Reversible 4D-printing of shape memory polymers using heat and ethanol swelling

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**REVERSIBLE 4D-PRINTING OF SHAPE
MEMORY POLYMERS USING HEAT AND
ETHANOL SWELLING**

LEE YILIN, AMELIA

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2020

**REVERSIBLE 4D-PRINTING OF SHAPE MEMORY
POLYMERS USING HEAT AND ETHANOL
SWELLING**

LEE YILIN, AMELIA

School of Mechanical and Aerospace Engineering

A thesis submitted to Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

29th June 2020

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Date

A handwritten signature in black ink, appearing to read 'Amelia', written over a horizontal dotted line.

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Lee Yilin, Amelia

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

23rd June 2020

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Date

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Asst Prof Zhang Yi

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 2 is published as Lee, A. Y., An, J., & Chua, C. K. (2018). Review on 4D printing of polymer and its Reversibility. *Proceedings of the 3rd International Conference on Progress in Additive Manufacturing (Pro-AM 2018)*, 529-534. doi:10.25341/D4F30V and Lee, A. Y., An, J., & Chua, C. K. (2017). Two-Way 4D Printing: A Review on the Reversibility of 3D-Printed Shape Memory Materials. *Engineering*, 3(5), 663-674.

The contributions of the co-authors are as follows:

- Prof Chua provided the initial study direction and edited the manuscripts.
- Dr An gave some insights and revised and edited the manuscripts.
- I researched the different studies and organised the manuscript flow. I also prepared the manuscript drafts.

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The contributions of the co-authors are as follows:

- Prof Chua suggested the initial direction of the study and revised the manuscript.
- Dr An helped with the flow of the study.
- I wrote the drafts of the manuscript and revised it with Dr An.
- Asst Prof Zhang provided insight to improve the manuscript.
- I performed all the 3D printings and various testing.

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- Asst Prof Zhang and Dr An assisted in the flow of the study and revised the manuscript.
- Aiwu helped to create the simulation model and ran the simulations at the early stages.
- I wrote the drafts of the manuscript and revised it with Dr An.
- Asst Prof Zhang and Prof Chua provided insight to improve and proofread the manuscript.
- I performed all the 3D printings, simulations in the later stage, and various testing.

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Abstract

The advancements in smart materials have boosted additive manufacturing into a new form of printing known as 4D printing. 4D printing provides the means to create a dynamic structure 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. With increasing improvements in design and using multiple stimuli, reversible 4D printing has been proven to be feasible. This technology would eliminate the need for human interference, as the programming is driven by external stimuli, which allows 4D-printed parts to be actuated in multiple cycles.

To combat the lack of reversibility in 4D-printing, this study introduces a new swelling, and the heat-driven reversible 4D-printing process developed to achieve contactless programming and recovery. The forward shape setting programming is realised by asymmetric swelling using ethanol and heating. The shape recovery is accomplished by drying and heating. The process was validated using a 4D-printed bilayer composite with a transition material (VeroWhitePlus) and an elastomer (TangoBlackPlus) that was printed with the PolyJet Connex500 printer. This et-swell (swelling by ethanol) and heat-driven process minimise the required materials to maintain the simplicity of the 4D-printed part.

An analytical model has been developed to determine the shape after programming using different parameters to attain control over the shape morphing. The analytical model could be used to predict the curvatures with the given conditions. The values predicted by the analytical model was compared to the experimental results and yield an average error of 10.1%. The error of the model reduced to $\sim 5\%$ under conditions of low temperature, low transition material thickness and an elastomer thickness of 2 – 3 mm. To overcome these limits and to attain a better accuracy in the prediction of curvatures, a finite element analysis was conducted. It produced a lower error of $\sim 4\%$ in shape morphing accuracy and provided stress study to gain insight into the swell and heat-driven programming process.

The study progressed to combine the stimuli to empower rapid response to the 4D-printing process. The entire shape morphing cycle could be completed within as short as 3 minutes. Twisting shape morphing motions were investigated to contribute more potential 3D-to-3D shape morphing during programming that are rarely achieved. The rapid response and twisting were incorporated into different designs such as flowers, butterfly and gripper to demonstrate potential applications for reversible 4D-printing of polymers in biomimetic and soft robotics.

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List of Symbols

A_a	actual area
A_e	area of elastomer
A_T	area of transition material
A_f	austenite-finish-temperature
A_s	austenite-start-temperature
c	concentration
c_∞	equilibrium concentration
c_t	concentration at any point as a function of time
$C_{10}, C_{01}, C_{20}, C_{02}, C_{11}$	material constants
c_e	neutral axis of elastomer
c_T	neutral axis of transition material
D	diffusion coefficient
D_0	maximal diffusion coefficient
E	elastic modulus
E_e	elastic modulus of the elastomer
E_T	elastic modulus of the transition material
E_a	activation energy for diffusion
F	deformation gradient
h	thickness
h_T	thickness of transition material
h_e	thickness of elastomer
I	second-order unit tensor
$\bar{I}_1, \bar{I}_2, \bar{I}_3$	Strain invariant
K	bulk modulus
k	constant that changes according to the network and geometric structure
M_c	mean molecular weight of the chains between each successive crosslink
M_∞	equilibrium mass
M_f	martensite-finish-temperature

M_s	martensite-start temperature
M_t	mass of the solvent as a function of time
N	number of replicates
n	diffusion exponential of the solvent
R	universal gas constant
r	radius of curvature of the neutral surface during bending
S	2nd Piola-Kirchhoff stress
S_∞	swelling content
S_t	swelling content as a function of time
t	time
T	absolute temperature
T_g	glass transition temperature
T_m	melting temperature
τ	difference between level average and total average
$\mathbf{u}$	displacement
v	volume
V_1	molar volume of the solvent
V_∞	the equilibrium volume of the swollen elastomer
V_d	the dry volume of the elastomer
v_2	polymer volume fraction
W	strain density function
w	width
w_e	width of elastomer
w_T	width of transition material
x	distance
z	furthest distance from the neutral axis
ε	strain
ε_x	strain on the elastomer along x-axis
κ	curvature
$\lambda, \lambda_1, \lambda_2, \lambda_3$	principal stretch
λ_t	linear swelling ratio

ρ	density of polymer
ρ_0	density of air
ρ_l	density of the liquid substance
Φ	angle of the bent material
χ	Flory-Huggins interaction parameter
μ	Poisson's ratio

List of Abbreviations

2D	Two dimensional
3D	Three dimensional
4D	Four dimensional
ABS	Acrylonitrile butadiene styrene
ANOVA	Analysis of Variance
CIE	Crystallisation induced elongation
DCM	Dual-component mechanism
DIW	Direct ink writing
DLP	Digital light printing
DSM	Dual-state mechanism
EBM	Electron beam melting
et-swell	Ethanol swelling
FDM	Fused deposition modelling
FEA	Finite element analysis
GO	Graphene oxide
hMSCs	Human bone marrow mesenchymal stem cells
LCE	Liquid crystal elastomer
L-PBF	Laser powder bed fusion
MIC	Melting induced contraction
MIR	Magnetically induced reorientation
MIT	Massachusetts Institute of Technology
MSM	Magnetic shape memory effect
NIR	Near-infrared
NiTi	Nickel Titanium
OWSMA	One-way shape memory alloy
OWSME	One-way shape memory effect
PAC	Printed active composite
PCL	Polycaprolactone
PE	Psuedoelasticity
PEG	Polyethylene glycol

PHA	Polyhydroxyalkanoates
PLA	Polylactic acid
PTM	Partial-transition mechanism
PTP	Phase transformation pathway
PU	Polyurethane
P μ SL	Projection micro stereolithography
SCG	Shape-changing gel
SDNPTP	Symmetry dictated non-phase-transformation pathway
SE	Superelasticity
SLA	Stereolithography
SLM	Selective laser melting
SMA	Shape memory alloy
SMC	Shape memory composite
SME	Shape memory effect
SMM	Shape memory metal
SMP	Shape memory polymer
SOEA	Soybean oil epoxidised acrylate
TBP	TangoBlackPlus
TWSMA	Two-way shape memory alloy
TWSME	Two-way shape memory effect
UV	Ultraviolet
VWP	VeroWhitePlus
ZE	Zeeman energy

Chapter 1 – Introduction

1.1. Background

Three-dimensional (3D) printing, also known as additive manufacturing or rapid prototyping, has been around for three decades, beginning with stereolithography (a subtype of 3D-printing) from 3D Systems commercialised in 1987 [5]. Parts produced by 3D-printing have been widely used for rapid prototyping of new products and the manufacturing of structures and objects that cannot be achieved via traditional manufacturing techniques. The use of 3D-printing is currently widespread, and 3D-printing is no longer merely used for industrial or academic research purposes [6]; instead, it is transforming from a prototyping method into a mature manufacturing method [7]. However, 3D-printing is still unable to replace most conventional manufacturing methods due to the limitations of materials, build size and cost [8]. Instead, it complements conventional manufacturing to produce new products with increased complexity and functions. Nevertheless, the prospect of more manufacturing applications with 3D-printing largely relies on the development of new materials that are suitable for 3D-printing techniques [7].

Over the past two decades, there were many studies on shape-memory materials [9-14], which are also known as “smart” materials. These materials change their shape or properties under the right stimuli. Metal alloys and polymers are most popular among these materials and have drawn a considerable amount of attention [15, 16]. However, shape memory polymers (SMPs) are preferred to shape memory alloys (SMAs) due to its more substantial recoverable strain. SMPs have a recoverable strain of up to 400%, whereas SMAs only possess 8%–12% [13, 17]. Also, the properties

of SMPs are more tuneable through adjusting molecular weights and by forming composites [18]; some of the composites are biocompatible and biodegradable and are therefore suitable for biomedical devices. As they are lightweight [19], they are highly desired by industries such as automotive and aerospace [3, 20-24].

The development of 3D-printable “smart” materials has driven 3D-printing to another level, known as four-dimensional (4D) printing. 4D-printing is an extension of 3D-printing to the fourth dimension, which is time [25-27]. This technique allows the properties of a printed object to undergo a designed transition over time when stimulated. The essential advantage of 3D-printing is the capability of producing customised designs of intricate architectures that cannot be fabricated by conventional methods. 4D-printing inherits this advantage. Moreover, 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. This breakthrough technology is mainly fuelled by the rapid development of smart materials and the latest progression of multi-material printing. Due to the development of multi-material polymer printing, the 4D-printing of polymers has been made possible [26], and more opportunities and applications await discovery.

The Massachusetts Institute of Technology (MIT)’s Self-Assembly Technologies Lab was among the first to develop and demonstrate the possibility of 4D-printing. In his 2013 TED (Technology, Entertainment, Design) talk, Skylar Tibbits, the co-director of the MIT Self-Assembly Technologies Lab and a pioneer of 4D-printing, demonstrated how 3D-printed materials could adapt to their surroundings (water, in his example) and self-assemble into different structures [28]. Since the introduction

of 4D-polymer printing, a wide variety of stimuli, ranging from heat, swelling, pH, and light, has been explored to induce the 4D transition [29-31].

However, 4D-printing is still a very raw and new technology with many challenges that require resolution. Most well-developed 4D-printing processes are confined to one-way shape morphing stimulated by a single mechanism, hence lack reversibility [32-34]. Reversibility is usually referred to as “two-way memory” because it gives the material two permanent shapes [35]. 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. Figure 1.1 depicts the effects of irreversible (one-way) shape memory and reversible (two-way) shape memory with heating and cooling as the stimuli. Adding reversibility into 4D-printing allows repetitive actuation and eliminate the need for reprogramming, which is time and labour consuming. Hence, there is a pragmatic need to develop reversible 4D-printing.

Figure 1.1 Process chains of shape memory effects. (a) Irreversible (one-way) shape memory effect; (b) Reversible (two-way) shape memory effect.

Introducing reversibility into 4D-printing enables repeated self-programming for many prospective applications such as soft robotics [36], packaging and logistics [33, 37], and biomedical applications [38-40]. 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, most of which had a long response time on the scale of hours to days [36, 41, 42] and only demonstrated the 2D-to-3D shape morphing (origami) or a mere change in size [41, 43-46]. There are two types of 2D-to-3D shape morphing. One type is printed in 3D and then manually programmed into 2D for later recovery back to 3D upon stimulation (e.g., origami). 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.

Currently, most reversible 4D-printing studies only conducted qualitative analysis on the feasibility of shape programming and reversibility [41, 42, 44, 47]. Secondary shapes were 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.

1.2. Objectives

The main objective of this study is to develop a predictable, rapidly responsive, reversible 4D-printed component to be used in applications that require such attributes. The five-fold objective is given as follows:

- To develop a reversible 4D-printing method with mechanisms for controllable programming and recovery
- To develop an analytical model to understand and predict the degree of bending of the reversible 4D-printed part during programming
- To conduct a finite element analysis to have an insight into the programming process

- To validate the feasibility of the reversible cycle and accuracy of the models using Polyjet and elastomer as an example
- To demonstrate controlled complex 3D-to-3D reversible shape morphing and potential engineering applications

1.3. Research issues and Scope

This work covers the development of a controllable reversible 4D-printing component of polymers which is achieved by controlling environmental stimuli in both programming and recovery stage. An in-depth review on reversible 4D-printing, along with the different mechanisms, are evaluated. This work focuses more on the programming stage of a controllable reversible 4D-printing.

The scope of this research is as follows:

- Possible mechanisms and cycles will be evaluated to obtain the most ideal mechanisms for both programming and recovery stages, and the feasibility of the selected mechanisms and cycle are investigated.
- An analytical model to predict the curvatures of the programmed structures is formulated using a series of different theories suitable for the mechanisms used.
- Independent variables such as temperature and thicknesses of the materials are varied to study their effect on the final curvature of the programmed structure. Using the analytical and simulation models, the variables and conditions required to obtain a certain curvature can be determined.

- The models are compared to the experimental results under the same conditions. ANOVAs are carried out to investigate if the predicted values are significantly different from the experimental values.
- The process of the cycle is sped up. 2D and 3D structures are created to demonstrate possible uses such as biomimetic and soft robotic functions.

1.4. Thesis Organisation

This first chapter gives an overview of the topic of 4D-printing and reversibility. The objectives are also covered in the first chapter. The literature review is covered in Chapter 2. In the literature review, different potential materials for 4D-printing are evaluated to investigate if they are suitable for the use of reversible 4D-printing. Following that, different mechanisms are introduced and studied for the programming and recovery stage. The existing reversible 4D-printing techniques are studied. Chapter 3 introduces a new mechanism for a 4D-printing reversible cycle where the mechanisms and processes are described. The materials used are also introduced and studied in this chapter. In Chapter 4, two different models that study the reversible 4D-printing process are developed. It comprises of a simple analytical model that is created to predict curvatures of a simple slab and a simulation model that studies final deformation and stress distribution in both simple and more complex structure. The reliability of the two models was investigated by comparing the theoretical results to the experimental results. Chapter 5 is the study of the various 4D-printed structures. Improvements to the initial reversible cycle are also implemented to increase the actuation speed and allow more rapid actuation in 3D structures. This study ends off with Chapter 6, the conclusion. Future

recommendations with regards to reversible 4D-printing and the list of publications arising from this research are included in Chapter 6 too.

Chapter 2 – Literature Review

2.1. Mechanisms of Smart Materials

Developments of 4D-printing technique were contributed by the advances in smart materials, also known as shape-memory materials. As 4D-printing is synonymous to the 3D-printing of smart materials, a thorough understanding of the mechanisms of smart materials is needed to achieve 4D-printing.

2.1.1. Shape Memory Metals (SMMs) and Shape Memory Alloys (SMAs)

SMAs belong to a particular group of metal alloys that can recover back to the original shape under certain stimuli. SMAs are usually subjected to a programming process between two transformation phases of metal alloys. These phases depend on differences in temperature [48] or magnetic field [49]. The transformation phenomenon is known as the shape memory effect (SME).

2.2.1.2. Mechanisms of SMMs and SMAs

1) Thermal Shape Memory Effect (SME)

Alloys can exist in different phases and attaining different crystal structures. Usually, SMAs exist in two different phases with three different crystal structures (twinned martensite, detwinned martensite and austenite), thereby giving rise to six possible transformations [50]. There are three categories of shape memory characteristics for SMAs [1, 51], namely, one-way shape memory effect (OWSME), two-way shape memory effect (TWSME) and pseudoelasticity (PE)/ superelasticity (SE), as shown in Figure 2.1. Emphasis is placed on OWSME and TWSME.

Figure 1.1 SMA phases and crystal structures (Permission obtained from [1])

In OWSME, the one-way SMA retains a deformed state after the removal of an external force. When heated, it recovers to its original shape. The driving force to achieve such transformation is the difference between the chemical-free energy of the phases above the austenite-start-temperature (A_s) which allows crystallographic reversibility [52]. At lower temperatures, the martensite structure is stable, but at higher temperatures, the austenite structure is more stable. There is a temperature range for transformation depicting the start and the end of the transformation. The start of the transformation of martensite is martensite-start-temperature (M_s), and the completion of the transformation is martensite-finish-temperature (M_f) [53]. It is usually in the structure of twinned martensite. When a load is applied to the SMA, the SMA forms a detwinned martensite structure. When it is unloaded, it is retained

in the detwinned martensite structure. The start of the transformation of austenite is A_s , and the completion of the transformation is austenite-finish-temperature (A_f). When heated beyond A_s , it begins to contract and transform into the austenite structure, resulting in shape recovery. If the austenite is heated beyond the temperature M_d , the highest temperature at which martensite can no longer be stress-induced, the SMA will be deformed permanently [54]. Once the SMA is cooled below M_s again, the transformation causes the austenite to revert to martensite structure, and the transformation completes below M_f .

Some SMAs obtained through a suitable thermo-mechanical treatment exhibit TWSME [17], otherwise known as reversible SME. Two-way SMA, unlike one-way SMA, can remember shapes at both high and low temperatures. The unique functionality of this effect is that the alloy does not need to undergo external mechanical stress [55]. For TWSME, the SMA transforms between two phases, mainly the austenite phase at high temperature and the detwinned martensite phase at low temperatures. TWSME is usually achieved by tailoring a biased one-way shape memory alloy (OWSMA) actuator that behaves like a TWSMA at the structural level [56].

Hysteresis is the measure of the difference in the transition temperatures between heating and cooling of SMA. It is generally marked by the difference between the temperature where the material is 50% transformed to martensite when cooled and the temperature where 50% transformed to austenite when heated [57]. For specification of applications, this is a very crucial property. A small hysteresis is required for fast actuation application, and a large hysteresis is essential for slow actuation application [58]. It is crucial to tailor the composition of the SMA material,

the thermomechanical processing and the working environment of the applications as they all influence the transition temperature and the hysteresis loop. The strain levels are also crucial in hysteresis as stress beyond the yield strength of martensite (approximately 8.5% for NiTi alloys [59] and up to 10% for the other alloys [60]) lead to permanent deformation.

2) Magnetic Shape Memory Effect (MSM)

Magnetic SMAs are also known as ferromagnetic SMAs. The mechanisms used for magnetic SMAs are twin boundary motion [61], also known as magnetoplasticity or magnetically induced reorientation (MIR), or a magnetic field induced phase transformation.

