstrated. These components have rectangular plates and their hinges were made up of SMPs with either different T_g temperatures or same T_g temperatures. The spontaneous and sequential folding process of a helical component with designed order of T_g temperatures is reproduced in Figure 10. The complete shape recovery of the component can be observed at different time through a series of photographs. Additionally, another helical component with the same T_g temperatures at the different hinges was also fabricated. However, this printed component with the same material properties exhibits a slower shape recovery speed and an incomplete shape recovery. Clearly, different materials having different T_g temperatures are required at different hinge sections in order to have a controlled sequential shape recovery or folding process of the printed component.

This result was again illustrated by the interlocking components. Controlled sequential shape recovery was demonstrated by an interlocking component with a designed order of T_g temperatures. However, when another interlocking component with a reversed order

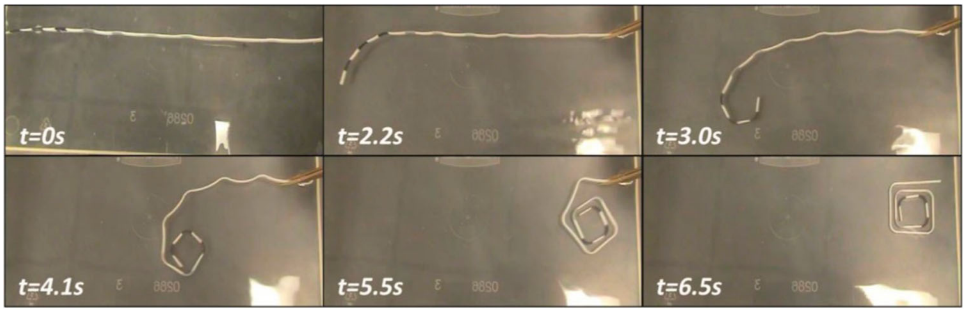

Figure 10. Spontaneous and sequential folding process of helical component with different material properties at various hinge sections (see (Yu *et al.* 2015) for details). Adapted from Procedia IUTAM, Vol. 12, pp. 193 – 203 under the CC BY-NC-ND license.

of T_g temperatures and one with the same T_g temperatures at the different hinge sections were tested, none of the two components successfully exhibit complete shape recovery. This observation further confirmed the above conclusion that the order and distribution of material properties at different hinge sections is important in achieving controlled and sequential shape recovery or folding process.

Overall, Yu et al. have demonstrated controllability over the shape recovery sequence through the fabrication of helical components and interlocking components (2015). The control over the sequence of the shape recovery is achieved by selecting and assigning different material properties with different T_g temperatures to the various sections. In terms of the potential of this research, the results obtained can have great contributions to the different applications such as permutations of complex deformation and the development of SMP solids that have the ability to self-adjust and self-reinforce to suit the changing environmental conditions (Yu *et al.* 2015). Furthermore, through the use of 3D printing, SMP structures with controlled sequential folding process could enjoy a larger design freedom and a higher resolution in the distribution of material properties (Yu *et al.* 2015).

Since 2014, we have been investigating the 4D printing with SMP materials and the design methodologies. Our research activities include both single materials and multiple materials for 4D printing and applications. Different from the researches carried out by Ge *et al.* (2013, 2014) who have adopted SMP fibres within an elastomeric matrix as the material for the hinges to achieve the *active origami* structures, in our research, we have adopted SMP as the sole material for the hinges of the *active origami* structures. The advantage of this approach is that SMPs comprising of multi-material with different percentage of each component enable better freedom in design and shape response. Instead of only using fibres to control the direction of response, our developed structures can response to any direction when the structure is being programmed. Thus, this allows for a better freedom in shape changing geometry, which results in a relationship between the material and dimensional difference reacting to thermal stimulus. Moreover, we have developed reconfigurable origami structures by exploiting the combination of multi-material fabrication and geometric design. Figures 11 and 12 illustrate the multi-stage folding structure and conceptual reconfigurable glider, respectively.

In the case of the sample shown in Figure 11, we have achieved controlled sequential folding process of a printed part with different materials printed at different hinge structures. Only the hinges were composed of SMP and the T_g temperatures for the various hinges were different. Hence, the hinges fold at different temperatures during continuous heating and have different stages of recovery, resulting in multi-stage folding as illustrated in Figure 11.

