3D printing of shape memory polymers via stereolithography process

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**3D PRINTING OF SHAPE MEMORY POLYMERS VIA
STEREOLITHOGRAPHY PROCESS**

CHOONG YU YING CLARRISA

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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II

ABSTRACT

Additive manufacturing (AM), also known as 3D printing, with the innovative combination of smart responsive materials such as shape memory polymers (SMPs) has brought about 4D printing as an emerging technology for creation of more dynamic devices. However, its applications have been impeded by the limited printable materials and inferior properties in terms of curing speed, mechanical strength and thermomechanical shape memory properties of currently available 4D printing materials. In recognition of these drawbacks, the motivation of this work is to develop photo-curable thermoset SMP resins that exhibit enhanced shape memory properties with rapid curing characteristics.

A tight coupling exists between material development and process development, hence the interaction between material properties of the developed SMPs and process parameters of the stereolithography (SLA) process was examined. While the SLA process can be divided into two major categories – projection and scanning type, the SMPs fabricated via these two systems were compared and found to have distinct curing characteristics. Theoretical calculations on critical energy density and threshold penetration depth were derived for the developed SMPs to enable the material to be successfully printable in any types of UV based 3D printing systems. Following which, characterizations and analysis of tailoring shape memory properties were carried out and the durability of the 4D printed structures was also evaluated. By tuning the material compositions, the flexibility of the developed SMPs allows tailorable thermomechanical properties including glass transition temperatures (from 54.9 °C to 74.1 °C), high shape recovery (from 90 to 100%) and prolonged shape memory durability (up to 22 cycles). The ability to freely tune the thermomechanical properties of 4D printed parts presents

a huge advancement for 4D printing technology to broaden the selection of suitable materials. The robustness of the developed SMPs also addresses the issue of thermomechanical durability of the materials to perform as engineering materials for wide industry adoption.

Moreover, for AM to be viable in mass production, print speeds must increase by at least an order of magnitude while maintaining excellent part accuracy. A shape memory polymer composite (SMPC) using nanosilica particles was developed to enhance the speed and performance of 4D printed parts. The nanosilica particles were discovered to promote remarkably fast curing due to nucleation enhancing activity. The curing time of each layer was reduced to 0.7s which effectively shorten the total printing time. The presence of nanosilica particles with high specific surface area promotes stress transfer, hence improving the tensile strength in the rubbery state by 2.4 - 3.6 times higher and the elongation in rubbery state reaches 85.2%. In particular, the shape memory durability was enhanced which offers a promising material for more robust applications. By comprehensively analysing and discussing the approach of process optimization and material evaluation, this work has enabled the use of the stereolithography technology to fabricate high performance responsive SMP components.

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TABLE OF CONTENTS

ABSTRACT.....	III
ACKNOWLEDGEMENT	V
TABLE OF CONTENTS.....	VI
TABLE OF FIGURES	X
LIST OF TABLES	XV
ABBREVIATIONS AND SYMBOLS.....	XVI
CHAPTER 1. INTRODUCTION	1
1.1 Background	1
1.2 Technology Gaps and Research Needs.....	4
1.3 Motivation.....	8
1.4 Objectives	10
1.5 Scope.....	11
1.6 Outline of Report	12
CHAPTER 2. LITERATURE REVIEW	13
2.1 General Aspects of SMPs	13
2.1.1 Classifications	13
2.1.2 Basic Molecular Requirements and Working Mechanism	16
2.1.3 Types of Shape Memory Polymers.....	18
2.1.4 Characterizing Shape Memory Effects	21
2.1.5. Mechanical Properties.....	27

2.1.6 Conventional Fabrication Technologies for SMPs	28
2.2 Additive Manufacturing.....	31
2.2.1 Introduction on AM or 3D Printing	31
2.2.2 Polymer Based AM.....	33
2.2.3 4D Printing.....	36
2.2.4 Single Thermoplastic Material.....	37
2.2.5 Multi-Thermoset Materials	38
2.3 Shape Memory Polymer Composites	40
2.3.1 Traditionally Fabricated SMPCs	41
2.3.2 3D Printing of SMPCs	43
2.4 Applications	44
CHAPTER 3. EXPERIMENTAL TESTS AND SETUPS.....	50
3.1 Syntheses of Photopolymer SMPs and SMPCs.....	52
3.2 Fabrication of SMPs via Stereolithography Process.....	54
3.2.1 Stereolithography Process.....	54
3.2.2 Optimization of Processing Parameters	56
3.2.3 Post-Processing of SLA SMPs	58
3.3 Thermal Analysis of SLA SMPs	59
3.3.1 Thermogravimetric Analysis	59
3.3.2 Dynamic Mechanical Analysis	59
3.3.3 Thermomechanical Analysis.....	59
3.4 Fourier Transform Infrared Spectroscopy (FTIR)	60
3.5 Mechanical Properties.....	60