The twin boundary motion of martensitic structure depends on the difference in magnetic energy which exceeds the mechanical energy required for displacement of atoms near the twin boundary. The difference of the magnetic energy is due to the various orientations of magnetic moments in twin related variants. This MIR results in a sudden increase in the magnetisation and leads to shape change [62, 63]. This allows the actuation frequency to be higher as the actuation energy is transmitted by a magnetic field which is much faster than heat transfer mechanism [64]. However, ferromagnetization is lost at high temperature, suggesting that magnetic SMA can only function at low temperatures [1].

The second mechanism is magnetic field-induced phase transformation. This mechanism is similar to the temperature-induced martensitic transformation mentioned earlier in thermal shape memory effect. In addition to the directional energy induced by the magnetic moments, the Zeeman energy (ZE) plays a crucial

role in this mechanism [65]. The ZE is the potential energy of a magnetised body in an external magnetic field, otherwise known as the external field energy. The ZE comes from the difference in the saturation magnetisations of phase transformation, and it increases continuously with the magnetic field. However, ZE only vaguely depends on crystal orientation, meaning that polycrystals can also be utilised as actuators. The ZE energy can be maximised by transforming between different phases such as ferromagnetic phase to paramagnetic or antiferromagnetic phase, or vice versa, as the difference between saturation magnetisation is much larger.

2.1.2. Shape Memory Polymers (SMPs)

2.2.1.2. Mechanisms of SMPs

There are two steps in a typical OWSME cycle: the programming process, in which the material is deformed into a temporary shape, and the recovery process, in which the shape is recovered. The programming step in one-way SMP is usually mechanical force; thus, the shapes are not reversible in both ways. The recovery step, on the other hand, has various mechanisms for SMP. While there are other mechanisms such as light and magnetic-responsive, the most thoroughly studied mechanisms are thermo-responsive and chemo-responsive.

1) Thermo-responsive SMPs

There are two parts to a thermo-responsive SMP, one being the matrix which stores the elastic energy during programming and the other being the reversible switch which can reversibly change in stiffness depending on the temperature range[66]. This reversible switch is usually the glass transition temperature or the melting temperature of polymers. There are three working mechanisms for thermo-responsive

SMPs to achieve the programming and recovery: dual-state mechanism (DSM), dual-composite mechanism (DCM), and partial-transition mechanism (PTM) [67] as shown in Figure 2.2.

Figure 2.2 Basic working mechanisms for thermo-responsive shape memory effect (SME) in polymers. (I) Dual-state mechanism (DSM); (II) Dual-component mechanism (DCM); (III) Partial-transition mechanism (PTM). (a) Original sample at low temperature; (b) Upon heating and compressing; (c) after cooling and constraint removal (d) after heating for shape recovery. (Permission obtained from [2])

a) Dual-state mechanism

The glass transition state is generally used in the DSM [68]. Above the glass transition temperature (T_g), polymers are in a rubbery state; for example, elastomers generally have a T_g that is lower than room temperature and, therefore, they are rubbery at room

temperature [67]. As such, they are more flexible and can be deformed easily. Below T_g , the polymer is in the glassy state and is more brittle and harder. When the distorted shape is maintained while cooling to below T_g , the micro-Brownian motion is frozen in the glass state. After the applied constraint is removed, the part retains its distorted shape. The polymer returns to its rubbery state only upon being heated to above T_g , which reactivates the micro-Brownian motion and results in shape recovery [69]. Therefore, all elastomers are naturally SMPs. It is named dual-state as it requires both glassy state and rubbery state to attain shape memory.

This mechanism, however, can only be operated at low temperatures and has to be maintained. For elastomers printed by Polyjet, the T_g s are below ice point. Hence, this mechanism is not very suitable for achieving reversible 4D-printing as the operating temperature is too low.

a) Dual-component mechanism

The DCM usually has two or more components, which can have an elastic matrix/transition inclusion [70]. The elastic matrix is relatively elastic throughout so that it can store elastic energy during programming. The transition inclusion has a stiffness that changes upon heating. The transition component prevents shape recovery at low temperatures due to higher stiffness at low temperatures. Reheating the component will soften the transition component to remove the constraints, and the stored elastic energy is activated to return the polymer back to its original shape [66].

b) Partial-transition mechanism

In the PTM, the polymer is heated to a temperature that lies within the transition range. This is different from DSM or DCM where the polymer is heated to above T_m or T_g . In this case, the unsoftened portion serves as the elastic component to store elastic energy, and the softened portion behaves as the transition component [67].

In this research, DCM is used as it is achievable using Polyjet as Polyjet can print two and more materials. The transition temperature is also tunable by creating digital materials. Digital materials are composite materials created by the Objet Connex 3D printing system. This mechanism has much more potential than DSM or PTM. As it has two different materials, the mechanical strength does not have to be compromised as in DSM when the temperature changes. As for PTM, it is very similar to DCM, but temperature control is very critical as compared to DCM, where it can have a broader working range.

2) Chemo-responsive SMPs

The plasticising effect is widely observed in polymers upon immersion into an appropriate chemical [71]. The plasticising effect reduces the T_g of the polymer; therefore, it may not be necessary to heat over T_g in order to trigger a transition. This effect provides an alternative for shape recovery. Chemo-responsiveness can be triggered by the pH value, ionic strength or quality of the agent [72].

There are three mechanisms for chemo-responsive SME: softening, swelling and dissolving. For chemo-responsive SME, gels and hydrogels have been widely used to achieve shape memory [73].

a) Softening

A study by Huang *et al.* [74] showed that actuation in polyurethane (PU) could be achieved through moisture or water as a stimulus. When a piece of pre-bent PU wire with an initial T_g of 35 °C was immersed in room-temperature water at 22 °C, it softened and gradually returned to its original shape. No swelling occurred, as the absorbed water was less than 5%. Ethanol was also shown to act as a stimulus to PU, at a much faster rate.

b) Swelling

A piece of pre-deformed polystyrene can recover its original shape upon immersion in room-temperature acetone for 16 h [2]. Similarly, although a soft contact lens is glassy without water, it becomes soft and rubbery after being soaked in water or solution, suggesting a decrease in T_g .

Another type of SMP that swells is a shape-changing gel (SCG), which is a hydrogel. The swelling is affected by changing the degree of crosslinking or by inducing a change in the miscibility of polymeric segments and solvent molecules [72]. For example, increasing the degree of crosslinking can be achieved by adjusting the pH value, and an increase in crosslinking density will reduce the amount of swelling.

In a study done by Varghese *et al.* [75], the hydrogel reversibly transformed from a cylindrical gel sample into a hollow spherical or ellipsoidal shape upon manipulation of the presence of metal ions such as Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , or Fe^{3+} . The hydrogel regained its initial shape after the metal ions were washed out using a hydrogen chloride solution. In this case, the concentration of the metal ions acted as the stimulus for chemo-responsive shape change.

c) Dissolving

When softening is taken to the extreme, the transition component will be removed by dissolving into the surrounding medium [76]. However, this mechanism is not useful in reversible shape memory process as the transition component is lost in the first actuation. As such, a second actuation cannot occur.

3) Photo-responsive SMPs

Light act as a high-power density force that breaks the chemical bonds to rearrange the cross-linked network. The reconfiguration of the crosslinks allows permanent shapes to be re-engineered. In a research led by Andreas Lendlein *et al.* [3], they reported that polymers containing cinnamic groups were able to form new temporary shapes when exposed to ultraviolet (UV) light illumination. They were stable for a long-time period and yet could recover to their original shape at ambient temperature when exposed to UV light of a different wavelength, as shown in Figure 2.3. In their test, the photo-responsive SMPs, like the thermo-responsive SMPs, required programming via an external force to induce a deformation in the polymer. Near original length was obtained after shape recovery and two cycles were carried out. Although there was no change in shape memory properties observed, the film changed from clear to pale yellow. However, it was also likely that partial cleavage of the photoreversible crosslinks might lead to changes in the mechanical properties. This indicated a high decay rate which would affect the amount of repeatability of the component. Even though the programming stage and recovery stage both used two different wavelengths, it could be a prospective method in achieving reversible SMP. The current technique required stress-induced to achieve photo-fixing of the temporary shape.

Many other studies used near-infrared (NIR) light to induce shape memory effect too. Bai *et al.* [77] proposed a thermoset polyurethane (PU)/graphene oxide (GO) composite with light-induced shape memory effect, solid-state plasticity and self-healing performance. The composite was programmed mechanically after being heated. It was able to recover more than 95% using NIR light with an intensity of 1.4 W cm^{-1} . At a higher intensity of 2.5 W cm^{-1} , it could even self-heal. A study by Zhou *et al.* used NIR light to actuate their modified $\text{W}_{18}\text{O}_{49}$ nanowire [78]. These actuators were able to respond to both NIR light and ultraviolet light, forming contraction and bending motion. Shape fixity was provided by chemical crosslinks formed by the acrylate group. The reversible phase of shape memory was provided by crystalline polyethylene glycol (PEG).

Figure 2.3 Molecular mechanism of light-induced shape memory polymer of the grafted polymer network: circles representing permanent crosslinks and diamonds representing photoreversible crosslinks. (Taken from [3])

4) Magnetic-Responsive SMPs

Polymers do not intrinsically possess magnetic properties. Magnetic nanoparticles have to be added to the polymer blend to form magnetic responsive SMPs or shape memory composites (SMCs) [79]. Some of which have nanoparticles dispersed in gels or elastomers creating soft magnetic materials. These materials can adaptively change their shape upon the presence of an external magnetic field. The shape programming occurs spontaneously when an external magnetic field is introduced and recovers once the magnetic field is removed. A magnetic gel was demonstrated lifting a load by contraction when an external magnetic field was applied. The

magnetic gel was also able to demonstrate bending, suggesting that magnetic response SMCs are capable of constructing worm-like actuators [79]. The advantages of this response are high repeatability and fast response rate of less than a second [80].

5) Summary of the mechanisms

However, most of these mechanisms are targeted to achieve recovery except a magnetic response. Self-induced stress by a stimulus during programming is essential to the component/material to accomplish reversible 4D-printing. A combination of stimulus will hence allow programming to be carried out by external stimulus instead of programming it manually.

2.2. 4D-Printing of Materials

The requirements to create a functional 4D-printed component are shape memory properties and printability. Also, the shape memory properties must be retained after being printed. In this study, the crucial additional functions required are reversibility and repeatability. Repeatability refers to the ability to repeat the entire cycle without fracture or significant change to the permanent shape.

2.2.1. 4D-Printing of Metals and Alloys

Emerging 3D-printed SMAs provide structural materials that can be applied on a larger scale as compared to polymers, in applications such as construction and medical devices [26]. New perspectives of shape memory application can be opened up as complex geometries can be realised via 3D-printing methods which are impossible to be realised by conventional methods. An example of how 4D-printing of metals can be applied is dental braces. As of now, nitinol wires are used for teeth correction. NiTi is also used in self-expanding stents [81]. By having 4D-printed

stents, the stents can be customised for the patient, and it can be activated without the balloon process, reducing the invasiveness of the surgery. Such SMAs have yet to maximise their potential as most conventionally produced SMAs are bounded by simple geometry [82]. While in the usual case of 3D-printing of metals desires minimal distortion due to stress build-up, the aim of 4D-printing of metals sets to induce programmability for transformation into another shape. The actuation is due to the application required.

One of the most popular and widely research SMAs is NiTi. While NiTi alloys have many outstanding functional properties and exhibit the best shape memory behaviours such as high percentage of shape recovery of 8%, they are not easy to be fabricated by conventional methods [82]. There are three main reasons. Firstly, for NiTi alloys, as mentioned in its mechanism, a change in composition can affect the transition temperature. Impurity elements can be picked up during high-temperature processing, and this results in oxidation and microstructural defects [82]. Secondly, the shape memory properties of NiTi alloys make it hard for precise machining and result in a substantial amount of tool wear [83]. Lastly, shape setting and heat treatments such as annealing can affect the phase transformation behaviour of NiTi alloy [84].

There are various additive manufacturing techniques used to produce NiTi alloys and other SMAs, namely, selective laser melting (SLM), electron beam melting (EBM) and laser powder bed fusion (L-PBF). They can eliminate various problems that arise from conventional methods.

1) Selective Laser Melting (SLM)

Additive manufacturing has come in as a possible solution to fabricate NiTi parts [7]. One of the additive manufacturing processes that was researched was selective laser melting (SLM) [85]. The use of additive manufacturing cut down the number of manufacturing cycles as minimal machining, and thermomechanical treatment is needed. It also allows the alloy to have a higher micro-hardness, as reported by Shishkovsky *et al.* [86]. It resolves the issue of increasing impurity level in conventional methods too. There was no increase in impurities in NiTi alloy produced by SLM [87]. This might be due to the inert gas in the chamber that prevents impurities from forming. The NiTi alloys produced were tested through deformation then heat recovery and were found to return to their original shape.

However, there were some problems presented by SLM nitinol parts. Nitinol produced by SLM has a lower content of Ni due to evaporation as Ni had a lower evaporation temperature than Ti, causing it to have a higher tendency to evaporate [87-89]. A decrease in Ni content led to an increase in the phase transformation temperature [90]. The decrease in Ni content could also be contributed by the formation of Ni-rich NiTi [83, 91, 92].

In a compression test carried out by Meier *et al.* [93] to study the mechanical and functional properties of SLM NiTi, they observed that SLM NiTi had lower fracture strain and stresses than the conventional NiTi parts. However, they did exhibit higher reversible strains and less irreversible strains than conventional NiTi. It is important to note that the tests were performed all under compression stress. Taheri Andani *et al.* have also conducted further testing on elastic modulus and ductility of the SLM fabricated NiTi SMA and found that these features were mostly dependent on

porosity and pore structure [94]. Further studies have to be carried out under tensile stress to have a more thorough understanding of the functionality of SLM NiTi alloys.

Besides NiTi alloys, research in additive manufacturing other types of shape memory alloys has also been explored. One example is the fabrication of Cu-Al-Ni-Mn SMA using SLM [95].

2) Electron Beam Melting (EBM)

Due to the strain recovery effect displayed by NiTi, Elahinia *et al.* saw the possibility of 3D-printed NiTi in biomedical applications, as nitinol has a much similar stress-strain curve as compared to the widely used stainless steel. They manufactured porous NiTi implant using electron beam melting (EBM) [82]. Both the benefits of shape memory and customisation were maximised using 4D-printing technique [96]. The shape-changing gave two benefits, enhanced bone fixation and minimisation of invasive surgery [97]. In a recent study by Le *et al.*, they managed to 3D-print a shape memory alloy penile prosthesis prototype [98].

3) Laser Powder Bed Fusion (L-PBF)

Another technique used to print SMA is laser powder bed fusion (L-PBF) [99]. Khademzadeh *et al.* studied the parameters and possibility of single-phase NiTi production by micro L-PBF. L-PBF was also used to fabricate Cu alloys [100].

One of the issues limiting the applications of SMA is the functional fatigue during repeated actuation through repeated mechanical or thermal loading. The increased accumulation of irrecoverable strain determines the functionality, durability and

service life of SMA [101-103]. Defect generation and transformation cycling are positively proportional as dislocations, grain refinement and formation of unique grain boundaries (Σ boundaries) occur during transformation cycling [104, 105]. In a review by Gao *et al.* [104], they suggested that other than the normal martensitic phase transformation pathway (PTP), there was an additional pathway activated during phase transformation cycling known as the symmetry dictated non-phase-transformation pathway (SDNPTP) which might play a pivotal role to functional fatigue. They also proposed several strategies to suppress SDNPTP to improve the fatigue resistance of SMAs.

Cyclic experiments carried out by Haberland *et al.* [83] have shown the degradation of SME. While in the first cycle, the SLM material displayed a broad hysteresis with a significant plateau, the irreversible strain accumulated in each cycle, and the hysteresis width decreased with it. However, in the first cycle, the SLM sample exhibited higher reversible strain than conventional NiTi sample. This suggested that they might likely have higher repeatability than conventional SMAs.

2.2.2. Reversibility in SMAs

As mentioned in the mechanisms, there is an effect known as TWSME in metals. The OWSMAs will need to undergo specific heat treatment [106] to be able to exhibit TWSME. One of such methods is thermomechanical training after heat treatment [107]. Wang *et al.* introduced the TWSME to a narrow hysteresis TiNiCu shape memory alloy. After that, the spring was able to contract when cooled and extend when heated. The recovery rate of this spring was up to 58%. Another method that

can induce TWSME to an alloy is by electrochemical hydrogenation [108]. However, the variation of the TWSME was minimal during the first 50 cycles.

TWSMAs are less applied commercially due to tedious training requirements and to the fact that it usually produces about half of the recovery strain provided by OWSMA for the same material and its strain tends to deteriorate quickly, especially at high temperatures. The main issue with TWSMA is that the maximum strain and deformation can go up to is 7% only [17].

As of now, there has not been any reversible 4D-printed SMA due to the issues that have not been resolved in 4D-printing such as low recovery strain, lower Ni content due to evaporation as most metal additive manufacturing requires high energy, and poor surface finishing [109].

2.2.3. 4D-Printing of Polymers

Unlike SMAs, there are more variety of materials for 4D-printing. SMPs generally respond to their environment by a stimulus that will affect the physical state of the polymeric chains or glass transition [110]. Glass transition is a function that is intrinsic to all polymers [111].

There are four categories of polymers: thermoset, thermoplastics, elastomer and hydrogels. Depending on the printing technique, the different polymers can be printed, e.g. thermosets can be printed by inkjet printing or stereolithography, thermoplastics can be printed by fused deposition modelling. Elastomers, depending on if it is a thermoset elastomer or thermoplastic elastomer, can be printed with different printing techniques too, making them one of the more versatile polymers; likewise, for hydrogel.

Some of the existing polymers that can be 4D-printed are polylactic acid (PLA), polyhydroxyalkanoates (PHA), polyurethane and other resins [112]. As polymers are synthesised using monomers, new printable SMPs can also be developed such as proprietary materials known as Vero and Tango [26]. Another popular material used for 4D-printing is hydrogel [113]. The advantages of the hydrogel are that the viscosity can be controlled to enable it to be printed, and it can be printed using an array of techniques such as bioextrusion, digital light printing (DLP).

There are mainly two types of additive manufacturing polymers used to realise 4D-printing: SMPs that are capable of temporary shape fixation and recover upon heating and gels that swell when solvent molecules diffuse into the network.

1) Polyjet

Polyjet uses inkjet printing technique. The inkjet printing technique can only print two class of polymers, and those are thermosets and thermoset elastomers. One of its limitations is, Polyjet, being a closed system, only prints their proprietary materials.

Chemo-responsive, particularly water-activated shape change is amongst the first of 4D-printing. Tibbits, together with Autodesk and Stratasys, looked into 3D-printing of smart materials that expanded when exposed to moisture [26]. They first started with a 1D strand self-assembling into a 2D word of MIT. Then they proceeded to carry it out on 2D plates folding into a 3D cube (Figure 2.4). The material was a hydrophilic polymer that swelled in water and expanded up to 150%. In their case, they used a rigid material as a framework and the smart material to programme the

object to create a hinge. Only the smart material section actuated when submerged in water.