In another example, the application of multi-folding in a 3D object represented by a reconfigurable glider is presented in Figure 12. The multi-material part is printed with

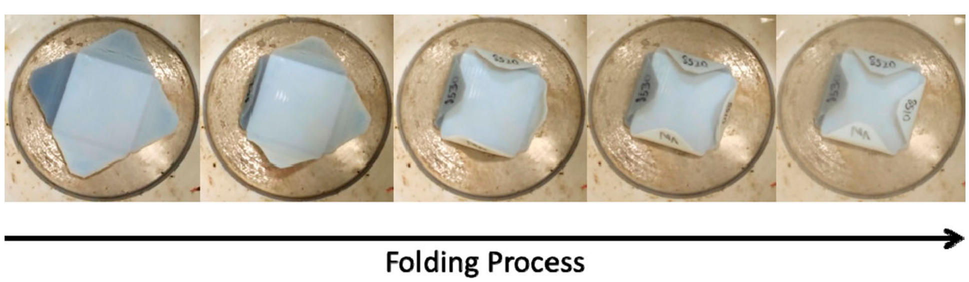

Figure 11. Multi-stage folding of 4D printed part with different SMP materials at different hinges.

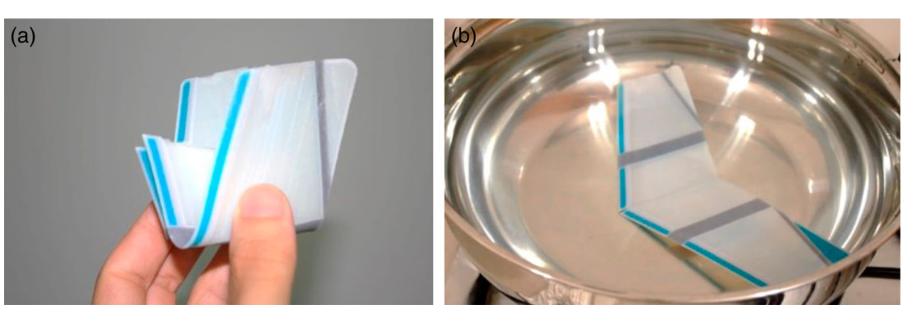

Figure 12. Multi-folding glider (a) before heating and (b) after heating.

the hinges consisting of SMPs. The SMPs are located specifically at the hinges such that the planar structure will not collide with the other areas during activation by thermal stimulus. As shown in Figure 12, the glider unfolds from Figure 12(a) to Figure 12(b) when it is heated.

2.3. *Summary of the developments in 4D printing*

After discussing the various developments of 4D printing, the following table can be used to summarise these developments for easier comparison (Table 1).

3. 4D Bio-printing

As the success rate of organ transplantation increases, the demand for transplantable organs increases as well. However, the supply of these organs is much lower than the demand for them and this causes a worldwide shortage of organs (Ozbolat and Yu 2013, Seliktar *et al.* 2013, Chua and Yeong 2015). Moreover, the current tissue engineering technology has a few major limitations such as non-automated manipulation, small manufacturing scale, inability to produce complex 3D organs and non-ordered and weak tissue microstructure (Ozbolat and Yu 2013, Chua and Yeong 2015). Thus, this gives rise to a new branch of tissue engineering called 3D bioprinting (An *et al.* 2015).

Bioprinting can be defined as 'the use of material transfer processes for patterning and assembling biologically relevant materials – molecules, cells, tissues, and biodegradable biomaterials – with a prescribed organisation to accomplish one or more biological functions'(Chua and Yeong 2015). The main advantages of bioprinting include the ability to mass produce tissue engineered products, high accuracy in positioning the different types of cells and capability to fabricate high cell density tissue (An *et al.* 2015, Chua and Yeong 2015). Bioprinting is a new emerging technology and the greatest benefit of this technology lies on its capability to fabricate living biological 3D structures such as tissues, organs, nutrients and cells (Seliktar *et al.* 2013, Murphy and Atala 2014, Chua and Yeong 2015).

Nevertheless, as the techniques of 3D bioprinting advance over the years, a new technique has been introduced recently, which is called laser-assisted bioprinting or 4D bioprinting (Poietis 2014, 2015). Laser-assisted bioprinting provides one of the highest resolution among all the other bioprinting techniques as the cells can be printed one by one to follow the biophysical mechanism. The high resolution of this technique allows more details and information to be integrated into the tissues to create tissues with high complexity. Laser-assisted bioprinting works by focusing a laser pulse on to a cartridge that leads to the removal of the material from the cartridge to be deposited on to a substrate in a layer-by-layer fashion. The fourth dimension of this laser-assisted bioprinting technique is the time dimension that is related to the self-organisation of the cellular processes such as cell communication and cell interaction (Poietis 2014, 2015).