3.5.1 Tensile Tests	60
3.6 Electron Microscopy	61
3.7 Shape Memory Characterizations	61
3.7.1 Thermomechanical Cyclic Tests.....	61
CHAPTER 4. SYNTHESIS AND CURING CHARACTERISTICS OF SMPS IN PROJECTION AND LASER STEREOLITHOGRAPHY PROCESS	63
4.1 Introduction.....	63
4.2 Synthesis and Resin Formulation	65
4.3 Results and Discussion	67
4.3.1 Theoretical Model for Energy Density	67
4.3.2 Curing Characteristics.....	71
4.3.3 Abnormal Shrinkage Phenomenon	73
4.3.4 Threshold Energy Density	74
4.3.5 Curing Depths with Varying Photoinitiator Concentrations.....	76
4.3.6 Curing Depths with Varying Crosslinker Concentrations	78
4.4 Summary	80
CHAPTER 5. TAILORING SHAPE MEMORY PROPERTIES	81
5.1 Introduction.....	81
5.2 Results and Discussion	82
5.2.1 Thermal Analysis of SLA SMPs	82
5.2.2 Thermomechanical Analysis.....	84
5.2.3 Mechanical Properties.....	85
5.2.4 Shape Memory Properties.....	88

5.3 Demonstration of SLA SMPs	99
5.4 Summary	103
CHAPTER 6. SHAPE MEMORY POLYMER COMPOSITES CROSSLINKED WITH NANOSILICA	104
6.1 Introduction.....	104
6.2 Results and Discussion	107
6.2.1 Enhancement in Curing Characteristics.....	107
6.2.2 SiO ₂ -SMP Formation	111
6.2.3 Thermal Analysis of SiO ₂ -SMP.....	112
6.2.4 Mechanical Properties.....	115
6.2.5 Dispersion of Nanosilica Particles	120
6.2.6 Shape Memory Properties.....	121
6.3 Demonstration of SLA SMPCs.....	125
6.4 Summary	126
CHAPTER 7. CONCLUSION	128
CHAPTER 8. FUTURE WORK & RECOMMENDATIONS.....	131
8.1 Study on the Thermal Responses of SMPs	131
8.1.1 Effects of Recovery Temperatures	131
8.1.2 Effects of Heating/ Cooling Rates	132
8.2 Study on Shape and Topology Variations	132
8.3 Multi-Shape Memory Polymers.....	133
8.4 Potential Applications.....	134
CHAPTER 9. PUBLICATIONS	136
CHAPTER 10. REFERENCES	138

TABLE OF FIGURES

Figure 1: Mechanism of shape memory effect (SME).....	1
Figure 2. Hysteresis loop of a SME cycle.	2
Figure 3: Technology gaps and research needs in the field of 4D printing.	7
Figure 4. Scope of the project.	11
Figure 5. Integrated insights into SMPs based on structure, stimulus, and shape–memory function (modified from [57]).....	13
Figure 6. Classification of SMPs.	15
Figure 7. Mechanism of amorphous SMPs with T_g as switching transition.....	17
Figure 8. Mechanism of crystalline SMPs with T_m as switching transition.	18
Figure 9: Cyclic stress-strain test.....	22
Figure 10. Schematic illustration of setup for shape recovery performance test.....	26
Figure 11. Solid state foaming of SMPs.	30
Figure 12. 3D printed PLA staple with self-tightening function using MakerBot Replicator II. (a) The SME in staple; and (b) demonstration of tightening function, before and after heating for shape recovery [106].....	37
Figure 13. 4D-printed laminates of complex shapes. (a) A two-layer laminate with alternating layer of oriented SMP fibers and pure elastomer matrix. The sample went through a process of heating, stretching, cooling before the stress is unloaded and the temporary shape presumes a complex shape according to the architecture. When reheated, the original shape returns to a flat strip. (b) A long rectangular strip in its original shape at room temperature and (c)–(h) show results of this process with differing fiber configurations [107];(i) Schematic view of the helical and (j) interlocking SMP component [41].....	39

Figure 14. A schematic representation of chemical crosslinking between CNT and SMP composites (Jung et al. [116]).	42
Figure 15. (a) CAD design of the smart valve; (b) Printing process of the hydrogels; (c) Opened valve in cold water; and (d) closed valve in hot water (Bakarich et al. [122]).	45
Figure 16. Demonstration of 4D printed stent being magnetically actuated (Wei et al. [121]).	46
Figure 17. 4D printed SMP gripper that enables gripping and releasing of objects when thermally actuated (Ge et al. [100]).	47
Figure 18. A flat sheet printed with SMP hinges which can transform its shape into a 3D box upon heating (Ge et al. [35]).	48
Figure 19: Applications of the 4D printing process (Momeni et al. [128]).	49
Figure 20. Process flow chart for development and characterizations of SMPs and SMPCs.	51
Figure 21: Synthesis process of SMP resins.	53
Figure 22: Synthesis process of SMPC resins.	54
Figure 23: Schematic of bottom-up scanning/ projection type SLA.	55
Figure 24. Experimental setup for curing depth studies of DLP and SLA.	57
Figure 25. Curing depth test illustrating cured resin array from 0.5 to 10 s.	57
Figure 26. Measurement of curing depth of a sample using stylus profilometer.	58
Figure 27. Experimental setup for thermomechanical cyclic tests.	62
Figure 28: Chemical structure of UV crosslinked tBA-co-DEGDA network.	65
Figure 29. Schematic diagram of laser scanning beam where d is the laser spot size and hs is the hatching space.	68