Figure 2.4 Folding of an unpacked cube in water (Permission obtained from [2])

Another activation method for 4D-printing, which is more common, is to utilise high temperature to trigger the shape change, by combining heat and stress [33]. The shape memory composite can bend at different rates and directions depending on the design of the hinges [4]. The research by Ge *et al.* created a printed active composite (PAC), printed via 3D multi-material polymer printer (Objet Connex 260, Stratasys, USA) which is a bilayer composite system comprised of the SMP fibres that are covered by the matrix. The matrix is an elastomer so that after the stress is released, it will return to the stress-free state. However, the SMP will retain the stretch configuration as the microstates of the molecules are frozen. When it is heated above the T_g again, the shape is recovered. This cycle is displayed in Figure 2.5, wherein earlier research [4], they studied the bending of the PAC lamina by aligning the SMP fibres differently, thus forming coils, twists and waves. This lays the foundation for their subsequent studies in making the PAC functional. They simulated the folding of a cube and a pyramid with the PACs as the hinges [33]. In a similar study, the mechanism of the

shape change and theoretical model were proposed and experimented on to understand the complex material behaviour [114].

Figure 2.5 Complex low-temperature shapes of active composite laminates obtained by the design of the laminate architecture. (a) A two-layer laminate designed with one layer being a lamina with fibres at a prescribed orientation and one layer being pure matrix material is printed, then heated, stretched, cooled, and released. Upon the release of the stress, it assumes a complex shape, depending on the laminate architecture. When reheating, it then assumes its original shape, a flat rectangular strip. (b) Shows an actual strip in its original shape and (c)–(h) show results of this process with differing fibre architectures. (Permission obtained from [4])

This concept of PAC bending during recovery has been improved to achieve sequential shape change and multi-shape change [115-117]. For sequential shape change, the percentage of fibres to the matrix was varied to achieve sequential shape change with the same materials [116, 117]. In earlier works in shape memory polymers, researchers have already achieved tri-shape memory effect by having multi-materials with two or more transition points [118-124]. To parallel the work of conventional manufacturing with 4D-printing techniques, Wu *et al.* demonstrated an approach to design and manufacture a flat layered composite with a myriad of digital

SMP fibres in the matrix. The parameters to achieve controlled bending and shape change were also studied and optimised to achieve the different desired temporary and permanent shapes. This is demonstrated further in implanting this concept in an orchid shape [125]. The morphing of the structure is achieved with creating different digital materials by varying the T_g yet using only two base materials.

2) Stereolithography

The limitation of the above method is that Stratasys' materials are proprietary, and therefore they cannot be manipulated. Another technique that prints thermosets and thermoset elastomers is stereolithography (SLA). There are different variations in technique that evolved from SLA, being the oldest form of 3D-printing [5]. A new 4D-printing method proposed by Ge *et al.* is using high-resolution projection micro stereolithography (P μ SL) [126]. The resolution and freedom to tune with material properties are the main advantages of this method. Shape memory was attained with a single material SMP with the T_g of 43°C. A similar study was reported by Choong *et al.* [127]. Several applications were proposed too, such as stents that can be reduced to a smaller diameter for minimally invasive surgery and microgripper. In another study, conductive ink of carbon nanotube was printed on stereolithography printed polycaprolactone (PCL) model that was supposed to function as a shape memory-based electronic device [128]. Two other applications proposed by Zarek *et al.* for 4D-printing using DLP printing were dynamic jewellery and fashionwear [129].

In a study by Miao *et al.*, they 4D-printed a new renewable soybean oil epoxidised acrylate using stereolithography based bioprinting [130]. 4D-bioprinting refers to groups of man-made programmable self-assembly, self-folding or self-

accommodating technologies that are triggered by the external environment [39]. The scaffold displayed shape memory effects by having the temporary shape fixed at -18°C and recovered fully at human body temperature of 37°C. This indicated a great potential in biomedical application. Also, statistically, the cytotoxicity test has proven that the multipotent human bone marrow mesenchymal stem cells (hMSCs) adhesion and proliferation were comparable to PLA and PCL.

3) Fused Deposition Modelling

Another 3D-printing technique that allows shape memory or shapeshifting via heating mechanism is fused deposition modelling (FDM) [131]. FDM, unlike the two techniques above, prints thermoplastics. The materials that are generally used are PLA and acrylonitrile butadiene styrene (ABS). To achieve 4D-printing, the material is printed in a manner where internal stresses were accumulated as there were heating and rapid cooling cycles during the fabrication process due to constraints of the platform or the existing layers. After printing, the internal stress in printed material was stored for a long time until the material was heated beyond T_g . This technique can be cost-saving as the materials are cheaper as compared to the other printing techniques. Also, using a 2D to 3D shape morphing with FDM, it is time-saving to achieve a 3D structure [132].

Another example of advancement in 4D bioprinting is the printing of bio-composite via FDM [133]. The printed wood reinforced bio-composite displayed poorer mechanical properties than conventionally produced wood bio-composites. However, the wood bio-composite studied was unlike the other conventional wood reinforced bio-composite that seek to increase strength and stiffness. The new functionality of

this composite is to achieve self-shaping actuation. FDM has led to a large increase in water intake, similar to PHA or PLA, thus allowing swelling as a stimulus [134]. Using natural bio-polymers can better suit the applications in the biomedical field.

4) Bio-extrusion

The materials used for bio-extrusion are usually gels or hydrogel, which are also known as bioinks. The composition of the bioink depends on individual study, as they have to consider printability and the properties after printing. Researchers at Harvard's SEAS (School of Engineering and Applied Sciences) have created a 4D-printing system inspired by biomimetic 4D-printing to simulate how a botanical system responded to external stimulus [135]. They developed a hydrogel composite that could be 4D-printed via extrusion into a programmable bilayer architecture. The hydrogel swelling was anisotropic to have control of the intricate shape changes upon hydration [136, 137]. Besides, the print path was manipulated to achieve different bending and twisting conformation. They managed to simulate an orchid and calla lily flower.

All of the above were only able to achieve a single direction shape memory. After every use, they have to be reprogrammed. Therefore, their functionality and application are in those that do not require reversible shape changing but more of complex structures that do not require shapeshifting or only require a single shape change, for example, cardiac stent [32].

2.2.4. Reversibility in SMPs

As mentioned earlier, the advancement in materials is a huge driving force for the advancement in 3D-printing. Likewise, the recent advancement in reversible SMP

has driven for more studies in reversible 4D-printing. Reversibility in SMPs promotes more practical usage in all industries as it reduces effort in constant reprogramming. This is particularly useful for biomedical application where, for example, implanted devices are not able to be reprogrammed manually. Thus, reversibility using external conditions is needed [138].

In most one-way SMP composite that uses heat as the recovery mechanism, it undergoes programming to attain a temporary shape. The programming step is usually manual stress [6, 26, 28, 32, 33, 116, 125, 126]. To achieve two-way shape memory effect, the programming step has to be removed or in another way be in-build into the SMP composite during manufacturing. The potential two-way shape memory properties were found in liquid crystal elastomer (LCEs). However, it has limited industrial application due to high manufacturing cost and unstable shape memory effect [139]. Therefore, a laminate of SMP with polyurethane is introduced to achieve such an effect [140]. After being heated to 60°C, the laminate curled. When cooled back to room temperature, the laminate uncurled. After the training cycle, it is proved to achieve good repeatability. Subsequently, many other similar polymer laminate types of research have shown to have similar promising results [141, 142]. Likewise, other research employs different mechanisms to achieve reversible SMP [143]. This presents a huge possibility in reversible 4D-printing.

In most of the 4D-printing techniques, they are not reversible and have to be programmed, inducing human interactive stress, then stimulated by external conditions to recover. Reversibility is crucial to enhance the functionality of 3D-printed SMPs. While it is not very common, there have been several breakthroughs that have attained reversible SMPs.

2.2.5. Reversibility in 4D-printing of polymers

In many studies carried out on reversible SMP, most of them create pre-internal stress to allow actuation and recovery. A pre-strained SMP polyurethane was combined with an unstrained polyurethane to achieve a reversible SMP laminate [139]. Another method is using semi-crystalline elastomers which exhibit crystallisation induced elongation (CIE) and melting induced contraction (MIC), which is similar to that of crystalline elastomer [144].

Comparing these conventional manufacturing methods to that of additive manufacturing, reversible SMPs have been achieved a few years beforehand. However, to produce a reversible SMP via the method of a composite, there are many steps to the fabrication. Also, the geometries that can be fabricated are simple shapes. On the other hand, though it is rare in additive manufacturing, it can achieve complex geometries. Therefore, by achieving reversible SMP in additive manufacturing, one can have a broader range of applications.

In recent years, there have been several successful studies on reversible 4D-printing [36, 44, 47, 145]. They are categorised into two main groups, hydrogel-based and LCE based.

The various study utilised hydrogels and gels to achieve shape morphing [36, 41, 47]. Naficy *et al.* were amongst the first to achieve reversible 4D-printing. They extruded a hydrogel composite that had two layers: a layer of inactive HEMA-based PEO₁₀-PU ink and a layer of temperature-sensitive NIPAM-based PEO-PU ink. The two stimuli were water swelling and heat. A similar study was carried out by Shiblee *et al.* to create soft robotics using shape memory gels derived from P(DMAAm-co-SA)

gels. Another study used soybean oil epoxidised acrylate (SOEA) as monomers for stereolithography-based reversible 4D-printing [42]. The printed part was able to shape change in ethanol/water. It relied on the resolution process with ethanol permeating the gradual crosslinked hydrophobic resin and the desolvation process with ethanol being removed and water not being able to permeate the hydrophobic resin due to its strong hydrophilicity. The reversible process took approximately 30 minutes. Nevertheless, there are still many limitations to hydrogels and gels. Firstly, the mechanical strength of the material is meagre, limiting the application to biomedical and specifically, the use of hydrogel. Also, the structure can most likely be only built in two dimensions. Upon actuation, the structure is converted to three dimensions with the process being reversible.

Amongst gels achieved shape morphing, a study by Mao et al. stood out [41]. While the stimuli were also water swelling and heat, the materials used were more than just gels and were more commercially available. The materials were printed using a multi-material printer Objet 260 Connex by Stratasys. The component was a three-layered component each with their functions. The Gray60 acted as the SMP where it was temperature-sensitive and contributed to shape fixations. The TangoBlack was used to store elastic energy to allow shape recovery. Hydrogel, encapsulated in TangoBlack, swelled upon hydration, creating internal stress within the component for programming to occur.

Although one of the actuation materials used was hydrogel, there were other components such as the Gray60 to compensate for the mechanical strength, allowing this printing method to have a large range of applications than that of the hydrogel printer. However, the hydrogel used in the experiment was not found in the common

materials provided by Stratasys that could be readily used. The exclusive access of the hydrogel material will limit the possibility of reversible 4D-printing available to the public and industries. Another issue is that Gray60 is a mixture of VeroWhite and TangoBlack. This mixture makes Gray60 highly susceptible to creep as the material is now more viscoelastic. It will not be able to retain its first permanent shape for long.

As mentioned earlier, there are two methods to achieve reversible SMPs; the second method is using LCE. Two other studies incorporated the use of LCEs as one of the various layers to achieved reversible 4D-printing [44, 145]. However, a complicated multi-technique and multi-platform 4D-printing process are entailed to print the multifaceted part. The entire printing process by Yuan *et al.* comprises two different printing techniques, inkjet printing, and direct ink writing (DIW). The silver ink was used to create joule heating to allow the LCE to expand and contract. Besides, a strip of LCE must be attached to the top of the device manually. Multi-technique and multi-platform are likely to incur more fabrication time and cost as a trade-off for the desired properties. The study by Kotikian *et al.* printed a photo polymerisable LCE ink at an elevated temperature using DIW. However, this technique is still limited shape morphing to planar-to-3D than 3D-to-3D.

Additive manufacturing can produce small parts which made it possible to produce better magnetic responsive SMCs. Most of these magnetic SMCs are produced by reorienting and aligning the magnetic domains of the magnetic nanoparticles that are suspended in either the resin or ink before right before being printed [146-149]. Various studies show that with different magnetic alignment, these magnetic responsive SMCs can operate in directions, simulating a range of movements such as

folding, twisting, crawling and swimming [146, 147, 149]. The magnetic responsive SMCs are produced in small sizes to maximise the bending effects [149]. While magnetic responsive SMCs can have rapid response, it cannot retain shape and can only primarily function as soft robotics. The use of soft materials implies that it is incapable of carrying out load-bearing functions.

2.3. Conclusion on 4D-Printing

The number of materials and techniques available in 3D-printing directly relate to the available mechanisms possible for 4D-printing. Reversibility is not impossible in 4D-printing, but the design of reversibility requires a thorough understanding of shape memory effects and limitations bounded by current printing methods and mechanisms of material activation.

There are various mechanisms available to SMPs and success in achieving reversibility in 4D-printing of polymers. The studies conducted by Mao *et al.* [41] and Naficy *et al.* [47] are very similar to the research conducted on reversible SMP fabricated by conventional methods where they design the components to induce internal stress via a different stimulus to allow the transformation to the second permanent shape. The two studies used the same mechanisms with different materials and applications in mind: chemo-responsive and heat-responsive. This proposed two or more stimuli to achieve reversibility in 4D-printing. The study by Shiblee *et al.* proposed the idea of a combination of stimuli to achieve and further control the bending [36]. Water swelling was the primary programming mechanism, but the temperature was a factor to speed up the programming. More stimuli provide reversibility and more controls for actuation. While there have been several

successful reversible 4D-printing, they are usually limited in a few areas. For example, the study by Mao *et al.* required at least three different materials [41], the study by Naficy *et al.* uses hydrogel solely [47] and, hence, the structure lack mechanical strength. Lastly, there are other examples which undergo long and tedious printing methods such as the study by Yuan *et al.* [44] which required complicated steps for printing. It is ideal for preparing reversible 4D printing within a single print and with a minimal amount of materials and still retains some mechanical strength to have load-bearing functions.

However, for 4D-printing of metals, as of now, there is limited reversibility achieved. This is because even via conventional fabrication, tedious training is required, and there is poor fatigue resistance leading to a quick loss of reversible strain. Besides, there are other limitations and challenges that need to be overcome even for the OWSMA, before they can proceed to develop reversible 4D-printing of alloys. The challenges are low recovery strain, poor finishing and mechanical properties.

Comparing both materials, SMPs have a brighter and faster development in additive manufacturing due to more stimuli and more variety of materials. This suggests that reversible 4D-printing of polymers is more plausible than metals.

2.4. Shape Morphing Models

While a new reversible cycle is introduced and proven feasible, there is a lack of predictability and control over the shape morphing. Predictability and control require the evaluation of the parameters that affect the shape setting. For most hinge-like movements, there are two methods to model the final shape change. The two methods are analytical models and FEA simulation models. In most reversible 4D printing, the

novelty is in the stimuli-based programming. Therefore, the modelling is focused on the programming stage.

There are two studies that used an analytical model based on beam theory to determine the hinge bending and curvature for bilayer structure so as to obtain the desired final 3D structure [44, 47]. To determine the curvature, a general equation of

$$\kappa = \frac{6\varepsilon(1+a)^2}{h(3(1+a)^2+(1+ab)\left(a^2+\frac{1}{ab}\right))} \quad (2.1)$$

Where κ is the curvature, ε is the strain, a is the stiffness ratio, b is the thickness ratio, and h is the overall thickness.

Both studies used experimental methods to obtain the strain to acquire an accurate prediction of the model. The strain value for the study by Naficy et al. was determined by the swelling ratios experimentally. The study by Yuan et al. [44] used an exponential function for the strain, and the constants were obtained using an experimental curve fitting method. The strain equation that is defined as

$$\varepsilon = \frac{A}{1+\exp(-B(T-T_r))} \quad (2.2)$$

Where A , B and T_r are fitting parameters. These methods are sufficient for prediction of the final 3D shape. As the strain was predetermined, it is tough to use them reversely to determine the conditions required to obtain a fixed curvature optimally.

A possible theoretical model for determining the strain for a swelling mechanism is the Peppas model [150]. It is a power law that is widely used for mass transport and swelling. It is given as [151]:

$$f_1 = kt^n \quad (2.3)$$

Where f_l is the fraction of the mass transport, k is a constant that changes according to the network and geometric structure, and n is the diffusion exponential of the solvent.

While an analytical model that ties in both the properties change due to stimulus and bending will enable us to predict the extent of bending and provide more controls over the extent of bending by adjusting other parameters. However, some of the specific physical properties and complex processes are challenging to quantify, and the relevance of analytical models is typically limited by the assumptions and approximations made [152]. Also, the prediction of shape morphing is confined to 2.5 D shape morphing (vertical projection from a 2D structure). The use of reversible 4D printing is expected to achieve more than just 2.5D shape morphing but also 3D-to-3D shape morphing.

The study by Mao et al. [41] used finite element method (FEM) simulation to better understand the thermomechanical properties of the SMP and the hydrogel swelling by using ABAQUS (Dassault Systems, Johnston, RI, USA).

Finite element method is a numerical method that solves partial differential equations in a few space variables and is useful in predicting stresses and structural responses [153]. Computational modelling allows simulation and the study of complex systems, which, in the case of the shape setting at the programming stage, has multiple variables leading to multiple physical fields [154].

2.5. Summary

Current 4D-printed parts lack reversibility. While there are studies that achieve reversible 4D-printing, the hydrogel-based printing lacks the mechanical strength and

the LCE based printing requires complex fabricating techniques. Although the studies each has limitations, both 4D-printings methods have common points in achieving reversibility. The studies suggest that the route to reversible 4D-printing is likely to be in achieving two or more different stimuli for actuation [29]. Inspirations can be drawn from the first few successful reversible 4D-printing [36, 41, 47] by using dual materials. For programming, it is necessary to introduce stress using a stimulus to the printed part. The expansion in one material of a dual material component can result in bending due to the difference in expansion. The expansion can be used for stress-inducing during programming. The mechanism for expansion can be chemo-responsive, specifically swelling. After devising a programming stage, it is essential to develop an analytical model so that the programmed 3D structure can be determined. Despite different programming mechanisms using different stimulus for inducing stress, a bilayer part can utilise beam theory to find the final curvature by combining other theories.

2.5.1. Mechanism for Programming

While the most widely used material for swelling is usually gels or hydrogels, there are other materials that are suitable for swelling too, as gels usually lack mechanical strength. Elastomers are generally capable of absorbing a large quantity of organic liquids [155]. Elastomer swelling has been observed by several studies to understand if the swelling will result in material degradation or fall in mechanical properties [156]. It has been used in the drilling of difficult oil and gas well [157, 158] in the last two decades too. Some fluids that have been tested are toluene and ethanol [159, 160]. In pure diffusion context, the lower the molecular weight, the faster the diffusion. This is known as Graham's law of effusion [161]. Therefore, it suggests

that low molecular alcohol swelling is a plausible solution, though the structure of the elastomer must have functional groups that attract alcohol groups. That will aid in the rate of swelling. In a review by Treloar [155], he reported the swelling and mechanical properties of rubber. A review by Ganji *et al.* on hydrogel swelling has a similar theoretical description of both elastomers and hydrogel [162]. Elastomer swelling will reduce the amount of materials needed as compared to the study by Mao *et al.* [41], and free the use of hydrogel due to the limitations in mechanical strength.

2.5.2. Mechanism for Recovery

For recovery, the mechanism used can be thermo-responsive. The DCM that was originally used for one-way shape memory uses a transition material and an elastomeric material. With the improvisation of the swelling of elastomer, the DCM can be used for reversible 4D-printing. Using a DCM requires a transition material and elastomeric material. This is particularly suitable because, in the programming stage, a swellable elastomeric material is already in place.