On the other hand, another category of 4D bioprinting will be the 3D printing of smart hydrogels (Wang *et al.* 2015). Smart hydrogels are matrixes with high water content that possess the ability to respond to external stimulus such as electric, ionic strength, light, magnetic field, pH and temperature. They have unique features such as shape memory, self-healing and controllable sol–gel transition. By utilising the potential of 3D printing to fabricate structures made of smart hydrogels, the fabricated 4D bioprinted structures or bio-origami hydrogel scaffolds can have the capability to self-fold or self-unfold in response to external stimulus. This will help to contribute greatly to the area of bioprinting of functional 3D tissues.

4. Challenges and future outlook

4D printing is a relatively new research area and has a lot of challenges ahead. These challenges can be classified into three areas; technological limitation, material limitation and design limitation. These limitations can come in combination of two or more types.

For instance, in the area of technological limitation, one of the challenges faced is the inadequate availability of 3D printing technologies. Currently, the developments in 4D printing mainly made use of PolyJet technology to fabricate multi-material components and SLM technology to fabricate metallic components. PolyJet printers utilise UV light to cure liquid photopolymers to create the 3D structures while the SLM equipment utilise laser to melt the powder particles. Thus in this case, the starting forms of the material have to fulfil either of the criteria. The polymeric smart materials or smart composites have to be in liquid form and they must be curable by UV light for it to be printable by PolyJet. The metallic smart materials have to be produced into powder form for it to be printable by SLM. As a result, this would greatly limit the types of smart materials to be explored in the development of 4D printing.

Another challenge faced under the category of material limitation is the properties of the smart materials or smart composites. One example is the NiTi SMA. As NiTi SMAs are extremely compositional sensitive, it requires great effort to fabricate NiTi components by both conventional and 3D printing methods without encountering problems such as microstructural defects,

Table 1. Summary of the developments in 4D printing.

Starting form of material	Type of materials/ structures	Smart materials/ composites used	Printing process	Resolution	Mechanisms	Positive results reported	Negative results reported/ * Limitations of research	Future Research
Single material/ form	Enhanced smart nanocomposites Kim et al. (2014)	Composite of piezoelectric nanoparticles and photoliable polymer	Digital projection printing (DPP)	Samples' resolution approximately 5 µm Printer's resolution 1 µm	Produces electrical charge when stress is applied and vice versa	Higher piezoelectric coefficient for chemically modified BTO nanoparticles embedded into PEDGA matrix	* Resolution limits of samples fabricated are about 5 µm	– Minimising DPP fabrication time – Reducing resolution limit of samples – Determining the upper limits of the piezoelectric coefficient and investigate their relationship with other parameters – Reducing the size of the nanoparticle to achieve a better optical transparency
	Shape memory alloys (SMAs) Meier et al. (2009, 2012), Dadbakhsh et al. (2014), our ongoing research	Nickel titanium (NiTi)	Selective laser melting (SLM)	–	Shape change is activated by temperature	– SLM process did not lead to an increase in impurity levels – SLM NiTi demonstrated higher reversible strains and less irreversible strains under compression as compared to conventional NiTi – SLM NiTi possesses shape memory effect (SME) and has a comparable functional stability to the conventional NiTi – SLM process has no significant impact on the composition of the fabricated parts as compared to that of the powder – SME of 0.5% was obtained under tension mode	– SLM process tends to lower the content of the Ni due to evaporation, leading to the formation of Ti_2Ni precipitates and an increase in the phase transformation temperatures of SLM NiTi by 30 K – SLM NiTi has lower fracture strains and stresses as compared to the fracture strains and stresses of the conventional NiTi parts – SLM process has substantial impact on the transformation temperatures of samples * The obtained SME under tension mode is rather small	– Further understanding on the relation among processing parameters, evaporation, composition, precipitation, porosity, microstructures, residual stresses, transformation characteristics, mechanical and shape memory properties of the SLM printed NiTi part – Design and fabricate complex shaped structures and investigate the shape recovery distributions both theoretically and experimentally. – Explore other types of SMAs – Study on the porosity of SLM NiTi parts – Improving the mechanical properties and SME – Achieving a good control of the transformation characteristics through controlling the SLM parameters
	3D printing of shape memory polymers (SMPs) Our ongoing research	SMPs	PolyJet	Printer's resolution 25 µm in X and Y direction and 16 µm in Z direction	Shape change is activated by temperature	– Glass transition (T_g) temperature can be manipulated by on-the-fly fabrication of two materials at different physical mixing ratios – Recovery rate of printed components can be pre-designed and sequentially controlled by graded heating in water.	* Currently only limited number/ type of materials have been explored Mechanical degradation has been found during repeated thermomechanical cycling	– To understand the science behind the physical mixing and the resultant material properties – Improve the mechanical and functional stability of the materials

(*Continued*)

Table 1. Continued.