Figure 30. Curing depth as a function of energy density for projection-type and laser-scanning-type SL process.	72
Figure 31. Shrinkage phenomenon in the lateral direction observed from curing depth samples with increasing UV exposure duration by projection type SL process.....	74
Figure 32: Excess curing width in x and y directions as a function of energy density.	75
Figure 33. Schematic illustration of overlap curing between layers.....	77
Figure 34. Curing depth of varying DEGDA crosslinker concentrations as a function of energy density.	79
Figure 35. DSC results showing amorphous nature of SMPs.....	82
Figure 36. Peaks of Tan δ curves denoting the T _g of SMPs with varying crosslinker concentrations.	84
Figure 37: TMA results of SLA SMP to determine softening temperature.....	85
Figure 38: Stress-strain plots for SLA SMPs at temperatures below and above T _g	86
Figure 39: Thermomechanical cycle of SLA SMPs.	89
Figure 40. Effects of strain loadings of 10% and 20% on fixity over repeated cycles.	91
Figure 41. Effects of strain loadings of 10% and 20% on recovery over repeated cycles.	92
Figure 42. Effects of increasing concentrations of DEGDA crosslinkers on shape fixity properties of the SLA SMPs over repeated thermomechanical cycles.	94
Figure 43. Effects of increasing concentrations of DEGDA crosslinkers on shape recovery properties of the SLA SMPs over repeated thermomechanical cycles.	96
Figure 44: Full thermomechanical cyclic tests of SLA SMPs.....	96
Figure 45: Thermomechanical cyclic tests of a) SMPs under free strain recovery of 10% and b) SMPs under free strain recovery of 20%.	98

Figure 46. Shape recovery properties of SLA SMPs as compared to typical thermoset SMPs.....	99
Figure 47. Overview of the processes involved in the design and fabrication of bucky-ball by stereolithography	100
Figure 48. SLA SMP Buckminsterfullerene (or C60 bucky-ball) in printing (Figure 48a), unfolded after printing (Figure 48b-c), and recovered its original bucky-ball shape by soaking at 65°C of water (Figure 48c-h).....	101
Figure 49. Shape memory structure printed via 3D projection type stereolithography process. (I-II) A ‘W’-shaped SMP was printed using ASIGA DLP, (III) The printed part was placed inside hot water where the temperature of the water acts as the thermal stimulus, (IV) the structure was fixed in its deformed state at room temperature, (V-VI) The original shape was recovered upon reheating.	102
Figure 50. Shape memory structure printed via 3D laser scanning type stereolithography process. (I) A complex SMP bucky ball was printed using DWS 029X. (II-IV) The SMP was heated up via thermal conduction in hot water and temporarily deformed and cooled down. (V-VIII) shows the shape recovery process when the SMP was reheated.....	102
Figure 51. Curing depth studies of SMP resin with and without nanosilica particles.	109
Figure 52. Schematic diagram of nanosilica particles acting as nucleation sites for initial polymerization.	111
Figure 53. FTIR spectra of (a) SMP without addition of SiO ₂ ; (b) SMP with addition of SiO ₂ in different concentrations.....	112
Figure 54. Loss factor $\tan \delta$ of SiO ₂ -SMP printed parts as a function of temperature.	113

Figure 55. Storage modulus of SiO ₂ -SMP printed parts as a function of temperature.	115
Figure 56. Comparison of mechanical properties of neat SMP and SiO ₂ -SMP printed parts at room temperature and at above T _g in terms of tensile strength.....	116
Figure 57. Comparison of mechanical properties of neat SMP and SiO ₂ -SMP printed parts at room temperature and at above T _g in terms of elongation.	117
Figure 58. Comparison of mechanical properties of neat SMP and SiO ₂ -SMP printed parts at room temperature and at above T _g in terms of Young's modulus.	119
Figure 59: (a) Macroscopic uniformity of nanosilica in developed resin; (b)TEM images of 2.5 wt% SiO ₂ -SMP.....	120
Figure 60. 3D representation of thermomechanical cyclic tests.	121
Figure 61. Shape fixity ratio (R _f) of SiO ₂ -SMP under varying applied strains.	123
Figure 62. Shape recovery ratio (R _r) of SiO ₂ -SMP under varying applied strains.....	124
Figure 63. Comparison of shape memory cycles in terms of shape fixity (R _f) and shape recovery (R _r) of SMPs with 0 wt% and 2.5 wt% nanosilica content under 20% applied strain.....	125
Figure 64a) Printing process of SMPCs on DLP; b and c) Fabrication of complex structures.....	126
Figure 65. Shape recovery process of SMPCs under hot air stimulation.	126
Figure 66: Dental aligners fabricated from the developed SMP photocurable resin..	135