By using these two mechanisms, the elastomer functions as both the material to induce internal stress in the system for programming and the material to store elastic energy for recovery. The transition material can be in place to restrict the swelling so that it only occurs to one layer during programming and help to shape set after programming and recovery. These mechanisms used in a bilayer structure is lightly to retain good amount of strength as it eliminates the use of hydrogel that were used in various studies [36, 41, 42, 47]. To achieve a printing of a transition material and an elastomeric material, a multi-material printer will be needed, and Polyjet is a suitable additive manufacturing machine for this work [26, 163]. This method of

printing also helps eliminate the need for multi-technique and multi-platform used by Yuan *et al.* which are likely to incur more fabrication time and cost as a trade-off for the desired properties [44].

While most reversible 4D-printing studies assert the feasibility of shape programming and reversibility, the secondary shapes were approximated based on the design without any quantitative study on the final shape [36, 41, 42, 44, 47]. The lack of predictability makes it tough to design any functional 4D-printed devices as the dimensions of the morphed shape is left unknown. Hence, it is important to develop an analytical model to study the effect of the mechanisms on the bilayer structure and to predict the secondary shape of the structure.

Chapter 3 – Feasibility Study on a New Ethanol-Swell (et-Swell) Heat 4D-Printing Reversible Cycle

3.1. Background

Reversible shape morphing in 4D printing calls for a new reversible process, in which the mechanisms for programming and recovery must be determined. As described in Chapter 2, many of the 4D printing processes are achieved with manual programming by physically applying a force to turn a structure from 3D to 2D that later recovers back to 3D upon stimulation [28, 32, 33, 132, 164]. It is known that elastomer swells when placed in a solvent, and this solvent-stimulated swelling force has the same effect on shape morphing. Therefore, a similar concept to one-way 4D printing can be used by replacing the mechanical force applied to a transition material with the swelling force in the elastomer to bend the transition material. With stimuli-induced programming and recovery, reversibility is achieved with 4D-printed bilayer composite. Stimuli-induced actuation ensures that the precise shape is achieved in each cycle with controlled stimulation conditions. When a 4D-printed part is used reversibly, it is also vital to ensure that the same part can achieve a repeatable result, otherwise known as the repeatability. The part can then be used for numerous times as the function will not degrade over time.

4D-printing a composite requires a multi-material 3D printer. The most suitable 3D printing technique, described earlier in the previous chapter, is Polyjet inkjet printing, a single platform that can fabricate the required composite. The material used as a transition material is VeroWhitePlus (VWP), and the material used as an elastomer is TangoBlackPlus (TBP).

As such, a reversible process, with respective mechanisms for programming and recovery, is introduced. The feasibility of the 4D-printing process is investigated by using a bilayer composite part printed with Polyjet. Material characterisations are also carried out on the two selected materials for a better understanding of the material properties. The importance of reversibility is that every cycle leads to a precise shape morphing consistently. Therefore, the short-term repeatability of the reversibility of the 4D-printed parts is also studied.

3.2. et-Swell Heat 4D-Printing Reversible Cycle

The reversibility of the bilayer is achieved by two stimuli—ethanol and heat. Ethanol is used to induce swelling in the programming stage to cause a shape change from permanent shape 1 to permanent shape 2, as shown in Figure 3.1. Then, in the recovery stage, the heat is applied to stimulate a shape change from permanent shape 2 back to permanent shape 1. In detail, a bilayered sample is placed in ethanol at 25 °C for an hour in the first step. This step is to allow the elastomeric material to swell. Due to the compatibility of ethanol and the elastomer, ethanol diffuses in and stretches the elastomer. However, the swell-induced expansion of the elastomer creates stress in the transition material due to its inability to expand. In the second step, the strip is then removed from the ethanol to stop the swelling and placed in a water bath at 60 °C for 5 min. The glass transition temperature of VWP is 58 °C [165]. Therefore, a temperature higher than 58 °C was necessary to cause the transition material heats above its T_g and soften. 5 minutes was used to allow sufficient time for the sample to be heated uniformly and bend till it stops shape morphing. The reduction in stiffness allows the transition material to change its shape to release stress. Thirdly, the strip is then removed from the warm water and submerged in ice

water for approximately 1 min to allow the shape to set into the second permanent shape. The first three steps constitute the programming stage, after which, in the fourth step, the strip is dried for three hours to ensure complete removal of the ethanol within the elastomer. Lastly, the strip is heated in the 60 °C water bath (above the T_g of VWP) again to recovery back to the first permanent shape. The entire reversible cycle focuses mostly on developing a contactless, and stimulation-induced programming mechanism (swelling in ethanol) that works hand-in-hand with the well-established recovery to achieve the full reversible cycle.

Figure 3.1 The two main stages of the reversible cycle: programming and recovery. In the programming stage, there are three steps. Step 1: The first permanent shape is exposed to ethanol. Step 2: The component is removed from ethanol and heated at 60 °C in water to allow the second

permanent shape to form. Step 3: The component is cooled to allow the component to fix in the second permanent shape. In the recovery stage, there are two steps. Step 4: The component is left to dry. Step 5: The component is heated to recover to the first permanent shape.

3.3. Materials and Methods

3.3.1. Materials

All the samples were fabricated using an Objet500 Connex3 Polyjet printer (Stratasys, USA). In the current printing system, all materials were supplied by Stratasys. The materials used in the present research were based on two materials provided by Stratasys (USA): VeroWhitePlus and TangoBlackPlus (product codes from Stratasys are RGD835 and FLX980). VeroWhitePlus (VWP) is a hard and rigid material at room temperature with a glass transition temperature of 58 °C, whereas TangoBlackPlus (TBP) is soft and rubbery material at room temperature with a glass transition temperature of ~10 °C [165]. The TBP liquid resin comprises urethane acrylate oligomer, exo-1,7,7-trimethylbicyclo hept-2-yl acrylate, methacrylate oligomer, polyurethane resin, and a photoinitiator. The VWP 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 APC. Chemical Industries.

3.3.2. 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 μm for the x and y axes. The resins were cured by ultraviolet (UV) light within the printer.

3.3.3. Tensile Tests of VeroWhitePlus and TangoBlackPlus

The replicates were determined with a level of significance of 95% using a two-tail z-test with a true difference of 50MPa. The number of replicates was found to be 2.2. Therefore, 3 replicates of VWP were tested. The same number of replicates were used for TBP as it required 2.58 replicates to achieve a 95% confidence level using a two-tail z-test with a true difference of 0.5MPa. The true differences for both materials are different due to the range of the material strength. 3 replicates were used for both materials in the following tensile tests.

Both materials—VWP and TBP—were tested with the Shimadzu Universal Tester AGS-X series at 10 kN with the test structure compliant with ASTM D638 and ASTM D412, respectively, to obtain the tensile properties. The samples were loaded at 10 mm/min. Both materials were tested at 25 °C and 60 °C with three replicates. Before the testing was carried out, the samples were stabilised at the desired temperature for 30 minutes.

To obtain the Poisson's ratios and bulk moduli of both materials, biaxial tensile tests were carried out with the Shimadzu Universal Tester AGS-X series at 10 kN with the test structures of both materials printed with a thickness of 3 mm, a width of 20 mm, and a gauge length of 40 mm. The samples were loaded at 20 mm/min and tested at 60 °C with three replicates. The samples were stabilised at the temperature for 30 min before the testing was carried out. The strains measured were along the gauge length and along the width.

The equation of the bulk modulus at 60 °C is given as

$$K = \frac{E}{3(1-2\mu)}, \quad (3.1)$$

where E is the elastic modulus, and μ is the Poisson ratio at 60°C.

3.3.4. Swelling tests of TangoBlackPlus

There are two types of swelling ratios that were tested, the linear swelling ratio and the volumetric swelling ratio.

The two-tail z-test in an initial linear swelling test was used to determine the sample size used. It gave a result of more than 2.13 replicates were required to achieve 95% confidence level with a difference in length of 1mm between each replicate. Hence, a sample size of 3 of a thin beam of TBP with the dimensions 2 mm × 2 mm × 50 mm were printed. The beam lengths were measured and recorded with a pair of Vernier callipers; the beams were then soaked in ethanol for 24 h in a temperature of 25°C (room temperature), 30°C, 40°C, 50°C and 60 °C. After the beams were removed from ethanol, the final length of the thin beam was measured and recorded with a pair of Vernier callipers.

A one-way analysis of variance (ANOVA) was used to identify if the change in temperature results in a significant change in linear swelling ratio at equilibrium. ANOVA uses the *F* statistic to test the null hypotheses. From the *F* distribution table, with a probability of 5 %, if the critical *F* value is lower than the value found by experimental test, the temperature is concluded to have a significant effect on the linear swelling ratios.

Another linear swelling test was carried out with TBP beams of three measurements: 2 mm × 2 mm × 50 mm, 3 mm × 3 mm × 50 mm and 4 mm × 4 mm × 50 mm. The

beams were soaked into ethanol and measured every ten minutes until sixty minutes. The same experiment was also carried out in a temperature of 25°C (room temperature), 30°C, 40°C, 50°C and 60 °C.

Lastly, using an initial volumetric swelling test, the number of replicates to achieve 95% confidence level using a two-tail z-test is 1.33. Therefore, 2 sets of different shapes were printed of TBP and VWP: a cube with sides of 58.4 mm and a block with the dimensions 50 mm × 50 mm × 80 mm. These dimensions were used to maintain an approximate total volume of 200 000 mm³. Two different shapes were used to investigate whether the elastomer also swelled isotopically. The dry mass of the samples was first weighed using a Mettler Toledo XS204 analytical balance and recorded as m_d . The samples were then placed in ethanol for 24 h at temperatures of 25 °C, 30 °C, 40 °C, 50 °C, and 60 °C. The samples were removed and weighed again. The wet mass was recorded as m_w . The volume was calculated using the formula $v = \alpha \times \frac{m_d - m_w}{\rho_o - \rho_l}$, where $\alpha = 0.99985$, ρ_l is the density of the liquid substance, and ρ_o is the density of air [166].

3.3.5. Et-Swell Heat 4D-Printing Reversible Cycle

To demonstrate the reversible effect, a bilayered sample measuring 40 mm by 10 mm with a thickness of 1.5 mm of TBP and 1.5 mm of VWP was printed for this test. The sample was placed in ethanol at 25 °C for 1 hour and heated at 60 °C for a minute before it was cooled in cold water at 10 °C for approximately one minute. The sample was then removed, and a 1 N weight was placed on it. The sample was then left to dry for 3 hours before it was heated in hot water at 60 °C.

3.3.6. Repeatability Test

The experiment for repeatability is designed to test if the difference in the curvatures is significant with increasing cycles. Using preliminary average for the curvatures, a two-tail z-test was carried out to determine the number of replicates required to achieve 95% confidence test. The minimum number of replicates required was found to be 1.62 (considering both programming and recovery) with true differences of 1.5 m⁻¹. The following experiment was then carried out with 2 replicates. The factor in this test was the number of cycles. A total of 5 cycles were used to provide insight on the curvatures, whether they decrease over a short number of repeats.

The samples were printed 40 mm by 10 mm with thicknesses of 1.5 mm of VWP and 2.5 mm of TBP. The bilayer samples were soaked in ethanol at 45 °C for 60 min, before being heated at 60 °C for a minute. The samples were cooled in cold water at 10 °C for approximately one minute. The samples were clipped at the end to allow it to hold an upright position and photographed against a graph paper. The curvature was then evaluated using ImageJ using the formula (3.2). The samples were then heated in hot water at 60 °C until the samples straightened. The same process was carried out for another four cycles, for a total of 5 cycles. The radius is given as follows:

$$R = \frac{d^2 + 4e^2}{8e} \quad (3.2)$$

where R is the radius of curvature, e is the chord height, and d is the chord length (Figure 3.2).

The curvature is:

$$\kappa = \frac{1}{R} \quad (3.3)$$

Figure 3.2 Measurements of the radius.

An ANOVA for a single factor experiment was carried out using a F test statistic to test for null hypothesis for a probability of 5%. If the F value of the different cycles is lower than the critical value obtained from the F distribution table, it suggests that the differences between each cycle are not significant.

3.4. Results and Discussion

3.4.1. Material Characterisation

As shown in Table 1, the elastic modulus of VWP falls once VWP is heated above the T_g . The much higher elastic modulus at 25 °C ensures that the bilayer will be fixed to a rigid structure when cooled. As for TBP, the elastic modulus decreases slightly when heated. This finding suggests that there is little change in the mechanical properties of the TBP.

Table 1 Elastic modulus of VWP and TBP at 25 °C and 60 °C (N = 3)

	25 °C	60 °C
VeroWhitePlus	2136.56 MPa	175.0316 MPa
TangoBlackPlus	3.0549 MPa	2.2462 MPa
Hydrogel	1–10 kPa [167]	–
Grey60	546.235 MPa [41]	–

The general elastic modulus of a hydrogel falls within the range of 1 kPa to 10 kPa [167], while the combined elastic modulus of a 1:1 ratio of our sample has an upper bound elastic modulus of 1070 MPa and a lower bound of 6.101 MPa—at least 600 times higher than that of hydrogels. In the mix that Mao *et al.* [41] used, which was referred to as Grey60 (also known as DM8530), the SMP layer had a thickness of 0.5 mm, the TBP layer had a thickness of 1.5 mm, and the hydrogel layer had a thickness of 0.5 mm. DM8530 has an elastic modulus of 546.235 MPa, as found by Teoh *et al.* [168] in a study of the various composites formed by TBP and VWP. The elastic modulus of DM8530 was almost a quarter of that of the original VWP, which would result in lower stiffness. Lower stiffness was also evident in their study, in which only the swelling of the hydrogel before heating was able to cause significant bending.

The Poisson's ratio of TBP and VWP at 60 °C were found to be 0.4447 and 0.3214 using the biaxial tensile test. The results for both materials were close to results that were found from other studies [169-171]. A study by Li *et al.* reported the Poisson's ratio of TBP and VWP to be 0.49 and 0.33, respectively [171]. Using the obtained Poisson's ratios, the bulk moduli of TBP and VWP at room temperature were

calculated to be 50.8 MPa and 2.09 GPa, respectively, and the bulk moduli at 60 °C were 6.78 MPa and 163 MPa.

The stress-strain relationship at an elevated temperature of 60°C was obtained and plotted using ANSYS Curve Fitting Tool to test for Mooney Rivlin model with five parameters, as shown in Figure 3.3. Figure 3.3 shows that the Mooney-Rivlin material model with five parameters, nearly incompressible material and quadratic volumetric strain, were suitable for both VWP and TBP. The fitted curve provided five material constants, as shown in Appendix A. C_{10} represents the elastic behaviour of the polymer [172]. Therefore, the results suggest that even above T_g , VWP still display much higher stiffness than TBP.

Figure 3.3 Stress-strain relationship of (a) VWP at 60°C and (b) TBP at 60°C and Mooney Rivlin with five parameters, curve fit

3.4.2. Effect of temperature on the swelling of TangoBlackPlus and VeroWhitePlus at equilibrium

The linear swelling ratio of TBP in ethanol at room temperature was found to be 1.226, and the volumetric swelling ratio of TBP was found to be 1.843 (Table 2). The swelling is also found to be isotropic as the average volumetric swelling for the bar shape, and cubic shape were almost identical. The linear swelling ratio reached up to 1.652, and the volumetric ratio reached up to 4.506 at 60 °C (Table 2). An analysis of variance (ANOVA) for a single factor experiment in Appendix B was carried out to determine if the results statistically show that temperature has an effect on the swelling ratio. From the F distribution table, the $F_{0.05, 4, 10}$ is 3.4780. The F_0 value for the temperature affecting the swelling ratio of TBP is 935.68, which is larger than $F_{0.05, 4, 10}$. Thus, this shows that temperature has a significant effect on the ethanol swelling of TBP at equilibrium. However, for VWP, the ANOVA shows that the F_0 value for the temperature affecting the swelling ratio of VWP is 3.409, which is less than the $F_{0.05, 4, 10}$, suggesting that temperature does not affect the swelling of VWP at equilibrium. The slight differences could be due to measurement errors. Since the volumetric swelling remained consistently low between 1 and 1.016, it was assumed to be negligible.

The one-hour linear swelling test was used to obtain the diffusion exponential coefficient, n . This duration was used due to the required duration in the et-swell heat 4D printing reversible cycle for swelling. The values range between 0.51 and 0.7 (Appendix C). Fickian diffusion will give a value of around 0.5. However, on average, the diffusion exponential is 0.61, which is much higher than the diffusion exponential of Fickian diffusion. 0.61 will fall in the range of anomalous transport. This value is

also further used in the prediction of the curvature of the programming stage of the bilayer model.

From the equilibrium swelling ratios, the Flory-Huggins parameter were estimated, and the amount of swelling content at equilibrium was obtained. The swelling content indicated the percentage of the volume of ethanol in the elastomer. As shown in Table 2, the amount of swelling content at the equilibrium state increased from 84.28% to 195.5%. Figure 3.4 shows that the Flory-Huggins parameter followed a negative power law, which suggests that as the temperature increases further, the change in the value of the parameter would be less significant than that at lower temperatures. This finding suggests that when the average temperature increases, the amount of swelling also increases.

Table 3 Linear swelling ratios ($N = 3$), Volumetric swelling ratios ($N = 4$) and the average swelling content at equilibrium.

Temperature (°C)	Linear swelling ratio	Volumetric swelling ratio	Swelling content at equilibrium
25	1.226	1.843	0.8428
30	1.362	2.527	1.0864
40	1.461	3.121	1.3841
50	1.550	3.722	1.6493
60	1.652	4.506	1.9550

Figure 3.4 Graph of the Flory-Huggins parameter against temperature.

The Flory-Huggins parameter is a unitless quantity that functions as an exchange parameter in the lattice model of the polymer solution [173]. The higher the Flory-Huggins parameter, the more resistance there is for the solution to enter the polymer matrix, and the less dissolution occurs. In this case, the increase of temperature encourages more mixing of the solvent into the polymer matrix, as the mixing is likely to occur for entropic reasons [174]. As the temperature increases, the affinity between the ethanol and the polymer structure increases. These swelling forces can be converted to the forces required to induce stress on the SMP, the transition material—in this case, VWP. However, it is essential to note that the method described here is

not the empirical method to obtain the Flory-Huggins parameter; rather, it is just an estimate using the Flory-Rehner equation for further study.

The temperature range for this study lay between the temperatures of 25 °C and 60 °C. The projected operating temperature should fall within this temperature range. Therefore, the temperature above 60 °C was not considered, as the solvent is volatile above 60 °C since the boiling point of ethanol is 78.37 °C. This range is particularly desirable because the T_g of VWP is 58 °C [165]. Between 25 °C and 50 °C, the cycle must be carried out in five separate steps. Between 50 °C and 60 °C, the cycle can be carried out in four steps, by combining Steps 1 and 2. However, the high-temperature heating of ethanol is not desirable. It was observed that the TBP tended to degrade after being removed from ethanol at 60 °C after some time. This degradation was likely due to the contraction and the evaporation of the surface ethanol molecules. After the TBP was removed from the heated ethanol, the surface cooled down faster than the core. Therefore, it contracted faster. This situation was exacerbated by the volatility of the ethanol molecules at 60 °C. When the swollen TBP was removed from the ethanol solution, the ethanol molecules near the surface would diffuse out or vaporise faster than the ethanol molecules in the core, resulting in the formation of cracks. Also, ethanol can dissolve some acrylics. At high temperature, the ethanol molecules might break up some of the polymer chains over time.