Starting form of material	Type of materials/ structures	Smart materials/ composites used	Printing process	Resolution	Mechanisms	Positive results reported	Negative results reported/ * Limitations of research	Future Research
Multiple materials	Actuators for soft robotics Rossiter et al. (2009)	Composite of dielectric elastomers and rigid material	PolyJet	Printer's resolution 42 µm in the X and Y direction and 29 and 16 µm in Z direction	Produces large strains upon activation by electricity	– Proved the workability of the 3D printed DEA	* No solution to printing a fully functional assembled DEA in one go as currently there is no 3D printing technology that is capable of fabricating a pre-strained membrane	– Manufacturing of multi-layered membranes, producing soft structures that do not require pre-straining, or fabricating uni-morph and bi-morph actuators
	Self-evolving structures Raviv et al. (2014)	Composite of hydrophilic polymer and rigid material	PolyJet	Printer's resolution approximately 85 µm in the X and Y direction and 30 µm in Z direction	Volume of hydrophilic polymer increases when exposed to water	– Printed components exhibiting shape changes according to the designed shapes – Degree of shape changes can be adjusted to the desired designs	– Mechanical degradation has been found to occur when the complex components undergo the transformation cycle of folding and unfolding (wetting/ drying) repeatedly – Degradation of the expanding material can be observed when the material was removed from the water and allowed to dry repeatedly – Component that displays linear stretching is fragile and the expansion is limited to 30% only	– Exploring new materials for fabrication – Exploring other activating mechanisms – Assessing the physical properties of the hydrophilic material – Predicting the behaviour of hydrophilic material by simulating on a molecular level
	Anti-counterfeiting system Ivanova et al. (2014)	Composite of QD suspension (mixture of QDs and photopolymer resin) and rigid material	PolyJet	No mention	Quantum dots absorb UV light and emit visible lights	– PUFs with visible QDs can be embedded into the PolyJet parts – PUFs could be made visible under the fluorescence microscope but non-visible to the naked eyes	* Manual deposition was adopted to embed QD suspensions into the printed part due to the risk of agglomeration and subsiding of QDs in the print head	– Evaluating the compatibility of the PolyJet system printhead with the QD suspensions – Understanding how the QDs affect the parameters of the photopolymerisation process
	Active origami and controlled sequential folding Ge et al. (2013, 2014), Yu et al. (2015), our ongoing research	Composite of SMP fibres and elastomeric matrix Composite of SMP and rigid material	PolyJet	Samples' resolution approximately 32–64 µm	Shape change activated by temperature	– Printed components that undergo thermomechanical programming recover to their original shapes via heating – Designed *active origami* components demonstrate the prescribed folding angles – SMP with different properties at different hinge sections in a prescribed order and distribution can lead to a controlled sequential shape recovery or folding process of the printed component – Developed reconfigurable origami structures with controlled multi-stage folding	* Directly printing a 3D object would require more materials, longer fabrication time, support structures and longer post-processing time due to the removal of the support structures	– Researching on the fabrication of a component with continuous and spatially varying material properties – Using other smart materials and computational design tools to achieve larger changes in the configuration of the components

oxidation and changes in the phase transformation behaviour. Besides, fabricating NiTi powders from NiTi ingot is expensive and normally results in significant waste of the materials. Hence, more research is required to overcome these constraints as these would hamper the developments of 4D printing.

Additionally, during the SLM fabrication of NiTi SMA, the metallic alloy was subjected to complex thermal history such as rapid solidification, directional cooling, repeated melting and phase transformations (Frazier 2014). These factors would introduce complications to the evolution of microstructures and properties that might not be found when the NiTi alloy was manufactured by conventional methods. Furthermore, the complications may even lead to unexpected failure of the components. Therefore, the lack of knowledge in the interaction between the smart materials and 3D printing technologies will pose a challenge to the progress of 4D printing.

In the area of design limitation, one of the challenges faced is the design of smart structures. Smart structures are able to adapt and adjust dynamically to their environment (Fisco and Adeli 2011). They can sense the changes in their environment and respond accordingly in real time. One example of smart structure is the antagonistic actuator for soft robotics. In order for the actuator to work, the membranes have to be in a pre-strain state. However, currently there is no report on design to create a pre-strain membrane directly. Moreover, this problem can also be classified under the technological limitation. At the current status, there is no 3D printing technology that is capable of directly fabricating a pre-strain membrane. Therefore, in this example, the development of 4D printing are hampered by the lack of feasible design of smart structures and the available technology to fabricate the final component.