LIST OF TABLES

Table 1. Properties of different commercialized SMPs for industrial use.....	25
Table 2. Thermomechanical properties of SMPs.....	27
Table 3. Classification of AM Technologies.	32
Table 4. Comparative chart of AM technologies utilized for SMPs fabrication.	34
Table 5. Process parameters setting for projection type stereolithography process.	70
Table 6. Process parameters setting for laser scanning type stereolithography process.	71
Table 7: Curing depths (C_d) measured with respects to different photoinitiator concentrations.	78
Table 8: Comparison between SLA SMPs and commercial thermoset Veriflex SMP.	87
Table 9. Properties of four commercial orthodontic aligner materials [172].	135

ABBREVIATIONS AND SYMBOLS

SMPs: Shape Memory Polymers

SME: Shape Memory Effect

TGA: Thermogravimetric Analysis

TMA: Thermomechanical Analysis

DMA: Dynamic Mechanical Analysis

FTIR: Fourier Transform Infrared Spectroscopy

TEM: Transmission Electron Microscopy

AM: Additive Manufacturing

3D: Three-Dimensional

4D: Four-Dimensional

SLS: Selective Laser Sintering

SLM: Selective Laser Melting

SLA: Stereolithography Apparatus

DLP: Digital Light Projection

PJ: PolyJet

MJ: Multijet

FDM: Fused Deposition Modelling

3DP: Three-Dimensional Printing

tBA: tert-Butyl Acrylate

DEGDA: di(ethylene glycol) diacrylate

SMPCs: Shape Memory Polymer Composites

SiO₂: Silicon dioxide/ silica

CHAPTER 1. INTRODUCTION

1.1 Background

Shape memory polymers (SMPs) belong to a class of polymeric smart materials that are stimuli responsive to conditions such as varying temperature, humidity, pH, light or magnetic field. SMPs are first processed or polymerized into its original permanent shape, then heated above its transition temperature (T_{trans}), which can be either glass transition (T_g) or melting temperature (T_m), to switch from glassy state to rubbery state so as to be mechanically deformed and fixed into a temporary shape upon cooling. The SMP remains stable unless it is triggered by an appropriate external stimulus to return to its original “memorized” shape, and this phenomenon of the SMP is known as shape memory effect (SME) [1, 2] which is illustrated in Figure 1. The SME cycle can also be represented by a hysteresis loop as shown in Figure 2. In step 1, the SMP in its original shape was heated and a stress is applied to deform it into a temporary shape. Step 2 and 3 involve cooling the SMP and fixing its temporary shape before the stress is unloaded. During the fixation stage, small strain recovery might be observed due to loss of stored energy upon release of stress. In the last step, the SMP is reheated for recovery. The shape memory capability gives rise to numerous applications particularly in biomedical fields [3-5], sutures or stents for minimally invasive surgery [6], sensors and actuators [7, 8] and even textiles [9].

Figure 1: Mechanism of shape memory effect (SME).

Figure 2. Hysteresis loop of a SME cycle.

However, the manufacturing and processing of SMPs still rely heavily on conventional manufacturing methods such as resin transfer moulding (RTM), compression moulding or solid state forming [10-12]. The SMPs come in uncured resin that are poured into moulds, photopolymerized under ultra-violet (UV) light or thermal curing before being laser cut into desired shapes [13]. The traditional manufacturing technologies require high temperature and labour-intensive processing with the use of expensive moulds while geometrical complexities of the parts are also restricted by the nature of the process. As such, the involvement of multi-machining steps results in cost-ineffective approaches which delay the production lead time for the final products. Accordingly, new processing methods are to be explored for fabrication of SMPs with high geometrical freedom so that the applications of SMPs can be significantly expanded.

Additive manufacturing (AM), also known as 3D printing, has advanced at remarkable speed, emerging as a robust technology to complement existing manufacturing in

increasingly complex tasks. All AM processes are based upon converting virtual models from computer-aided designs or 3D scanning, followed by software slicing of the 3D objects which is transmitted to the 3D printer for fabrication by adding materials successively layer-by-layer [14]. The great design freedom enabled by AM capabilities has made possible the manufacturing of functional parts with huge design freedom that were challenging for conventional technologies and improved economic value for high mix low volume production.

AM has been used across a diverse array of industries, including automotive, aerospace, biomedical, energy, consumer goods and also expanding into food engineering [15-18]. Its applications include conformal, flexible electronics [19]; products with embedded multimaterial sensors and actuators [20, 21]; lightweight, high-strength aerospace structures with material gradients [22, 23]; multifunctional houses [24]; part production with functionally graded materials (FGM) [25-27]; custom-shaped orthopedic prostheses or dental aligners [28, 29]; and even human organs [30]. In general, AM enables the printing of complex shapes with controllable compositions and active functions.

Recently, there is a radical shift in AM with an addition of a fourth dimension – the transformation over time. 4D printing (a scaling up of 3D printing) as described by Skylar Tibbits is “a process that entails multi-material prints with the capability to transform over time, or a customized material system that can change from one shape to another, directly off the print bed” [31]. The multi-material printer allows a choice of different materials to be programmed into specific areas of the designed geometry and to activate the self-assembly process upon external stimuli. Once printed, the printed

part possesses the embedded properties and geometrical designs to allow it to have controlled transformation into another shape.