3.4.3. Printing Design

As mentioned in section 2.3., mechanisms used for programming and recovery respectively can be swelling and heat. The working principle of the printing design in this study is akin to the use of DCM in conventional one-way 4D printing. During

the programming stage of conventional DCM one-way 4D printing, a mechanical force is usually applied to the printed part when it is heated above the T_g . Inspired by the swelling of the hydrogel in the study by Mao *et al.* [41], this study used the swelling to replace the mechanical force that is applied too. However, instead of the swelling of a hydrogel, the swelling of elastomer was used. The swelling due to diffusion of ethanol molecules into the free volume of the elastomer and not the transition material creates an asymmetrical swelling and difference in strain between the elastomer and the transition material. The induced strain exerts a force on the transition material. After the swelling, the part is heated above T_g to allow shape change. As the entire printed part is heated above T_g , the transition material becomes rubbery, and the bilayer part bends under the exerted strain. The part is then quenched in cold water to freeze the microstructure of the transition material by cooling the transition material below its T_g to restore its stiffness and fix the shape. During the process of drying, elastic energy is restored in the elastomer. When heated above the T_g , the elastomer acts as a spring pulling the component back into its original shape. In the end, the printed part is allowed to cool down to room temperature to fix the shape again.

Similar to Mao *et al.* [41], multiple materials and multiple stimuli were used. However, a bilayer was deployed instead of a triple-layer, as shown in Figure 3.5. The first layer is an elastomer, and the second layer is a transition material, also known as the shape-setting polymer. The shape-setting polymer does not swell in the presence of the solvent that is used to swell the elastomer. The elastomer replaces the function of the hydrogel in the trilayer component. The swelling of the elastomer elongates the elastomeric section and creates a difference in length. Due to the

mismatch in length, the elastomer exerts a force on the shape-setting polymer. After the shape-setting polymer is heated past the T_g , bending occurs, thus enabling self-actuation in the programming stage. By introducing elastomer swelling into the design, the number of layers is reduced to two. The elimination of the hydrogel reduces the materials required to achieve reversible 4D printing. The use of fewer layers and materials simplifies the design and brings convenience to the designer.

Figure 3.5 A comparison of (a) our new design with (b) the existing design.

In the new design, VWP is used as the transition material, as its T_g is 58 °C, according to its manufacturer, Stratasys [165]. The high T_g of VWP enables the bilayer to operate at about 60 °C; furthermore, this material is known to have a reasonable recovery rate of about 97% [168].

TBP is used as the elastomeric material, as its T_g is ~10 °C, according to Stratasys [165]. TBP has a sufficiently low enough T_g to ensure that it stays rubbery which is required to retain elastic energy when the material is cooled down. Besides, a large amount of volumetric swelling (described in Section 3.4.2.) suggests that this is a suitable material to carry out the dual function of exerting stress in the programming stage and storing elastic energy for the recovery stage.

3.4.4. Demonstration of Reversibility

Reversibility was demonstrated using a simple print of the dual flat layers. Figure 3.6 shows the feasibility of using a swellable elastomer to achieve the intended shape, shown in the schematic diagram earlier in Figure 3.1.

Figure 3.6 Experimental samples of the et-swell heat 4D printing reversible cycle. Programming steps: (a) Side view of the original printed sample; (b) side view of the sample after being soaked in ethanol at 25 °C for one h; (c) side view of the sample after it was placed in 60 °C water and then into ice water, and then removed. A 1 N weight is placed on the sample. Recovery steps: (d) Side view of the sample left to dry for 3 h; (e) side view of the sample after being heated at 60 °C.

There were three steps in the programming stage and two steps in the recovery stage of the cycle. Step 1 was to immerse the part that is shown in Figure 3.5a in ethanol. Ethanol diffused into the elastomeric section. The overall volume of the elastomeric section increased, as the ethanol molecules diffused into the free volume and space between chains. However, the internal stress caused by the difference in volume and strain is insufficient to overcome the mechanical stiffness of the transition material at a temperature below the glass transition temperature, as the material is still glassy as shown in Figure 3.5b. The bilayer part could only bend slightly. The part was soaked in 60 °C of hot water to heat the part above the glass transition temperature of the transition material. This step is carried out to soften the transition material; the mechanical strength of the material will decrease significantly. The internal stress is relieved by the shape change, leading to a second permanent shape formation. Step 3 was to cool the component. Step 3 is a necessary step to bring the temperature to below the glass transition temperature of the transition material will freeze the microstructure of the transition component. The mechanical strength will return to the original state where it is stiff and set the shape as depicted in Figure 3.5c. A payload of 1 N was placed on the sample to demonstrate the load-bearing capability of the part after shape-changing. Step 4 is to allow the component to dry. As the ethanol evaporates and diffuses out of the elastomeric material, the elasticity of the material will return. The volume decreases, and the elastomer will act as a spring pulling the component back into its original shape; however, it is unable to overcome the mechanical strength of the transition material. The shape retention ability is shown in Figure 3.5d, where the curvature still looked similar to the curvature in Figure 3.5c. Elastic potential energy was stored in the elastomeric material. Step 4 is

a transition step; after the first three steps, the component can already be at full functionality. Once Step 5 is carried out, heating the material above the glass transition temperature, the transition material softens and decreases in mechanical strength. The elastic energy of the elastomer pulls it back into the first permanent shape, as shown in Figure 3.5e, thus completing a cycle. The whole process takes a total of slightly more than four hours from programming to drying and recovery. This duration suggests that this technique is only suitable for slow actuation.

3.4.5. Repeatability

A reversible 4D printed part is not practical if it is not able to withstand shape change multiple times. The part needs to be able to repeat its performance. The test was carried out with 2 replicates for 5 cycles. Only 5 cycles were recorded as the purpose of this test was to assert the short-term repeatability. Figure 3.7a shows the photos taken after the programming and recovery stages. After the first, second, or even fifth actuation, the amount of curvature remained similar at approximately 25 m^{-1} , as shown in Figure 3.7b. The ANOVA to determine if the curvatures after programming at different cycle were significantly different was carried out and shown in Appendix D. A null hypothesis will suggest that the number of cycles has no effect on the curvatures after the programming stage. Since, F_0 (1.8841) is smaller than $F_{0.05, 4, 5}$ (5.1922), statistically, it shows that the curvatures were not affected by the number of cycles. Similarly, after the recovery stage, the sample was able to return to a straight shape of a curvature $\sim 0 \text{ m}^{-1}$. The ANOVA result for the recovery stage shows that the F_0 (1.083449) is smaller than $F_{0.05, 4, 5}$ (5.1922), suggesting that the curvatures obtained after recovery was also not affected by the number of cycles it has experienced. However, it is essential to note that after multiple recoveries and up to

10 repeated cycles, the VWP started to creep slightly when the structure was left to dry. As mentioned in section 3.4.2, ethanol could have dissolved some of the acrylics. It might have damaged the polymer chains of VWP in the long run too.

Figure 3.7 Actuation results showing the actuation and recovery. a) Snapshots of the bilayer sample before actuation, after actuation and after recovery. b) Curvatures of the bilayer sample in cycle 1-5.

3.5.Conclusion

Using a design that previously could only achieve one-way 4D printing, the introduction of the new et-swell heat 4D printing reversible cycle allows a dual component composite to achieve reversibility. The proposed cycle is driven by stimuli-based programming and recovery. The feasibility of this et-swell heat-driven reversible cycle is proven in this chapter using VWP as the transition material and TBP as the elastomer in a bilayer slab. A large amount of swelling of the TBP in ethanol makes it a suitable elastomer to induce stress on the transition material, VWP. VWP makes a good transition material too, as it has a high stiffness when it is in room temperature, making it an excellent material for shape-setting. The bilayer

samples are also tested to be repeatable within 5 cycles as the curvatures obtained for subsequent programming are similar, showing no significant decrease in curvature.

Chapter 4 – Analytical and Simulation Models

4.1. Background

The earlier chapter has shown that the new reversible cycle using just two materials are feasible. In this chapter, the predictability and possible control over the shape morphing are introduced. Up to now, the extent of the shape morphing during programming is only mostly investigated experimentally. An analytical model that combines a series of theories is created to assist in predicting the curvature of the 4D printed structure after programming by adjusting other parameters such as temperature and thickness.

However, as described in Chapter 2.4, analytical models are insufficient for in-depth studies such as stress distribution and the physics involved [152]. Therefore, another modelling method, Multiphysics FEM, is also suggested in this chapter. Multiphysics is able to study the structural responses in complex systems [153], making it ideal for studying the programming stage and also to predict the programming deformation of the bilayer composite due to multiple space variables. By utilising a more accurate material model, the simulation results obtained may provide better precision in the prediction and control in the shape morphing.

4.2. Analytical Model

Since the recovery stage has been widely studied in one-way 4D printing actuated by heat, our focus is on shape-setting stimulated by swelling, which comprises steps 1 and 2. A model is essential to predict the curvature that can be obtained in shape-setting.

A predictive analytical model was obtained by improving on the Flory Rehner equation, the Peppas model, and the mechanics of composites. The swelling of the elastomer can be described and predicted with the Peppas model. The swelling rate of the equilibrium is determined by the Flory Rehner equation [175].

$$\ln(1 - v_2) + v_2 + \chi v_2^2 = -\frac{\rho V_1}{M_c} v_2^{\frac{1}{3}} \quad (4.1)$$

where v_2 is the polymer volume fraction, χ is the Flory-Huggins interaction parameter, ρ is the density of the polymer, V_1 is the molar volume of the solvent, and M_c is the mean molecular weight of the chains between each successive crosslink.

From the Flory Rehner equation, the polymer volume fraction of v_2 can be found. The equilibrium volume is given as follows:

$$\frac{V_\infty}{V_d} = \frac{1}{v_2} \quad (4.2)$$

where V_d is the dry volume of the elastomer and V_∞ is the equilibrium volume of the swollen elastomer.

The swelling content, which is also known as the ratio of swelling agent to the dry volume of elastomer, is found using the following equation:

$$S_\infty = \frac{V_\infty - V_d}{V_d} \quad (4.3)$$

To determine the swelling content at various time points, two models are used separately, as each has its own limitations. For short diffusion times, where the fraction of swelling content $\frac{S_t}{S_\infty} < 0.6$, the Peppas model will be used. This model is described by a power law:

$$\frac{S_t}{S_\infty} = kt^n \quad (4.4)$$

where S_t is the swelling content at time t , k is a constant that changes according to the network and geometric structure, and n is the diffusion exponential of the solvent. The constants can be obtained by solving Fick's second law of diffusion [176], which is given as follows:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(\frac{\partial c}{\partial x} \right) \quad (4.5)$$

where c is the concentration of the solvent and x is the distance.

For diffusion into a slab of thickness $2h$, the concentration c_t at any point within the film at time t can be found by the following:

$$\frac{c_t}{c_\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left(\frac{-D(2n+1)^2 \pi^2 t}{4h^2} \right) \times \cos \left(\frac{(2n+1)\pi x}{2h} \right) \quad (4.6)$$

where D is the diffusion coefficient.

By integrating Eq. (6), the following equation can be obtained:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left(\frac{-D(2n+1)^2 \pi^2 t}{4h^2} \right) \quad (4.7)$$

where M_t is the mass of the solvent as a function of time, and M_∞ is the equilibrium mass.

For short times, Eq. (7) is reduced to be somewhat similar to the Peppas model [150] in Eq. (4),

$$\frac{M_t}{M_\infty} = \frac{2}{h} \left(\frac{D}{\pi} \right)^n t^n \quad (4.8)$$

Therefore, the constant k is $\frac{2}{h} \left(\frac{D}{\pi} \right)^n$.

The mass diffusivity is governed by an exponential equation that is temperature dependent:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4.9)$$

where D_0 is the maximal diffusion coefficient, E_a is the activation energy for diffusion, R is the universal gas constant and T is the absolute temperature.

Combining Eq. (9) with Peppas' model, the following equations are obtained:

$$\frac{S_t}{S_\infty} = \frac{2}{h} \left(\frac{D_0 t}{\pi} \exp\left(-\frac{E_a}{RT}\right) \right)^n \quad (4.10)$$

For the 4D-printed component, the swellable elastomer on only one side of the slab allows the solvent to diffuse in; therefore, the whole equation is divided by two for the component.

$$\frac{S_t}{S_\infty} = \frac{1}{h_e} \left(\frac{D_0 t}{\pi} \exp\left(-\frac{E_a}{RT}\right) \right)^n \quad (4.11)$$

where h_e is the thickness of the elastomer.

To find the swelling content that is present in the elastomer at a given time, temperature, and thickness, the following equation is used:

$$V_t = S_t V_d + V_d \quad (4.12)$$

Assuming that the swelling is isotropic, the linear swelling ratio at time t will be

$$\lambda_t = \left(\frac{V_t}{V_d} \right)^{\frac{1}{3}} = (S_t + 1)^{\frac{1}{3}} \quad (4.13)$$

Since

$$\varepsilon_x = \lambda_t - 1 \quad (4.14)$$

where ϵ_x is the strain along the x -axis.

Therefore,

$$\epsilon_x = \left(\frac{S_\infty}{h_e} \left(\frac{D_0 t}{\pi} \exp \left(-\frac{Ea}{RT} \right) \right)^n + 1 \right)^{\frac{1}{3}} - 1 \quad (4.15)$$

In the case that the two layers of transition material and elastomer are not bonded, the swelling of the elastomer will bring about an increase in the strain that does not exist for the transition material. When they are bonded, the mismatch in strain will result in stress that forces the transition material to bend. However, the mechanical strength of the transition material is high at room temperature. The bending force created is insufficient to cause considerable bending (Figure 4.1). Therefore, the transition component is heated above its glass transition temperature. Now, the stiffness of the transition material decreases, enabling the component to bend further. This structure is a dual-layer composite, and the curvature is calculated using the mechanics of composites. The difference in strain due to the difference in thermal expansion coefficient is assumed to be negligible [32].

Figure 4.1 Illustration of the effects of elongation of the elastomer when unbonded and bonded to the transition material. When bonded, the mismatch in strain results in curvature.

To simplify the model, it is assumed that there are two laminates in the model. In the mechanics of a composite, the plane sections normal to the longitudinal axis remain plane and normal during bending. Hence,

$$\epsilon_x = \frac{(r+z)\Phi - r\Phi}{r\Phi} = \frac{z}{r} \quad (4.16)$$

where r is the radius of curvature of the neutral surface during bending, Φ is the angle of the bent material, and z is the furthest distance from the neutral surface defined by the xy plane, which is the neutral axis of the bilayer. z is taken to be the furthest distance, as the elastic modulus of the elastomer tends to be much lower than that of the transition material. To determine the neutral axis of the bilayer, it is first necessary to determine the ratio of the elastic modulus of VeroWhitePlus to the elastic modulus of TangoBlackPlus:

$$\text{ratio} = \frac{E_T}{E_e} \quad (4.17)$$

where E_T is the elastic modulus of the transition material at 60 °C, and E_e is the elastic modulus of the elastomer at 60 °C.

The bilayer is shown in Figure 4.2.

Figure 4.2 Height and width of the bilayer.

The actual area of the cross-section is given as follows:

$$A_a = w \times h \quad (4.18)$$

Using the smaller elastic modulus as a base, the area of the elastomer will be:

$$A_e = w_e \times h_e \quad (4.19)$$

Assuming the bending occurred in a homogeneous material, the difference in the elastic modulus is considered and the centroid axis for the transition material must be normalised; hence, it is necessary to factor in the ratio of the elastic modulus of the transition material to the elastic modulus of the elastomer to the area:

$$A_T = w_T \times h_T \times \frac{E_T}{E_e} \quad (4.20)$$

The distances from base to the neutral axes, c_T and c_e , for the respective materials are as follows:

$$c_T = h_e + \frac{h_T}{2} \quad (4.21)$$

$$c_e = \frac{h_e}{2} \quad (4.22)$$

The neutral axis of the bilayer, z , will be:

$$Z = \frac{c_T \times A_T + c_e \times A_e}{A_T + A_e} \quad (4.23)$$

$$Z = \frac{c_T \times w_T \times h_T \times \frac{E_T}{E_e} + c_e \times w_e \times h_e}{w_T \times h_T \times \frac{E_T}{E_e} + w_e \times h_e} \quad (4.24)$$

The equation for the curvature κ obtained is as follows:

$$\kappa = \frac{1}{z} \left(\frac{S_\infty}{h} \left(\frac{D_0 t}{\pi} \exp \left(-\frac{Ea}{RT} \right) \right)^n + 1 \right)^{\frac{1}{3}} - 1 \quad (4.25)$$

$$\kappa = \frac{w_T \times h_T \times \frac{E_T}{E_e} + w_e \times h_e}{c_T \times w_T \times h_T \times \frac{E_T}{E_e} + c_e \times w_e \times h_e} \left(\frac{S_\infty}{h_e} \left(\frac{D_0 t}{\pi} \exp \left(-\frac{Ea}{RT} \right) \right)^n + 1 \right)^{\frac{1}{3}} - 1 \quad (4.26)$$

where κ is the curvature.

For example, the predicted curvature of a bilayer sample with a TBP thickness of 1.5mm and VWP thickness of 1.5 mm and length of 60 mm at 25 °C for 60 minutes can be obtained using the analytical model. The plotted χ values in Figure 3.4 at 25 °C were used to obtain the χ value which is 0.79. The polymer volume fraction v_2 can be calculated using equation (4.1). The material constants are obtained from Appendix E.

$$\ln(1 - v_2) + v_2 + (0.79)v_2^2 = -\frac{(1.13)(58.5)}{11429}v_2^{\frac{1}{3}} \quad (4.27)$$

$$v_2 = 0.5427 \quad (4.28)$$

Replacing, v_2 , the equilibrium volume of the polymer into equation (4.2) can be obtained:

$$\frac{V_\infty}{200} = \frac{1}{0.5427} \quad (4.29)$$

$$V_\infty = 368.5 \text{ cm}^3 \quad (4.30)$$

The equilibrium swelling content using equation (4.3):

$$S_\infty = \frac{368.5-200}{200} = 0.843 \quad (4.31)$$

The other independent variables such as thicknesses, time and temperature are substituted into equation (4.26). The Young moduli were obtained experimentally in Chapter 3.4.1.

$$\kappa = \frac{0.06 \times 0.0015 \times \frac{E_T}{E_e} + 0.06 \times 0.0015}{0.00225 \times 0.06 \times 0.0015 \times \frac{E_T}{E_e} + 0.00075 \times 0.06 \times 0.0015} \left(\frac{0.843}{0.0015} \left(\frac{D_0(60)}{\pi} \exp \left(-\frac{E_a}{R(298.15)} \right) \right)^{0.61} + 1 \right)^{\frac{1}{3}} - 1 \quad (4.32)$$

$$\kappa = 15.19 \text{ m}^{-1} \quad (4.33)$$

4.3. Simulation Model

Likewise, the FEA was conducted on the programming stage. Using COMSOL Multiphysics 5.4 software, the FEA can be carried out by determining the amount of stimuli acting on the designed bilayer. To achieve accurate results, the material model has to be determined. The material model defines how the materials respond to stimuli. The material models and the specific study used in COMSOL MultiPhysics 5.4 are further introduced in the following subsection.