Nevertheless, the advancement from 3D printing to 4D printing has brought about great application potentials. One of the future applications in 4D printing lies in overcoming the limitation of requiring manpower to work in an extreme environment.

One such example is the fabrication of a 3D printed self-assembled satellite components with its hinges made of smart materials such as NiTi. When the self-assembled satellite component is being manufactured on Earth, it could be designed to assume a compact structure before it is being launched. Once the satellite has been brought up to the outer space, the hinges would then open up and the satellite component will adopt a deployed structure either by solar heating or joule heating.

Another possible application of 4D printing is the development of personal responsive products (Tibbits *et al.* 2013). Such products are able to react to the demands of the users or react to the physical conditions of the users such as body temperature, perspiration and biometric information. Furthermore, such products can be made more durable as well as they can be designed to adapt to environmental changes such as humidity level or moisture content, temperature, altitude and pressure (Tibbits *et al.* 2013).

Besides, 4D printing can help to simplify the design of the 3D printed products. One example will be the *active origami* structures. The printed *active origami* products could assume a planar shape for the ease of transportation in limited space before they are activated at the designated time and location. Hence, this might help to decrease the logistic cost as the printed products can be stored as compactly as possible before activated to full volume and functionality. In addition, 4D printing can also provide an alternative solution to the fabrication of smart materials or structures since they are difficult to produce by conventional technologies.

One interesting research direction in 4D printing is the 'Programmable Material', which aims to fully programme a wide range of materials (Self-Assembly Laboratory, Guberan, C., Demaine, E., Carbitex LLC, and Autodesk Inc. 2015). For instance, when active materials (smart materials) are printed on the surface of a carbon fibre, the carbon fibre gained the ability to change its shape under the influence of heat. Such methodology can be applied to various types of conventional materials such as carbon fibre, wood grain and textiles (Self-Assembly Laboratory, Guberan, C., Demaine, E., Carbitex LLC, and Autodesk Inc. 2015), which will allow the shapes of conventional materials that are coupled with smart materials to alter under the application of various types of stimulus not limiting to heat.

Moreover, as 4D printing is a relatively new research area, a lot of smart materials have not been explored yet. However, one thing we can expect in the near future is that the range and variety of printable smart materials will definitely increase, together with the improvements in the properties of printed components such as strength, durability and quality of surface finish. This continual advancement of 4D printing may even bring about a change in the trend of 4D printing as the current research activities focus mainly on shape changes of the printed components. With a larger variety of printable smart materials, the future printed components may not only just exhibit shape change. With the added functionalities into the printed components, they may not need to be just designed for a specific application (Donnell *et al.* 2014, Pei 2014). Instead, they can be designed in such a way that they are able to reconfigure continually to suit to the changing environment, satisfying more than one application along the way.

5. Conclusion

In this paper, some of the developments in 3D printing of smart materials, also known as 4D printing, were reviewed together with some of the results from our ongoing research. These developments were classified according to the starting form of the printing material.

In 4D printing of single material such as a single smart material or smart composite, 3D printed enhanced smart nanocomposites, SMAs and SMPs were reviewed and discussed. For the 4D printing of multi-material, we have reviewed and discussed the developments in 3D printed actuators for soft robotics, self-evolving structures, anti-counterfeiting system, *active origami* and controlled sequential folding.

The difference between 4D printing of single material and multiple materials lies on their limiting factor of changes. In 4D printing of single material, the limiting factor is the smartness of the smart materials. It is this factor that determines how readily the printed single material components react upon activation. For the 4D printing of multiple materials, the extent of the changes in the multi-material components, especially changes in the overall shape, is usually determined by the design of the basic 4DP components (stretching, compression, bending, twisting, etc.) and the complexity of the integral design of these basic components.

3D printing of a single smart material is the basic form of 4D printing, where 3D printability of the material and the relationships among process, microstructure and material 'smartness' need to be researched. 3D printing of multiple smart materials or a combination of smart materials and conventional materials requires both design knowledge, material knowledge and process knowledge, which currently represents the state of the art of 4D printing. The most popular printing method is the PolyJet. However, 4D printing method will continue to evolve with no predictable form. The only predication is that 4D printing will not be limited to shape change.

Another trendy research in AM is 4D bio-printing, though lack of consensus on the exact definition, it has the potential to physically replicate the development path of biology and bring organ printing one step closer to reality.

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