The innovative convergence of 3D printing with the use of stimuli-responsive materials gives rise to 4D printing, which has gained great scientific interest in recent years. As of today, 4D printing is still primarily based on polymer-based AM processes where these printed SMPs offer greater flexibility with more degree-of-freedom and are able to withstand significantly larger recoverable strains for shape transformation as compared to metals or alloys [32, 33]. The combination of functionalities with greater liberty in terms of complicated geometries makes the fabricated SMPs more versatile and effective as an active material. Applications for 4D printing have and can be greatly broadened to include the fabrication of actuators for soft robotics [34] that demonstrated the capability of developing soft robotics in an easier and less labor-intensive method. The recent fabrication of active origami using multi-material printer [35] also successfully proved the concept of self-folding and self-unfolding which offers potentials of compacting sizable objects to smaller space-saving parts that remain compacted and only be expanded when intended.

1.2 Technology Gaps and Research Needs

While AM techniques have progressed greatly in recent years, many challenges remain to be addressed, such as limited materials available for use in AM processes, inferior properties of currently available materials and insufficient repeatability and consistency in the produced parts [36]. Research is needed to expedite the transformation of 3D printing from rapid prototyping to the additive manufacture of advanced materials.

To date, research and developments in 4D printing are largely based on the few limited commercial systems in the market: Fused Deposition Modeling (FDM) or Inkjet printing such as Polyjet that utilizes multi-materials printing. Typical SMP filaments such as polyurethane used in FDM systems (a solid extrusion based system) reported high recoverable strain when thermally activated due to its physically crosslinked thermoplastic characteristics [37]. However, the physical networks are prone to creep and the irreversible plastic deformation can result in poor shape fixity and recovery [38]. FDM is also known to produce thermoplastic parts with poorer surface finish, especially when the parts require supports for overhanging features, which can cause surface defects during folding and unfolding, resulting in shorter shape memory thermomechanical cycles. Parts also experience more chances of delamination due to poorer dimensional precision such that layer thickness are generally more than 100 μ m [39].

On the other hand, inkjet multi-material printing systems are liquid based AM techniques that have multiple nozzles to jet out photo-sensitive materials and photocured heterogeneously. In terms of shape memory properties, the printing systems produce thermoset SMPs formed by covalently crosslinked networks which are considerably better shape memory materials as compared to thermoplastics since they exhibit inherent lower creep properties due to cross-linkages formed [40]. Multi-material thermoset parts printed by Polyjet technology have demonstrated spontaneous and precisely controlled shape recovery abilities [41], showing that chemically crosslinked SMPs usually exhibit better chemical, thermal, mechanical and shape memory properties than physically crosslinked SMPs [40]. Nevertheless, multi-material printing of SMPs have its limitations too. The proprietary thermoset materials alone do not react to external

stimulus, whereby a single material itself cannot form SMP because it is either too rubbery or too rigid containing highly cross-linked networks that are mainly glassy and brittle which cannot be reshaped once cured. A mixture of elastomeric matrix with rigid plastic have to be cured heterogeneously in order to exhibit shape memory properties [42]. Moreover, multi-materials are more vulnerable to failures due to interface or boundary cracks between dissimilar materials.

In the case of multi-material printing, the shape memory effects depend principally on the design of the components [42]. It has been reported that the active motion of the 4D printed parts were restrained to only 30% of the linear stretch [43]. This induces a limiting factor in the smartness of the multi-materials printed parts since the extent of the shape memory changes are determined by the design in terms of stretching, compression, bending or twisting. Moreover, thermo-mechanical durability were also identified as one of the limitations [44]. For a manufacturing process to be adopted widely by industry, the repeatability and consistency of the manufactured parts are essential. Currently, the inability of current 4D printing materials to perform as engineering materials is inhibiting its wide industry adoption. There is lack of confidence in investors that the AM technology can guarantee material properties, hence this drawback has placed a large constraint on the potential applications for 4D printing.

In general, not all traditional SMP materials are suitable to be used in AM systems. The materials developed for molding purposes are suited for photo-curing with UV exposure under extremely long polymerization time [13, 45]. Long curing time is unfavourable in AM processes as fast curing is one of the process requirements, otherwise the fabrication process will be slow and time-consuming, losing its advantages to traditional molding

methods. Moreover, fabrication of traditional SMP parts has all along been molded as a bulk, hence when these materials are used in 3D printing system to be cured layer by layer especially in a bottom-up process, the initial thin-printed layers do not have the mechanical strength to withstand the accumulation of mass during the printing process. The fabricated part eventually delaminates and collapses due to gravity and this has been experimentally proven to show that some of the traditional SMP materials tested were unsuitable for 3D printing.