4.3.1. Material Model

Similar to the analytical model, the part is assumed to be a bilayer part bonded at the interface. In the analytical model, the materials were assumed to be linear elastic. However, in reality, elastomeric materials are usually hyperelastic [177]. In Chapter 3, the material characterisation shows that both materials used were hyperelastic at above T_g . At a temperature of above T_g , even the transition material displayed elastomeric properties. Hence, it is safe to assume that both the transition material and elastomeric material may share the same material model. The material model chosen was the Mooney-Rivlin model, one of the various models that are used for hyperelastic materials [178]. For a uniaxial tensile test, the Mooney-Rivlin material model was able to give a good prediction to experimental results from Treloar [155, 177]. There are variations of the Mooney-Rivlin model with different parameters

such as two, three, five or nine parameters. The number of inflection points in the stress-strain curves determines the number of parameters used [172].

The uni-axial tensile tests show that both materials fit well with the five-parameter Mooney-Rivlin model. Hence, this model is used in this study. The strain density function, W , of the five-parameter Mooney-Rivlin model is given as [179]:

$$W_{(5)} = C_{10}(\bar{I}_1 - 3) + C_{01}(\bar{I}_2 - 3) + C_{20}(\bar{I}_1 - 3)^2 + C_{02}(\bar{I}_2 - 3)^2 + C_{11}(\bar{I}_1 - 3)(\bar{I}_2 - 3) + \frac{1}{2}K(J - 1)^2 \quad (4.27)$$

where C_{10} , C_{01} , C_{20} , C_{02} and C_{11} are the material constants, K is the bulk modulus, and $\bar{I}_1$ and $\bar{I}_2$ are the strain invariant. The material constants can be obtained from experimental data.

The strain invariants are functions of principal stretch, λ_1 , λ_2 and λ_3 . However, due to the assumption of incompressible materials, the invariant $\bar{I}_3$ is equal to one [180].

$$\bar{I}_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2, \quad (4.28)$$

$$\bar{I}_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 \quad (4.29)$$

$$\bar{I}_3 = \lambda_1^2\lambda_2^2\lambda_3^2 \quad (4.30)$$

Under the assumption of incompressibility ($J = 1$), the principal stretches for uniaxial deformation of an isotropic, hyperelastic material are given as:

$$\lambda_1 = \lambda, \lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}} \quad (4.31)$$

4.3.2. Multiphysics software

The solid mechanic module of COMSOL MultiPhysics 5.4 with a stationary study is used to conduct the simulation of the shape morphing. The materials, as established in section 3.3.1., are hyperelastic, and the material model was five-parameter Mooney-Rivlin. For a stationary study:

$$0 = \nabla \cdot (FS)^T + Fv, F = I + \nabla \mathbf{u} \quad (4.32)$$

where F is the deformation gradient, S is the 2nd Piola-Kirchhoff stress, I is the second-order unit tensor, and $\mathbf{u}$ is the displacement.

The 2nd Piola-Kirchhoff stress is defined as

$$S = S_{\text{ext}} + \frac{\partial W(S)}{\partial \varepsilon}, \sigma = J^{-1}FSF^T \quad (4.33)$$

Where $J = \det (F)$.

The strain is given as

$$\varepsilon = \frac{1}{2}(F^T F - I) \quad (4.34)$$

4.4. Validation of the analytical model and simulation model

The validation of both models was carried out by comparing the obtained values with the experimental results. The initial results of the curvature test show that a minimum number of replicates to achieve 95% confidence level with an acceptance difference of 5 m^{-1} in a two-tail z-test is 2.00. For better assurance, a sample size of three replicates of bilayer components of TBP and VWP with a length of 40 mm, a width of 10 mm, TBP of varying thickness of 1.5 mm, 2 mm, 2.5 mm, 3 mm, and 3.5 mm, and VWP of a standard thickness of 1.5 mm were used. They were printed and soaked in ethanol at the four different temperatures of 25 °C, 35 °C, 45 °C, and 55 °C for 60

min. Next, the components were heated to above 60 °C (which is above the T_g of VWP) in water for 1 min to allow the VWP to be heated past its T_g . The components were quickly removed and placed in cold water at 10 °C in order to cool the component rapidly. The samples were then removed and placed on grid paper. The curvatures were determined by measuring the chord length and chord height with a pair of Vernier callipers and calculated using the equations (3.2) and (3.3).

Similarly, three bilayer components of TBP and VWP with a length of 40 mm, a width of 10 mm, VWP of varying thickness of 1.5 mm, 2 mm, 2.5 mm, 3 mm, and 3.5 mm of VWP, and TBP of a standard thickness of 1.5 mm were printed and soaked in the four different temperatures of 25 °C, 35 °C, 45 °C and 55 °C for 60 min.

Two-way ANOVAs were carried out on the derived analytical and simulation models to evaluate the significances of the models. An F statistic is used to test the null hypothesis. The null hypotheses are that the analytical model and the simulation model provides an accurate prediction of the curvatures. From the F distribution table, with a probability of 5 %, if the F values of the models are lower than the critical value, models are concluded to be able to accurately predict the model within the set of conditions.

4.5. Results and Discussion

4.5.1. Validation of the analytical model

The analytical model was created primarily based on a mixture of theories such as the Flory-Rehner equation, Peppas model, and mechanics of composite. Flory-Rehner equation is used to describe the equilibrium swelling of a lightly crosslinked polymers in terms of crosslinked density and quality of solvent. However, to optimise

the swelling time, equilibrium swelling is too time-consuming. Therefore, in the analytical model, it is used to determine the equilibrium swelling only. Peppas model, on the other hand, is a power law that is able to predict the swelling of a gel matrix. However, it is usually used to describe a diffusion/drug release mechanism. In this analytical model created, it is used to determine the swelling content over time. The novelty of the analytical model is translating the swelling content into strain so that it can be used in mechanics of composite as a laminate to predict the shape change in 2D.

To validate the above model, experimental curvature results and the calculated curvature values from the above model were compared with varying temperatures and thicknesses of the materials. Some constants such as n , S_{∞} , E_e and E_T were obtained in Chapter 3.4.1 and 3.4.2. S_{∞} corresponds to the swelling content at equilibrium in Table 2. n was found to be 0.61. The model considers that the sample is placed in ethanol and the sample is heated above its T_g , so E_e and E_T at 60 °C are 2.2462 MPa and 175.0316 MPa, respectively, which correspond to the elastic moduli of TBP and VWP at 60 °C. The maximal diffusion constant is assumed to be 1.15×10^{-5} , as shown in Appendix E, and the activation energy is assumed to be 14000 J, by determining the mass diffusivity experimentally. The swelling time was fixed to 1 hour as the above constants were determined at 1 hour of swelling time.

The curvatures predicted by the analytical model and experimental results are plotted against temperature and the different material thicknesses: the thickness of elastomer and the thickness of transition material. The materials used to simulate the curvatures were TBP, as the elastomer, and VWP, as the transition material.

4.5.1.1. Effect of the thickness of elastomer and temperature on the curvatures of the bilayer slab

The curvatures were calculated using Eq. (4.26) with the material parameters listed in Appendix E. A parameter that will affect the curvature is the thickness of the elastomer. The thickness of the elastomer plays a role in two sections of the final equation, Eq. (4.26). It contributes to the z value, which helps to determine the stiffness of the bilayer, and it also contributes to finding the swelling content in the elastomer. The swelling content and the thickness of the elastomer are inversely correlated, as shown in Eq. (4.11). However, the increase in the thickness of elastomer only increases the z value slightly as the elastic modulus of the elastomer (2.25MPa) is over 80 times smaller than the elastic modulus of the transition material (175.0MPa). Therefore, a change in curvature, with varying thickness of the elastomer, is primarily caused by the decrease in swelling content.

The curvature is plotted against the thickness of the elastomer, TBP, at four different temperature points from 25 °C to 55 °C, which are the expected operating temperatures of the bilayer part, as shown in Figure 4.3. A 1.5–3.5 mm thickness is used in consideration of diffusion. Further increase in thickness results in negligible induced curvature. In theory, the smaller the thickness of the elastomer, the larger the curvature, as shown in Figure 4.3. The same relationship is reflected in the experimental results too. A smaller thickness allows a larger exposed surface area, resulting in a higher percentage of the volume of ethanol to the volume of elastomer, which gives rise to more bending. With a smaller thickness, the z value decreases too, allowing slightly more bending due to lower stiffness. The time of swelling is limited

to 1 h. It is faster for the ethanol molecules to penetrate and diffuse into the area nearer to the neutral axis for a smaller thickness than for a larger thickness.

Figure 4.3 Graphs of curvature against the thickness of TBP at different temperatures. (a) 25 °C; (b) 35 °C; (c) 45 °C; (d) 55 °C with a fixed 1.5mm-thick VWP (N=3). The experimental results were plotted using a curve-dot plot.

The curvatures at each thickness across the temperature range are higher when the temperature is higher. The results were expected as higher temperature indicates a higher mass diffusivity (Eq. (4.9)). Higher mass diffusivity suggests that more ethanol can diffuse into the matrix of the elastomer, providing a larger bending force as there is a more significant difference in strain. As mentioned earlier, the temperature also affects the affinity between the elastomer and the ethanol.

Figure 4.3a shows that at 25 °C for every thickness, the theoretical model and experimental results are very close. The average degree of discrepancy is 3.92 % at

25 °C (Appendix F). This result demonstrates that at 25 °C, the model can predict the curvature with a high degree of accuracy. At the temperatures from 35 °C to 55 °C, the results show a considerable parity between the theoretical and experimental results at smaller thicknesses (Figure 4.3b–d). The difference narrows down at about 3 mm for 35 °C and 45 °C (Figure 4.3b and c). This intersection occurs at 3.5 mm at 55 °C (Figure 4.3d). The percentage of parity for rising temperature increases at an increasing rate from an average of 3.92 % at 25 °C to 14.24 % at 55 °C. On average, the model can predict the curvatures at higher accuracy as the thickness increases, especially between 2 mm to 3 mm where the difference of approximately 5%. When the thickness is smaller, the total surface area of the elastomer exposed is higher. Once the bilayer strip is removed from ethanol and exposed to the air, ethanol diffuses out quickly. Therefore, the larger the exposed surface area is, the larger the loss of the percentage of ethanol from the elastomer will be. Likewise, at a higher temperature, ethanol will be more volatile. Thus, once the dual-layer strip is removed, a significant amount of ethanol will diffuse out of the elastomer and reduce the amount of swelling force.

The increasing parity at a smaller thickness and higher temperature can be attributed to the percentage of swelling content in the elastomer too. The equation that is used to predict the behaviour is based on the Peppas model and it can model up to a swellable content of 60%. At higher temperatures, especially at 55 °C with a thickness of less than 2.5 mm and with soaking for 1 h, the amount of swelling content exceeds 60% and deviates from the Peppas model. Hence, the model is not able to predict the curvature accurately at higher temperatures.

Another possible reason could be the analytical model assumed that the materials are linear elastic. However, in reality, TBP is more hyperelastic than linear elastic. Therefore, it accounts for the increase in parity between experimental and theoretical results when the temperature increased.

Generally, based on the ANOVA results, shown in Appendix G, the analytical model is only able to predict the curvature accurately at 25 °C, as the theoretical results do not have a significant difference from the experimental results. Beyond that, there is a significant difference between the theoretical and the experimental curvatures.

Combining the qualitative analysis and the statistical analysis of the model and the experimental results, while the model is not able to predict as accurately at extremes, within the temperature range of 25–45 °C and for a thickness ranging from 2 mm to 3.5 mm, the model is still able to predict the curvature to a high degree of accuracy with an average discrepancy of less than 10%, especially at 25 °C where this is no significant difference between the two.

4.5.1.2. Effect of the thickness of transition material and temperature on the curvatures of the bilayer slab

The other parameter that affects the κ value is the thickness of the transition material, the VWP section. The effects of the thickness of VWP and temperature have on curvatures of the bilayer are shown in Figure 4.4. The increase in the thickness of the transition material leads to a decrease in curvature. The reason is, however, slightly different from the thickness of the elastomer. A fixed thickness of TBP suggests that the swelling force exerted on the transition material is the same as it has the same swelling capacity throughout the samples. However, the increase in the thickness of

the transition material increases the stiffness of the entire sample, making it harder to bend and gives a smaller curvature. The thickness of the transition material only contributes to the z value when calculating the curvature. The increase in the thickness of the transition material contributes to higher stiffness.

Figure 4.4 Graphs of curvature against VWP thickness at different temperatures. (a) 25 °C; (b) 35 °C; (c) 45 °C; (d) 55 °C with a fixed 1.5mm-thick TBP (N=3). The experimental results were plotted using a curve-dot plot.

The experimental results with a VWP thickness between 1.5 mm and 2.5 mm were close to the theoretical results at all temperatures. This finding suggests that at a smaller thickness when the stiffness is slightly lower, the model can accurately predict the curvatures. However, when the thickness of the VWP increased further, the experimental curvatures fell short of the theoretical curvatures. After a thickness of 2.5 mm, there is a sudden dip in curvature. The average percentage difference at a

thickness of 3 mm and 3.5 mm were more than 15% (refer to Appendix H). The significant difference between the theoretical and experimental results at 3 mm and 3.5 mm can be attributed to an inability to attain uniform heating in Step 2, which is limited to 60 s. Therefore, at the end of the 60 s heating, the elastic modulus of the VWP is still high, and the force created by the swelling is unable to induce much curvature, as it is smaller than what is required to create a slight deflection. However, the duration for heating during the programming stage cannot be too long because the ethanol that has entered the elastomer matrix will start to diffuse out once the sample is removed from ethanol and submerged in water. Also, high temperatures will result in a faster diffusion rate out of the TBP, thus reducing the amount of bending and making it difficult to predict the curvature. The results at and below 2.5 mm produced an average percentage difference of less than 3%. Hence, it is safe to consider that the model can make accurate predictions at a VWP thickness of at or less than 2.5 mm.

Based on the two-way ANOVA results in Appendix G, the F_0 values for all temperatures are consistently below the critical F value. This suggests that there is no statistical difference between the predicted curvatures obtained by the analytical model and the experimental results. The analytical model is generally accurate in this instance. Also, based on raw results, the average percentage differences at all temperatures were consistent at about 9% to 14%. Differences in results at the thickness of 3 mm and 3.5 mm contributed to the significant error. The increase of temperature, in this case, does not affect the accuracy of the analytical model.

4.5.1.3. Response surface plots of the analytical model

Response surface plots of the models are used to describe the relationships of more than one parameter with the curvatures. These response surface plots allow the programming of the curvature of the first actuation to be predicted.

The curvatures predicted by the model concerning temperature and the thickness of elastomer were shown in Figure 4.5, considers a fixed thickness of the transition material of 1.5 mm. Similar to the experimental results shown in section 4.5.1.1., the increase in temperature and the decrease in thickness of elastomer, respectively, increases the curvatures. The response surface plot also suggests that a combination of low elastomer thickness and high temperature yields a more prominent curvature.

Figure 4.5 Response surface plot of the thickness of elastomer, swelling temperature, and resultant bilayer curvature.

Figure 4.6 shows the effect of temperature and the thickness of the transition material on the curvature. A fixed thickness of the elastomer of 1.5 mm was used for the plot. It suggests that a low thickness of the transition material and high temperature provide a more considerable curvature.

Figure 4.6 Response surface plot of the thickness of transition material, swelling temperature, and resultant bilayer curvature.

Lastly, the thicknesses of both materials are compared against the curvatures at a fixed temperature of 55 °C in the response surface plot displayed in Figure 4.7. Individually, the change in thickness of the elastomer resulted in a more significant change in curvature than the change in the thickness of the transition material. Together, the increase in the overall thickness of the materials in equal thickness gives an exponential drop in curvature. This is the combined effect of increased stiffness and lower swelling content in the elastomer to drive the bending.

Figure 4.7 Response surface plot of the thickness of transition material, the thickness of elastomer, and resultant bilayer curvature at 55 °C.

These response surface plots allow the programming of the curvature of the first actuation to be predicted. Ideally, the response surface plots can be used in a reversed manner to obtain parameters for the actuation of a given curvature. The right selection of parameters will offer more control over 2D shape morphing, such as bending. For example, to obtain an approximate curvature of 25 m^{-1} , there are a set of parameters to select. It can correspond to a combination of 1.5 mm of elastomer and 2.5 mm of transition material or a combination of 2 mm of elastomer and 1.5 mm of transition material. The selection of thickness depends on the design of the structure. If the overall thickness is consistent with the other parts of the structure have, for instance, 4mm, then the former is more suitable.

4.5.2. Validation of the simulation model

Simulation allows the final deformation to be predicted and the stress plot to be studied. The simulation uses a fixed strain; therefore, experimental results for an external strain are still required. The strain at 25 °C after an hour is found to be approximately 1.075. Hence, in the following simulations, a fixed external strain of 1.075 is used to emulate the programming process. In the first step of programming, the bilayer sample is placed at 25 °C of ethanol for an hour. The second step is to heat the entire sample so that the transition material is heated above T_g to turn it rubbery.

4.5.2.1. Simulating stress plot and deformation of the bilayer slab

Figure 4.8 illustrates the deformation and stress accumulation in the bilayer sample with both materials thickness of 1.5 mm before and after heating at 60 °C. The bilayer is shown in Figure 4.8a with the elastomer stacked on the transition material. Visually, the experimental result is compared to the simulated deformation, which both are shown in Figure 4.8b and d, respectively.

Figure 4.8 Experimental demonstration and finite element modelling of actuation phase of the 4D-printing a) The schematic diagram of the bilayer sample that is modelled. b) Snapshot of a sample with 1.5mm of TBP and 1.5mm of VWP after swelling in ethanol for 60 minutes c) Stress (solid) plot of the bilayer sample with a 1.5 mm thickness for both transition material and elastomer before heated d) Stress (solid) plot of the bilayer sample with a 1.5 mm thickness for both transition material and elastomer after heated.

The stress plots in Figure 4.8c and d justify the need to heat the bilayer sample after swelling in 25 °C. When only the elastomer experiences an external strain (swelling) in all dimension, the interface between the two materials limits the possible deformation in the x and y-direction. Before the transition material is heated above T_g , the elastic modulus of the transition material is relatively high, which gives rise to a high bulk modulus. The bulk modulus is a measure of the compressibility of a material [181]. Although there was a slight deformation, the curvature of the bilayer is not maximised as there is a tremendous amount of stress acting on the transition

material across the entire cross-section. The slightly higher amount of stress is accumulated in the transition material along the interface of the two materials and furthest from the interface. As there is no delamination between the two materials, interfacial stress forms near the interface. The transition material experiences a tensile force from the elastomer to stretch out caused by the increase in strain in the elastomer due to a shared interface. Whereas, the stress experience furthest away from the interface is a compressive force as a difference in length will lead to bending.

As the sample is heated above T_g for stress relaxation, Figure 4.8d shows a more considerable amount of deformation, which agrees with the experimental result. Also, the stress along the transition material section is low. When the transition material transits into the rubbery state, the elastic modulus decreases. A decrease in the elastic modulus results in a lower bulk modulus too. However, two regions have high stress. The stress is still slightly higher along the boundary of the two materials as the boundary stress prevents the materials from delamination. Also, there is a sharp increase in stress at 2 cm along the y-axis (midpoint of the long axis). The bending stress exerted on the transition creates a high-stress concentration in the middle region.

4.5.2.2. Effect of thicknesses of both material on the curvatures

Unlike the analytical model, the simulation model does not take into account of temperature as it is not one of the parameters in a stationary study, so in this section, only the thicknesses of the different materials will be evaluated. The experimental curvatures were compared against the simulated results at 55 °C, as shown in Figure 4.9. The simulation was able to closely simulate the curvatures of the bilayer sample with an overall percentage discrepancy of 3.73 % (Appendix I). In both Figure 4.9a and b, the simulated results and experimental results follow similar trends.

Figure 4.9 Graphs of curvature against the thickness of a) TBP and b) VWP at 55 °C. The experimental and simulated results were plotted using a fitted curve plot.

The change in curvature due to the change in thickness of the elastomer (TBP) was previously explained in 4.5.1.1. The simulated results for increasing thickness of TBP at with VWP at a fixed thickness of 1.5 mm were mostly within the error range of the experimental results, as depicted in Figure 4.9a. With the exception at 1.5 mm thickness of TBP, the simulated curvatures were generally higher than that of the experimental results. At elevated temperature, once the sample is removed from ethanol, the ethanol within the elastomer was likely to diffuse or evaporate out of the matrix resulting in lower curvatures than the simulated curvature.

With the increase in the thickness of transition material, there is a decrease in curvature, as shown in Figure 4.9b. The force applied remains the same due to the same strain with the same thickness of elastomer; a larger area will lead to smaller stress distribution and result in a smaller deflection. The simulated curvatures and experimental curvatures for increasing thickness of VWP at a fixed 1.5 mm thick TBP were almost identical. The simulated curvatures were mostly within the error plots of the experimental curvatures. The simulated curvatures were highly accurate, with a discrepancy of 2.09 %.

The simulation model was validated against the experimental results using a two-way ANOVA. F_0 values of both the simulation model with changing thickness of TBP (1.428) or VWP (1.101) were smaller than the critical F value (4.965) when the probability is 5%. This shows that the results simulated from the simulation model and the experimental results statistically had no significant differences, once again, showing that the simulated curvatures are highly accurate.

4.5.2.3. Response surface plots of the simulation model

A response surface plot obtained from the simulation results is plotted in Figure 4.10. The curvatures were compared against the material thicknesses. The plot shows that the decrease in the overall thickness of both materials will result in a higher curvature.

Figure 4.10 Response surface plot of the thickness of transition material, the thickness of elastomer and resultant bilayer curvature at 55 °C.

With the thickness of transition material at 1.5 mm, an increase in the thickness of elastomer leads to a decrease in curvature. But with the thickness of transition material at 3.5 mm, an increase in the thickness of elastomer seeming lead to a slight increase in curvature. This could be due to the uniform external strain that is input into the model. In reality, there may be a decrease instead of an increase as the swelling ratio may decrease as the thickness of elastomer increases.

4.5.3. Comparison between the Analytical model to the Simulation model

The analytical model is a simplified model to make a quick prediction of the curvature.

The main benefit of the analytical model is that the final curvature can be set, and the

temperature and thicknesses can be determined in a reverse manner. However, it is only capable of predicting the final curvature, a 2D prediction. From the validation results in Chapter 4.5.1, it shows that the analytical model has a small range of operating temperature range to ensure the accuracy of the predicted results, due to the various assumptions made, such as assuming the material being linear elastic.

By comparing the accuracy of the two models, the simulation model was able to predict the results more accurately than the analytical model. The overall error of the simulation model compared to the experimental result was merely 3.73%, yet it was approximately 10% for the analytical model. The individual accuracy for each thickness was also higher with the simulation model than the analytical model. Also, the ANOVA results show that the analytical model is significant only when predicting results that at 25 °C for varying TBP thickness whereas the simulation model is generally useful for both varying thicknesses of TBP and VWP at 55 °C.

Besides, the analytical model is only capable of providing the final curvature, a 2D perspective; however, the simulation model is able to provide the full deformation of the sample in 3D. Also, the stress distribution can also be studied from the simulation.

While the simulation model is much more capable in the final curvature prediction and helps in studying the stress distribution, it possessed a critical limitation. The limitation of the simulation model is that the external strain has to be predetermined experimentally to obtain an accurate swelling ratio to yield realistic results. The increase in the thickness of the transition material to 3.5 mm will lead to an increase in simulated curvatures (Figure 4.10). The predetermination of swelling ratios is also required for different temperature as the model account for a change in temperature.

The analytical model, on the other hand, requires less experimental data for the model to function. Most of the parameters are material parameters or independent variables such as time and temperature. This makes it less time consuming to predict the curvatures.

The response surface plot of the analytical model and the simulation model is shown in Figure 4.11. The simulation results gave smaller values when the thicknesses of both materials are small. When the thickness of the elastomers increases, the simulation model provides a more significant curvature than the analytical model.

Figure 4.11 Response surface plot of the analytical model (red) and simulation model (blue) at 55 °C.

4.6.Conclusion

An analytical model was created from a myriad of principles. The analytical model allows the curvatures of simple bilayer slabs to be predicted easily as most parameters are independent variables or material parameters. The parameters can also be selected using the response surface plots of the analytical model to control the amount of bending. The accuracy of the analytical model, however, is only good within a limited range where there is a mix of low temperature swelling between an elastomer thickness range from 2 mm to 3.5 mm and low transition material thickness. Also, the model confines the estimation of shape-changing to bending as it was built for quick analysis of bending.

The simulation model, on the other hand, requires more experimentally predetermined parameters to be functional. The simulation model, however, provides higher accuracy in obtaining the curvatures. The Multiphysics software also provides deformation in 3D and stress study, which helps to study the movements of the bilayer slab sample further. The 3D simulation of the possible deformation aids in the control of shape morphing using more designs. More deformation movements are studied in the next chapter and to provide better control for 3D shape morphing.

Chapter 5 – Controllable Complex 3D Shape Morphing

5.1. Background

To enable biomimetic morphing such as flapping wings and flower blooming, the material actuation speed and degree of bending are important. However, an issue with the earlier study, much like other reversible 4D processes, is the long response time on the scale of hours to days [41], making biomimetic morphing challenging along the time dimension. With a good understanding of how the reversible 4D-printing process can be achieved, strategies for faster and improved reversible actuation can be devised. Previously, stimuli acting on the composites were implemented in separate steps. Numerous steps resulted in an arduous contactless programming shape setting. By combining multiple stimuli into a single step, which is a proved feasible strategy, rapid programming and recovery can be accomplished. In addition, reducing material thickness can also reduce actuation time. In this chapter, it will be shown that the reversible actuation process is reduced from hours to minutes by using these two strategies. A faster actuation promotes practical applications in areas such as soft robotics. Also, a faster actuation encourages designs of more complex 3D structures as slight differences in parameters such as thickness can naturally give rise to different degrees of bending. The faster response allows easier manipulation to obtain more distinct shape change over time, e.g. hinges with slightly different thickness and length within the same structure can achieve multi-stage folding effect [164, 168]. A slow actuation will require a greater change in parameters to achieve the same effect.

Another challenge in biomimetic morphing is complex motion such as twisting and 3D-to-3D shape morphing. At present, there is only a handful of reversible 4D-printing demonstrations with the majority demonstrating 2D-to-3D shape morphing (origami) or size enlargement. Much like reversible SMPs fabricated by conventional methods, the as-built devices are mostly 2.5D at best (a vertical projection from 2D) instead of 3D, which limits the structure complexity and functionality [44, 47]. Only upon stimulation, could the device be converted to a simple 3D structure. However, these 2.5D actuation can be modified to implemented in true 3D structure to achieve true reversible 4D shape morphing. By further implementing the simple reversible process into different designs, other forms of motions such as twisting can be achieved. The designs that induce a twisting effect are investigated in this chapter before being applied in demonstrations. The presentation of more 3D structures illustrates the possible application in biomimetics.

5.2. Materials and Methods

5.2.1. Response rate and recovery rate

The two-tail z test, using a preliminary test, with an acceptable difference of 5 m^{-1} required a minimum of 2.95 replicates to achieve 95% confidence level. Two separate response rate experiments were carried out. A preliminary test for varying overall thickness was carried out, the 3 mm sample which was shown to achieve the largest curvature in Chapter 4.5 and the thickness providing the maximum curvature while still capable of shape retention after swelling was compared. The response rate of the samples with different overall thicknesses (1 mm and 3 mm), each thickness was printed with three replicates of 10 mm by 60 mm and the respective overall thickness

of 1 mm (0.5 mm of TBP and 0.5 mm of VWP) and 3 mm (1.5 mm of TBP and 1.5 mm of VWP).

The second response rate test was to compare between a various mix of the thickness of TBP and VWP while maintaining an overall thickness of 1 mm, the three sample slabs were printed with a dimension of 1 cm by 6 cm by 1 mm (overall thickness). The samples were placed in ethanol at 60°C. 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 experiment was repeated to obtain another set of readings of the same sample. The curvature was plotted as a function of time, and each data point was an average of three measurements.

Likewise, three samples of the same dimension were used to study the response 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 for 20 seconds. The recovery was carried out in an oven heated to 70°. A snapshot was taken every 10 seconds until the sample was fully straightened. The experiment is repeated for another set of readings. The images were also processed with ImageJ to extract information on curvature. A scatter graph was then plotted in Originlab for the recovery rate study.

5.2.2. Preparation for parts with alternating stripes

The samples were designed and printed in three layers. The TBP and VWP layers were to carry out the reversible 4D-printing process, and the middle layer was designed to twist in a specific direction. 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 thicknesses were determined using the response rate studies. 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 1 cm by 6 cm, with an overall thickness of 1mm. 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. An average of three sets of samples was obtained as a minimum of 2.41 replicates are required for a difference of 5° to achieve a 95% confidence level in a two-tail z test.

In the simulation for this study, a fixed strain of 1.05 was used instead. The value is obtained by placing a $40 \times 1 \times 1$ mm TBP in ethanol at 60 °C for 60 s. An average of three samples gave an average of 1.05 fixed strain for 60 s.

5.2.3. 2.5D and 3D-to-3D demonstrations

The samples were printed according to the schematics that were described in each of the studies. 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, 220-240V, 1600W.

5.3.Results and Discussion

5.3.1. Improved Actuation Speed

5.3.1.1. Combination of stimuli

In the previous chapter, the et-swell heat 4D printing cycle required the sample to be soaked in ethanol at a fixed temperature which is usually lower than the T_g of the transition material (VeroWhitePlus, VWP). However, to speed up the actuation process, which lasted at least 4 hours in the previous chapter, a combination of swelling and heating was used in this chapter.

The improved cycle is shown in Figure 5.1. In the programming stage, the printed part with a bilayer structure was programmed into the second shape in heated ethanol that acts as the first stimulus for rapid contactless shape-setting. The elastomer (TangoBlackPlus, TBP) was swelled via the diffusion of ethanol. The ethanol was heated to speed up the rate of diffusion. The high temperature also heated the transition material (VWP) above its T_g to reduce its stiffness for easy reshaping. This asymmetric swelling resulted in a difference in strain between the elastomer and the transition material, which caused the printed bilayer to curl. The part was then quenched in cold water to fix the second shape by cooling the transition material below its T_g to restore its stiffness. In the recovery stage, the printed part was dry-heated using an air gun or in a convection oven to recover its original shape. Dry heating was 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 elastomer recovered back to its original shape after ethanol evaporation. In the end, the printed part was allowed to cool down to room temperature to fix the shape.

Figure 5.1. Et-swell heat 4D-printing reversible cycle stimulated with heated ethanol and heat.

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, minimises the duration required for programming and recovery. There are also other advantages in using the new process. Previously, high-temperature swelling was not recommended due to the degradation of TBP over time. However, with a much shorter time frame for programming, high temperatures can be used with a negligible amount of TBP degradation. Originally, the cycle took at least 4 hours to complete. With the new process, the entire reversible cycle only takes 3 – 4 minutes to complete.

5.3.1.2.Reducing the overall thickness

The overall thickness of the bilayer slab was reduced to speed up the bending further. A comparison between the overall thickness was carried out. In the previous study, the thinnest layer had an overall thickness of 3 mm, which yielded the most considerable curvature. It was compared against an overall thickness of 1 mm. Both samples had a 1:1 ratio of VWP to TBP. The response rates of two parts with different overall thickness are shown in Figure 5.2. The curvatures were measured every 10 seconds and plotted against time. It was evident that by limiting the overall thickness

to 1 mm, 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. These results are also supported by the response surface plots in Figure 4.8 and Figure 4.11, where generally a decrease in thicknesses of both TBP and VWP yield a much larger curvature. 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 would ensure uniform heating during recovery; A thin layer would also lead to a more rapid transition of mechanical properties, such as stiffness, of the transition material (VWP).

Figure 5.2 The response rate of bilayer samples, overall 1mm (0.5 of TBP and 0.5mm of VWP) and overall 3mm (1.5mm of TBP and 1.5mm of VWP). (N=3)

A reduction in thickness and the combined use of stimuli resulted in relatively faster 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 for 30 seconds to fix its shape, during which VWP became stiff. The sample was then heated with a heat gun until it was straightened, which took 90 seconds. The entire reversible 4D-printing process took approximately 3

minutes to complete, making it one of the fastest among all swelling and heat-driven contactless reversible 4D-printing processes.

5.3.2. Geometrical Size Effect

The improved actuation speed initiated by the slight change in the programming and reduction in thickness allowed swelling to be reduced to 60 seconds and still produce a considerable amount of swelling. Although the overall thickness of the bilayer slab could be 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 increase in peaked curvature after 60 s of swelling at 60 °C is contributed by a reduction in stiffness and increased swelling content. However, the relatively constant curvature from sample 3 to 5 shows that, within 60 s, there is a limit to the amount of bending.

Table 3 Geometrical size effect on the curvatures

Sample	Thickness of VWP (mm)	Thickness of TBP (mm)	Ratio of VWP to TBP	Peaked curvature (m^{-1})
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

5.3.3. Response Rate of the Curvature of Thin Bilayer Slabs

To better understand the effect of the stimuli, the response rates of the thin bilayer samples were studied. Figure 5.3 depicts the response rates 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 $1.82 \text{ m}^{-1}\text{s}^{-1}$ in the first second, drastically lower than the other four samples which had the initial response rate in the range of 14 to $19 \text{ m}^{-1}\text{s}^{-1}$ 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 $1.56 \text{ m}^{-1}\text{s}^{-1}$ for the first 10s, with the rate from 2-10 seconds being $1.53 \text{ m}^{-1}\text{s}^{-1}$. While the other four samples showed a high response rate for the first 10 s, and most of the increase in curvature happened within the first second with a response rate of up to $19 \text{ m}^{-1}\text{s}^{-1}$.

The average rate from 2-10 seconds was approximately 0.6 to $1.2\text{ m}^{-1}\text{s}^{-1}$. 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. Therefore, the samples with optimal performance of good shape retention and large curvatures are samples 3 and 4.

Figure 5.3 Response rates of the samples when soaked in ethanol at 60°C

5.3.4. Recovery Rate of the Curvature of Thin Bilayer Slabs

The recovery rates of the five samples have also been studied at a constant temperature of 60°C, as shown in Figure 5.4. In general, the smaller the ratio of VWP to TBP for a given overall thickness, the more rapidly 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 rapid 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. In addition, the elastomeric recovery 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 might not have as much pre-stored stress as the other samples due to the thinner TBP layer. The ability to recover was primarily due to the residual stress formed as the ethanol evaporated. Hence, it had a more uniform but slower recovery rate.

Figure 5.4 Recovery rate of the samples when heated at 60°C.

5.3.5. 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 5.5. 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 in Figure 5.5a, which helped to maintain the asymmetric swelling for shape morphing. The presence of the thin VWP layer is to prevent ethanol from entering from that face. This layer was intended to be as thin as possible to achieve substantial

curling and twisting. Therefore, a minimum of 0.1 mm is used. In the response rate studies in Chapter 5.3.3., it is shown that Sample 5 (0.9 mm of TBP and 0.1 mm of VWP) gave the largest curvature. The middle layer with alternating stripes of 0.4 mm of VWP and TBP, 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. The sections with 0.1 mm of VWP and 0.9 mm of TBP provide the largest curvature, and the sections with 0.5 mm of VWP and TBP provide minimum curvature in 60 s, as studied earlier in Chapter 5.3.3. This difference in curvature results in the slab curling 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 5.5b). Figure 5.5a shows the schematic diagrams of the orientations of the stripes. Figure 5.5c 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 5.5d. 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.

Figure 5.5 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: The simulated and experimental samples of the five different print angles

5.3.6. Reversible 4D Demonstrations

One of the potential prospects of reversible 4D-printing application is soft robotics. A few 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.

5.3.6.1. 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 5.6. 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 5.6a illustrates how the 2.5D flower morphs into the 3D shape over time. The curled flower was heated to full recovery using a heat gun.

Figure 5.6 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.

The alternating stripes were also included in the butterfly, as illustrated in Figure 5.6b. The hinge was designed with just a simple bilayer structure with a ratio of 1:4 of VWP to TBP. The ratio is designed 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 5.6c shows that butterfly before programming, after programming and after recovery. The recovered

structure was also similar to that of the initial shape. However, as it was recovered using a heat gun, the temperature might be too high and resulted in a significant difference in heat expansion of the two materials. This deduction is based on the observation that the tips of the wings remained slightly curled despite ethanol being removed entirely.

Figure 5.6d 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. Thus, the relaxed shape differed slightly from the as-printed shape. 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 heat gun until it fully recovered. Figure 5.6e illustrates that the 3D flower has a similar shape before programming and after recovery.

5.3.6.2. 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 5.7a. 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.

Figure 5.7 Demonstration of the gripper. a: Top view and front 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.

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. Unlike the other two 3D structures, the gripper was

soaked in ethanol for 5 minutes to ensure that the gripper fully enveloped the block so that it would not slip out, as shown in Figure 5.7b. 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 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 [182].

The current technique is demonstrated with the PolyJet printer, which only prints proprietary materials due to its close platform system. 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.

5.4.Conclusion

The improved rapid contactless shape-setting has overcome the drawbacks, such as slow response, complicated fabrication, and confinement to 2.5D shape morphing, that limit the real-world applications of previously reported SMP-based reversible 4D-printing processes. This chapter has shown that having a combination of stimuli for programming and recovery is beneficial, as it also overcame some issues faced previously. Biomimetic reversible morphing was demonstrated with flowers and a butterfly. Also, our study has indicated that reversible 4D-printing could be very useful in soft robotics with the demonstration of a gripper. While all these processes and techniques may still be insufficient to achieve truly functional 4D reversible structures that can be used in industries, it is an advancement to achieving practical 4D reversible printing.

Chapter 6 – Conclusions and Future Work

6.1. Conclusions

6.1.1. Review on Reversibility of 4D printing

An in-depth and critical review of reversible 4D-printing is conducted in Chapter 2 introduces different mechanisms of smart materials, namely SMAs and SMPs. This review is the first to look into the reversibility of 4D-printing as most reviews focused on one-way 4D-printing. The usage of different mechanisms in the area of 4D-printing is discussed. Amongst the two materials, reversibility in the shape morphing is attained in SMPs. This led to further study in reversible 4D-printing. The printing techniques, materials and working principles are discussed in detail. These working principles suggest that reversible SMPs achieve reversibility with the implementation of more than one stimulus; each actuation warrants a type of mechanism for actuation. Multi-responsive materials or composites are highly encouraged.