Furthermore, mass production is another potential frontier for AM. Fabrication speed is the key to mass production, but most 3D printing technologies operate at under 10 mm/hour, and have a maximum deposition rate of under 50 cm³/hr [46]. There is a concern that these machines do not provide good Return on Investment (ROI) because of the fabrication speed. The speed-limiting process for polymer printing systems is due to its slow resin curing. Most commercially available machines print at speeds between 1.3 mm/hr (Polyjet) and 30 mm/hr (digital light processing SLA), where a macroscopic object several centimetres in height can take hours to construct. For additive manufacturing to be viable in mass production, print speeds must increase by at least an order of magnitude while maintaining excellent part accuracy.

Figure 3: Technology gaps and research needs in the field of 4D printing.

1.3 Motivation

More intensive materials research and development is needed in order to broaden the selection of suitable materials. The motivation of this work is to develop photo-curable thermoset SMP resins that exhibit enhanced shape memory properties with rapid curing characteristics. Research is also needed to understand how the process parameters affect the material properties and part performance, including strength, ductility, geometric accuracy and stability. A tight coupling exists between material development and process development, such that the challenges include a lack of access to the build chamber and integrating process control through the machines' proprietary controllers creates another significant barrier.

There are several polymer-based additive manufacturing systems suitable for fabricating SMPs parts. The popular photo-curing systems are Polyjet (3D inkjet printers) and stereolithography process (which is a mould-less fabrication approach that utilizes UV projection or laser to cure the surface of photopolymer resin in a resin vat layer-by-layer). However, Polyjet are mostly closed systems where they use their own proprietary materials, hence materials and parameters cannot be easily changed. Any failure of jetting material through the nozzle during material development may result in clogging and complete breakdown of the expensive printhead. Material development of SMPs and fabrication using stereolithography process will be more straightforward since it has less restriction in material options due to its open build environment and easily accessible resin vat. The utilization of a bottom-up stereolithography also allows minimal use of resin, which makes it more economical in developing SMPs. In this work, process optimization and material evaluation on the developed SMPs are performed using stereolithography process. This printing system is also recognized for its high

resolution and excellent surface finished parts among all other AM techniques [47]. This ensures that the printed SMPs are of better quality with lesser surface defects to avoid defect-induced failure during repeated thermomechanical cycling. Hence, research is required to determine the interaction between the process parameters of stereolithography process and the newly developed materials.

Moreover, the curing behavior and performance of the developed SMP materials can be further enhanced by introducing nanofillers into the polymer matrix to form shape memory polymer composites (SMPCs). Although the addition of fillers in AM have been extensively reviewed, this approach is still challenging for liquid resin-based 3D printing technologies such as the stereolithography processes due to the incurrence of high viscosity and serious light shielding/scattering. The widely used carbon nanotubes (CNTs) fillers in AM systems are discovered to be strong UV absorbers and this significantly affected the curing efficiency of the polymers [48]. Hence, the nature of the fillers especially in photopolymer resins that cure under UV exposure must be taken into consideration.

The development of SMPCs are recognised to reinforce the mechanical strength, whereby most of the fillers can significantly improve the elastic modulus and recovery stress of SMPs [49]. While there are many different types of fillers based on sizes (micro- and nano-), shapes (rod-shaped and spherical-shape) or new stimuli effects (electroactive, magnetic-active or water-active), the motivation of this work will be investigating on fillers that have chemical bonding with the SMP chains. In particular, the influences of nanosilica (SiO_2) particles not only function as crosslinking agents to

reinforce the properties of the SMPs [50], but also discovered that the particles remarkably accelerates the curing rate, which improves the fabrication speed.

1.4 Objectives

Based on the motivations of this work, the objectives focus on several areas:

1. Synthesize and develop a homogenous thermoset SMP photopolymer resin printable in stereolithography process.
2. Study and compare the curing characteristics and behavior of the developed SMP between projection and laser based stereolithography process.
3. Develop and characterize a series of SMP resin with tailorable functions and properties.
4. Develop and fabricate SMPCs for stereolithography process to further enhance SMP properties.

1.5 Scope

This project is designed to develop and analyze a new smart and stimuli-responsive photo-sensitive resin for stereolithography process to print shape memory polymers. The scope of the research is carried out from four aspects, namely material development, fabrication process, characterizations for tailorable properties and lastly enhancement through development of composites as shown in Figure 4.

Figure 4. Scope of the project.

1.6 Outline of Report

This report begins with the introduction, describing the background, research gaps and motivation for this research. The objectives, scope and outline are all covered in Chapter 1.

Chapter 2 details the literature review on the general aspects of SMPs in terms of classifications, working mechanisms, materials and characterization methods. Conventional fabrication techniques for SMPs is also reviewed in this chapter, while an evaluation based on the current AM systems is carried out to determine their suitability for development of new SMP materials. This chapter also provides a review on SMPCs and its 4D printing applications.

Chapter 3 discusses the synthesis process and experimental methods to perform characterizations on the formulated SMPs using stereolithography process. Theoretical calculations to evaluate the shape memory properties of the SMPs are also listed.