6.1.2. Mechanisms for Reversible Shape Memory Polymers

The accomplishment of the et-swell heat 4D printing reversible cycle is developed from the detailed study of mechanisms and potential materials in Chapter 2 to determine the mechanisms used for programming and recovery. This reversible cycle minimised the amount of materials required to achieve reversibility in 4D-printing of polymers and managed to reduce the time taken for programming drastically while still retaining some mechanical strength. In the study, the mechanisms used in programming are swelling and heating. As for recovery, diffusion and heating are used. A bilayer composite comprising a transition material and an elastomer is used. The novelty of the reversible cycle is using the unique properties of elastomers in

both the programming and recovery stage. The good affinity between the elastomer (TBP) and ethanol allows it to swell as the ethanol molecules diffuse into the bulk volume of the elastomer used. The swelling force from the diffusion of ethanol functions as an external force acting on the transition material. The swelling of the elastomer provides stress on the transition material, which deforms upon heating above its T_g . The elastomer plays a dual role in the reversible cycle. In the recovery stage, the elastomer acts as a spring to pull the part back to its original shape. After the removal of the ethanol from the elastomer, due to evaporation, the composite is heated above T_g to recover to its original shape. Initially, the mechanisms were used individually in separate steps to provide a distinct understanding of how each mechanism acts on the 3D printed bilayer parts. However, it led to the whole process being too time-consuming. Therefore, in the latest chapter, a combination of each mechanism is carried out concurrently. The programming is contributed by swelling and heating, and the recovery is made with dry heating so that the faster removal of ethanol could be done simultaneously. The experimental response rate proves that the time taken for the entire reversible process can be reduced from hours to minutes, making it one of the fastest swelling and heat-driven contactless reversible 4D-printing processes.

6.1.3. Predictability of the Reversible 4D-Printing of Polymer

An analytical model is devised to give a quick prediction of the bending of a 3D printed bilayer slab. The analytical model was created based on Peppas power-law model and beam theory in mechanics of composite due to the nature of programming. The analytical model only requires mostly material constants or environmental parameters to give the final curvature of the part. It can also be used in a reverse

manner to control the input parameters so to obtain desired curvatures. However, this model is only highly accurate under certain circumstances. Overall, it has an error of 10.1 %. It functions best in low-temperature range, an elastomer thickness between 2 mm to 3 mm and low transition material thicknesses with 2.5 mm or less. Within this operating limit, it yields a percentage error of approximately 5 %, and it is statistically accurate. Another issue with this model is that it confines its prediction to bending. The analytical model is a simplified model that can be used to obtain estimated optimal conditions only. Hence, a finite element simulation model is introduced to overcome the limitations to predict the shape morphing of the 3D printed slabs. The model can predict the movement of the slabs to high accuracy with an error of only ~ 4 %. The multiphysics study shows the simulated deformation of the designed structure and provides the stress study, showing the stress accumulation progression after swelling and then after heating. This helped to study the physics behind the shape morphing. However, the simulation model has its limitations too as it requires a lot of experimental data of extensive characterisation of material properties before it can produce an accurate simulated condition.

6.1.4. Proof-of-concept: Demonstration with Reversible 4D-printed Parts

A mix of different print orientation is first introduced to produce motions other than bending. The print orientation is proven to correspond to the twisting angle. The twisting and bending are integrated into different designs. The 2.5D flower shows the twisting actions being incorporated into a design can show the wilting of a flower. The flower, however, unlike other 4D-printing, is programmed and recovery based on stimuli and not manually re-programmed. Other biomimetic structures are demonstrated too. A fully 3D flower is demonstrated to bloom and close upon

actuation. The other structure is a butterfly. The repeated actuation can mimic the motion of a butterfly flapping its wings. Lastly, a gripper is demonstrated to be able to carry payload and deposit it. The 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. This proposes the possibility of reversible 4D-printing being used in real-life applications such as soft robotics that responds to its environmental stimulus.

6.2. Future Work

The limitations of the current work are closed system printing and the reversible process. Printing with PolyJet limits the materials to the proprietary materials provided by Stratasys. Improvements and adjustments to materials are restricted; hence, it also limits the possible mechanisms that can be used. Also, the printable polymers are only thermosets. The contactless programming method is also confined to the use of ethanol, which presents many challenges for industrial adoption as it is flammable and requires a fume hood to work safely with it. More work can be done on developing a different reversible 4D-printing process that uses more industrial and commercial friendlier stimuli and mechanisms. The next step is to overcome the challenges of materials and mechanisms. Having more materials and mechanisms options can deliver more 4D-printing processes.

6.2.1. Different Printing Techniques

A different printing technique can be explored to continue leveraging on the idea of using a dual-component composite. Some possible printing techniques are FDM and

SLA. Some FDM machines allow dual nozzles with each nozzle carrying a different material. The advantage of FDM over PolyJet printers is that it is an open system. Therefore, non-proprietary materials can be used, expanding the choice of materials. FDM uses thermoplastics instead of thermosets which are more recyclable and more environmentally friendly if bio-thermoplastics are used.

6.2.2. Different Mechanisms

By using other techniques, other possible mechanisms that can be used are light and magnetic stimuli. The current use of ethanol has a diminutive chance for practical use. The use of any liquid will require large storage space or operating space as it needs to cover the entire actuation part. Therefore, stimuli such as light and magnetic can be more useful in an industrial sense. Light can provide localised deformation, and the operating environment is less demanding than heating and solvent selling. Also, near-infrared (NIR) light can be used as localised heating to reduce the operating danger. Several successful one-way 4D-printings actuate using NIR light suggest a possibility in implementing them in a reversible 4D-printing process. The other possible stimulus is the magnetic field. A magnetic stimulus is highly desired due to fast actuation. The time taken for actuation is less than a second [80]. Magnetic-responsive 4D printing has a huge potential in biomedical application due to the safe environment it operates in. They usually operate at temperatures that do not endanger lives [183]. While they are usually printed as a composite with FDM, the surface finish of FDM is poor as compared to other techniques. A possible solution is to print using an open system with magnetic nanoparticles dispersed in the photopolymers and magnetised subsequently.

6.2.3. List of Publications

Published Journal Papers

- [1] Lee, A. Y., An, J., & Chua, C. K. “Two-Way 4D Printing: A Review on the Reversibility of 3D-Printed Shape Memory Materials,” *Engineering*, 3(5), 663-674. (2017)
- [2] Lee, A. Y., An, J., Chua, C. K., & Zhang, Y. “Preliminary Investigation of the Reversible 4D Printing of a Dual-Layer Component,” *Engineering*, 5 (6), 1159, (2019)
- [3] Lee, A. Y., Zhou, A.W., An, J., Chua, C. K., & Zhang, Y. “Contactless Reversible 4D-Printing for 3D-to-3D Shape Morphing,” *Virtual and Physical Prototyping*, 15(4) , 481-495 (2020)

Conference Papers

- [1] Lee, A. Y., An, J., & Chua, C. K. “Review on 4D printing of polymer and its reversibility”. *Proceedings of the 3rd International Conference on Progress in Additive Manufacturing (Pro-AM 2018)*, 529-534. (2018)
- [2] Lee, A. Y., An, J., & Chua, C. K. “ Preliminary Results of The Feasibility of Alcohol As A Stimulus For 4D Printing,” *Proceedings of the 5th International Conference on Additive Manufacturing and Bio-Manufacturing (ICAM-BM 2018)*, 52

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Appendix A – Five Parameters of the Mooney-Rivlin model

This appendix contains the five parameters of the Mooney-Rivlin model that was obtained using the curve fitting of the stress-strain curves of TBP and VWP.

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

Appendix B – One-way ANOVA of the Temperature Change for TBP and VWP

This appendix contains the raw numerical results from one-way analysis of variance in Chapter 3.4.2.

Results for TBP

<i>Observations</i>						
<i>Temperature</i>	1	2	3	Total	Average	τ
25	1.2875	1.28	1.275	3.8425	1.281	-0.1802
30	1.3575	1.36	1.3675	4.085	1.362	-0.0993
40	1.47	1.4625	1.45	4.3825	1.461	-0.0002
50	1.5625	1.55	1.5375	4.65	1.550	0.0890
60	1.65	1.65	1.655	4.955	1.652	0.1907
				21.915	1.461	

<i>Source of variation</i>	<i>Sum of Squares</i>	<i>Degrees of Freedom</i>	<i>Mean Square</i>	F_0	$F_{0.05, 4, 10}$
<i>Between Temperatures</i>	0.2598	4	0.064951	935.68	3.4780
<i>Error</i>	0.0007	10	6.9417×10^{-5}		
<i>Total</i>	0.2605	14			

Results for VWP

<i>Observations</i>						
<i>Temperature</i>	1	2	3	Total	Average	τ
25	1	1	1.0025	3.0025	1.001	-0.006
30	1	1.005	1.01	3.015	1.005	-0.002
40	1.005	1.0025	1.0075	3.015	1.005	-0.002
50	1.0025	1.005	1.0125	3.02	1.007	0.000
60	1.005	1.005	1.01	3.02	1.007	0.000
				15.0725	1.005	

<i>Source of variation</i>	<i>Sum of squares</i>	<i>Degrees of Freedom</i>	<i>Mean Square</i>	F_0	$F_{0.05, 4, 10}$
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<i>Between</i>	1.188×10^{-4}	4	2.969×10^{-5}	3.409	3.4780
<i>Temperatures</i>					
<i>Error</i>	8.708×10^{-5}	10	8.708×10^{-6}		
<i>Total</i>	2.058×10^{-4}	14			

Appendix C – The Calculated Diffusion Exponential, n , at Different Temperatures

This appendix contains the average calculated diffusion exponential. The overall average value is used in the prediction in the analytical model.

<i>Thickness\ Temperature</i>	<i>25°C</i>	<i>30°C</i>	<i>40°C</i>	<i>50°C</i>	<i>60°C</i>
1mm	0.58	0.61	0.61	0.61	0.59
1.5mm	0.56	0.52	0.58	0.57	0.66
2mm	0.54	0.61	0.58	0.59	0.59
2.5mm	0.59	0.61	0.65	0.60	0.58
3mm	0.68	0.67	0.63	0.60	0.61
3.5mm	0.70	0.63	0.68	0.58	0.63
Average	0.61	0.61	0.62	0.59	0.61
overall average					0.61

Appendix D – One-way ANOVA of Repeatability for a 2.5mm thick TBP with 1.5mm thick VWP

<i>Programming</i>					
<i>Cycle</i>	1	2	Total	Average	τ
1	25.286	26.677	51.963	25.982	0.639
2	24.560	23.706	48.266	24.133	-1.210
3	26.057	22.604	48.661	24.331	-1.012
4	26.674	27.385	54.059	27.029	1.687
5	25.442	25.036	50.478	25.239	-0.104
			253.427	25.343	

<i>H_(p)</i>					
<i>Source of variation</i>	Sum of Squares	Degrees of Freedom	Mean Square	F ₀	F _{0.05, 4, 5}
<i>Between Cycles</i>	11.5019	4	2.875477	1.8841	5.1922
<i>Error</i>	7.6310	5	1.526204		
<i>Total</i>	19.1329	9			

<i>Recovery</i>					
<i>Cycle</i>	1	2	Total	Average	τ
1	0.140	0.476	0.615	0.308	0.147
2	0.021	0.300	0.321	0.160	-0.001
3	0.153	0.068	0.221	0.110	-0.051
4	0.000	0.005	0.005	0.003	-0.158
5	0.332	0.116	0.448	0.224	0.063
			1.610	0.161	

<i>H_(r)</i>					
<i>Source of variation</i>	Sum of Squares	Degrees of Freedom	Mean Square	F ₀	F _{0.05, 4, 5}
<i>Between Cycles</i>	0.1062	4	0.026546	1.083449	5.1922
<i>Error</i>	0.1225	5	0.024502		
<i>Total</i>	0.2287	9			

Appendix E – Assumed Material Constants Used in Analytical Model

This appendix is consisted of the material constants that were used in the analytical model. For the model, some constants are assumed because they are either obtained from research papers or the material parameters of similar polymers.

Material Constants	Symbol	Value	Units	Remarks	Reference
Density of TBP	ρ	1.13	g/cm^3	From datasheet	[184]
Mass diffusivity of ethanol	D_0	1.15×10^{-5}	m^2/s	Ethanol diffusivity in air	[185]
Molar volume of ethanol	V_1	58.50	cm^3/mol	n.a.	[159]
Average molecular weight between crosslinks	M_c	11429	g/mol^{-1}	n.a.	[186]

Appendix F – Percentage Difference between Analytical and Experimental Results with Varying Thickness of TBP

This appendix contains the percentage difference between the curvatures obtained from the analytical model and the experimental results with varying thickness of TBP between the temperature of 25 °C and 55 °C.

<i>Thickness of TBP</i>	$\kappa(\text{m}^{-1})$				<i>Average (same thickness)</i>
	<i>25 °C</i>	<i>35 °C</i>	<i>45 °C</i>	<i>55 °C</i>	
1.5mm	8.70%	22.32%	26.51%	18.10%	15.43%
2mm	2.43%	1.61%	10.64%	5.80%	4.50%
2.5mm	2.42%	5.81%	3.93%	6.90%	4.31%
3mm	1.93%	0.13%	7.88%	16.83%	5.95%
3.5mm	4.11%	6.69%	10.41%	23.58%	9.66%
Average	3.92%	7.31%	11.87%	14.24%	7.97%

Appendix G – Two-way ANOVA of the accuracy of the Models in predicting the curvatures

Analytical Model

Varying TBP thickness

$H_{TBP(25\text{ }^{\circ}\text{C})}$					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F_0	F_{crit}
<i>Thickness</i>	163.430	4	40.857	713.490	3.478
	0.229	1	0.229	4.007	4.965
<i>Model/Experiment</i>					
<i>Interaction</i>	1.095	4	0.274	4.781	3.478
<i>Error</i>	0.573	10	0.057		
<i>Total</i>	165.327	19			

$H_{TBP(35\text{ }^{\circ}\text{C})}$					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F_0	F_{crit}
<i>Thickness</i>	290.303	4	72.576	128.106	3.478
	31.236	1	31.236	55.136	4.965
<i>Model/Experiment</i>					
<i>Interaction</i>	51.569	4	12.892	22.756	3.478
<i>Error</i>	5.665	10	0.567		
<i>Total</i>	378.773	19			

$H_{TBP(45\text{ }^{\circ}\text{C})}$					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F_0	F_{crit}
<i>Thickness</i>	295.634	4	73.909	101.828	3.478
	34.146	1	34.146	47.045	4.965
<i>Model/Experiment</i>					
<i>Interaction</i>	104.096	4	26.024	35.855	3.478
<i>Error</i>	7.258	10	0.726		
<i>Total</i>	441.135	19			

$H_{TBP}(55\text{ }^{\circ}\text{C})$						
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F_0	F_{crit}	
<i>Thickness Model/Experiment</i>	384.566	4	96.142	88.483	3.478	
	25.258	1	25.258	23.246	4.965	
<i>Interaction</i>	94.595	4	23.649	21.765	3.478	
<i>Error</i>	10.866	10	1.087			
<i>Total</i>	515.285	19				

Varying VWP thickness

<i>H_{VWP} (25 °C)</i>					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F ₀	F _{crit}
<i>Thickness</i>	123.226	4	30.806	17.098	3.478
<i>Model/Experiment</i>	2.912	1	2.912	1.616	4.965
<i>Interaction</i>	8.715	4	2.179	1.209	3.478
<i>Error</i>	18.018	10	1.802		
<i>Total</i>	152.871	19			

$H_{VWP} (35\text{ }^{\circ}\text{C})$					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F ₀	F _{crit}
<i>Thickness</i>	117.741	4	29.435	43.872	3.478
<i>Model/Experiment</i>	0.614	1	0.614	0.915	4.965
<i>Interaction</i>	2.721	4	0.680	1.014	3.478
<i>Error</i>	6.709	10	0.671		
<i>Total</i>	127.785	19			

$H_{VWP} (45\text{ }^{\circ}\text{C})$					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F ₀	F _{crit}
<i>Thickness</i>	164.041	4	41.010	21.892	3.478
<i>Model/Experiment</i>	2.810	1	2.810	1.500	4.965
<i>Interaction</i>	7.962	4	1.990	1.062	3.478
<i>Error</i>	18.733	10	1.873		
<i>Total</i>	193.545	19			

$H_{VWP} (55\text{ }^{\circ}\text{C})$					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F_0	F_{crit}
<i>Thickness</i>	537.217	4	134.304	28.903	3.478
<i>Model/Experiment</i>	17.522	1	17.522	3.771	4.965
<i>Interaction</i>	76.380	4	19.095	4.109	3.478
<i>Error</i>	46.467	10	4.647		
<i>Total</i>	677.585	19			

Simulation Model

$H_{TBP} (55\text{ }^{\circ}\text{C}) (S)$					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F_0	F_{crit}
<i>Thickness</i>	181.513	4	45.378	41.764	3.478
<i>Model/Experiment</i>	1.551	1	1.551	1.428	4.965
<i>Interaction</i>	13.871	4	3.468	3.192	3.478
<i>Error</i>	10.866	10	1.087		
<i>Total</i>	207.801	19			

$H_{VWP} (55\text{ }^{\circ}\text{C}) (S)$					
<i>Source of Variation</i>	Sum of Squares	Degree of Freedom	Mean Square	F_0	F_{crit}
<i>Thickness</i>	769.995	4	192.499	41.427	3.478
<i>Model/Experiment</i>	5.115	1	5.115	1.101	4.965
<i>Interaction</i>	9.319	4	2.330	0.501	3.478
<i>Error</i>	46.467	10	4.647		
<i>Total</i>	830.896	19			

Appendix H - Percentage Difference between Analytical and Experimental Results with Varying Thickness of VWP

This appendix contains the percentage difference between the curvatures obtained from the analytical model and the experimental results with varying thickness of VWP between the temperature of 25 °C and 55 °C.

$\kappa(\text{m}^{-1})$					
<i>Thickness of</i> VWP	25 °C	35 °C	45 °C	55 °C	<i>Average (same</i> <i>thickness)</i>
1.5mm	0.61%	1.69%	0.25%	9.32%	2.97%
2mm	0.99%	3.94%	0.65%	4.88%	2.62%
2.5mm	4.70%	0.15%	3.38%	1.74%	2.49%
3mm	14.57%	14.30%	16.98%	14.87%	15.18%
3.5mm	51.48%	25.04%	41.22%	32.77%	37.63%
Average	14.47%	9.02%	12.50%	12.72%	12.18%

Appendix I - Percentage Difference between FEA and Experimental Results with Varying Thickness of TBP and VWP

This appendix contains the percentage difference between the curvatures obtained from the FEA model and the experimental results with varying thickness of TBP and VWP at 55°C

<i>Thickness</i>		<i>Percentage error</i>	
<i>VWP</i>	<i>TBP</i>	<i>55 °C</i>	<i>Average Error</i>
1.5	1.5	4.87%	5.37%
	2	4.78%	
	2.5	7.33%	
	3	6.01%	
	3.5	3.85%	
1.5	1.5	0.79%	2.09%
2		0.33%	
2.5		2.93%	
3		2.15%	
3.5		4.28%	
<i>Average</i>		3.73%	