The experimental results and discussions are categorized into three separate chapters to highlight the significant findings in each section. Chapter 4 presents the synthesis and mechanism behind the development of the SMPs, while an analysis and comparison on the curing characteristics between the two different types of stereolithography process – projection and scanning type were studied. Chapter 5 covers the investigation of developing tailorable SMPs by manipulating material compositions and characterizing the fabricated SMPs. Chapter 6 examines the influences of nanosilica particles on the development and properties of SMPCs fabricated using stereolithography process.

Lastly, the conclusion of this report is summarized in Chapter 7 and recommendations for future research in this area are proposed in Chapter 8.

CHAPTER 2. LITERATURE REVIEW

2.1 General Aspects of SMPs

2.1.1 Classifications

The classifications of SMPs have been widely discussed in the literature in which Figure 5 presents an integrated insight into the classification of SMPs by polymerization [51-53], structure [54, 55], stimuli [56, 57] and shape-memory functionality [3, 58].

Figure 5. Integrated insights into SMPs based on structure, stimulus, and shape-memory function (modified from [57]).

Another classification approach will be categorizing SMPs based on the type of SMPs - thermoplastic or thermoset SMPs. The next section will introduce the two types of SMPs and their syntheses.

2.1.1.1 Thermoplastic SMPs

Thermoplastic SMPs are generally physically crosslinked SMPs and the fundamental mechanism behind lies in the formation of a phase-segregated morphology. One phase provides the physical cross-links while another phase acts as a molecular switch [32]. Among thermoplastic SMPs, the polyurethane SMP performs many advantages when compared with other available SMPs, including higher shape recoverability (maximum recoverable strain more than 400%) [59], a wider range of shape recovery temperature (from -30 to 70°C), better biocompatibility and better processing ability [40].

2.1.1.2 Thermoset SMPs

For the chemically crosslinked SMPs, there are two methods to synthesize covalently cross-linked networks [9, 32]. Firstly, the polymer network can be synthesized by adding a multi-functional crosslinker during the polymerization. The chemical, thermal and mechanical properties of the network can be adjusted by the choice of monomers, their functionality, and the crosslinker content.

The second method to obtain polymer networks is the subsequent crosslinking of a linear or branched polymer. The networks are formed based on many different polymer backbones, such as polystyrene, polyurethanes, and polyolfines. Covalently crosslinked SMPs possess chemically interconnected structures that determine the original macroscopic shape of SMPs. The switching segments of the chemically cross-linked

SMPs are generally the network chains between netpoints, and a thermal transition of the polymer segments is used as the shape-memory switch. The chemical, thermal, mechanical and shape-memory properties are determined by the reaction conditions, curing times, the type and length of network chains, and the crosslinking density. Compared with physically crosslinked SMPs, the chemically crosslinked SMPs often show less creep, thus the occurrence of irreversible deformation during shape recovery is reduced. Chemically crosslinked SMPs usually show better chemical, thermal, mechanical and shape memory properties than physically crosslinked SMPs. Additionally, these properties can be adjusted by controlling the crosslink density, curing conditions and curing duration [40]. Figure 6 presents the classification scheme for existing polymer networks that exhibit shape memory effect [60].

Figure 6. Classification of SMPs.

2.1.2 Basic Molecular Requirements and Working Mechanism

The SMP enabling mechanism relies mainly on the thermal phase switches from a rigid plastic at room temperature to soft rubbery state upon heating above its shape memory transition temperature T_{trans} [60]. The T_{trans} can be either a glass transition temperature T_g or a melting temperature T_m . According to the thermal transition of the switching segment, SMPs can be divided into glassy type or crystalline type to explain its different shape memory mechanisms.

2.1.2.1 Shape Memory Mechanism in Amorphous SMPs

If the SMP is a glassy type, its thermal transition belongs to a glass transition. The micro Brownian motion of the network chains is frozen and the temporary shape is fixed at low temperatures; correspondingly, the network chain segments are in the glassy state. The SMPs will remember the temporary shape and store the strain energy. When heating at or above T_g , the micro Brownian motion will be triggered and the ‘switch’ will be opened. The mechanism is depicted in Figure 7. In the case of glass transition, glass transitions always extend over a broad temperature range.

Figure 7. Mechanism of amorphous SMPs with T_g as switching transition.

2.1.2.2 Shape Memory Mechanism in Crystalline SMPs

If the SMP is a crystalline type, its thermal transition belongs to a melting point. The switching segments crystallized at low temperature as a fixed segment to store the strain energy, and it was concluded that high crystallinity of the soft segment region was a necessary prerequisite to demonstrate shape memory behaviour [61]. At elevated temperatures at or above T_m , the SMP recovers to its original shape. In the case of melting temperature, the transition presents a relatively sharp transition in most cases unlike the amorphous reversible segments which often show broad transition temperature range.

Figure 8. Mechanism of crystalline SMPs with T_m as switching transition.

2.1.3 Types of Shape Memory Polymers

In recent years, there have been significant advances in shape memory polymers where there are many new features found in traditional shape memory materials (SMMs) and new emerging types of SMMs. However, in this report, the focus will be directed on reviewing possible resin based SMMs that are suitable for 3D printing. Since as mentioned above that thermoset SMPs exhibit better shape memory properties than thermoplastic SMPs, resin based thermoset SMPs will be looked into. In the field of additive manufacturing, the common types of resins used for fabricating polymers are usually either acrylate or epoxy-based. Consequently, acrylate and epoxy based SMPs will be further evaluated.

2.1.3.1. Epoxy Based SMPs

Epoxy resins are widely accepted for use in many areas of coating, sealants, adhesives, etc. due to excellent thermal, adhesive and mechanical properties. Conferring the shape memory properties to these versatile resins has been the subject of many researchers leading to some advances in the development of shape memory epoxy polymers (SMEPs). SMEPs merit a special reference among the diverse shape memory polymers such as polyurethane, polynorbornene, crosslinked polyethylene, styrene rubbers and acrylate systems as they are unique thermoset shape memory polymer systems with excellent thermal, thermomechanical and mechanical properties along with ease of processability into engineering components [62].

Epoxy polymers perform better as they are capable of recovery from compressive strains of up to 90%, depending on the thermomechanical cycles [63]. Unfortunately, foaming processes for epoxy resins are very complex and expensive, and chemical and processing details of the materials are generally proprietary [64]. Moreover, its cure kinetics is based on cationic polymerization which takes a longer time to cure [65], thus it might be less suitable for 3D printing which emphasizes on rapid fabrication.

2.1.3.2. Acrylate Based SMPs

On the other hand, acrylate polymers represent an ideal system for SMP studies since the copolymerization of linear acrylates (mono-functional monomers) with acrylate cross linkers (multifunctional monomers) yields SMPs with tunable properties that can be optimized for specific applications [45, 66]. Previous investigations have shown that tert-butylacrylate-co-poly(ethylene glycol) dimethacrylate (tBA-co-PEGDMA) networks have shape memory ability with thermal and mechanical properties that can

be readily tailored [4, 59]. Furthermore, unlike epoxy SMPs that is cured by cationic polymerization, the underpinning mechanism for acrylate SMPs is through free radical polymerization in which the curing process propagates very rapidly with the initiation of free radicals [67].

In this work, acrylate based resins are chosen for formulation since they exhibit more desirable properties for 3D printing as compared to epoxy based resin. The acrylate based SMP has higher chain mobility than epoxy based SMP, making it more flexible and suitable for large deformation in SMP. Moreover, the mechanism of acrylate based SMP is through free radical polymerization in which the curing process propagates very rapidly with the initiation of free radicals. The curing is also controlled and precise due to inhibition of oxygen from the environment which stops the reaction quickly, producing high dimensional accuracy in the cured parts [68, 69]. On the other hand, the epoxy based SMP is initiated by cations, which takes a longer time for curing and requires higher light intensity, while polymerization can still continue in the dark once exposed with enough UV at the start, hence it may lose accuracy and precision during printing [70]. Fast curing is one of the process requirements in the AM processes, as long curing time is unfavourable which makes the fabrication process long and slow, losing its advantages to traditional moulding methods. Therefore, acrylate SMPs are fast in curing, which is more appropriate for 3D printing.

2.1.4 Characterizing Shape Memory Effects

There are no standard procedures for the characterization of the shape memory effects of polymeric materials. The development of SMPs as smart materials has garnered a lot of attention in research and inventions but the applications are not widely established. There are various typical applications such as biomedical applications of vascular stents [2], surgical sutures [13] or morphing devices in aerospace applications [49], hence the performance parameters for a SMP become very diverse. The essential ones would be the shape memory transition temperature, shape fixity ratio (R_f) and shape recovery ratio (R_r). Depending on the circumstances, when the recovery speed is of concern, average and instantaneous recovery rates can be calculated; when the robustness of the shape memory performance over multiple consecutive cycles is critical, it is necessary to run a cycling experiment to determine the cycle lifetime of the SMP.

To allow a comparison to be made between different SMPs, the quantification of the shape memory effect is realized through mechanical tests with specific procedures and parameters. In general, the procedures described in this literature consist of (i) stress-strain or (ii) bending tests with a temperature programme based on the transition temperature of the materials.

Stress-Strain Test

The stress-strain test is the procedure more commonly reported in the scientific literature to characterize the shape memory effect [33, 71]. It can be represented in a two-axis system, the variables of which are stress and strain for a fixed temperature. A more efficient representation of this test represents these variables in a three-axis system, by adding the temperature axis. This will allow the observation of temperature behaviour and location the transition temperature. Figure 9 shows a typical stress-strain test in a three-axis system. The complete shape memory test is constituted by a four-step cycle:

Figure 9: Cyclic stress-strain test.

1. Strain deformation

The sample is deformed to a predetermined strain (ϵ_i) at the deformation temperature $T_d \geq (T_{trans} + \Delta T)$, where ΔT is often arbitrarily fixed at 20°C. Most shape memory polymeric elements are practically used in the strain of below 20% and a large deflection is easily obtained in the range of small strain through bending [72].

2. Cooling

Under the imposed deformation constraint, the sample is cooled from T_d to the setting temperature $T_s \leq (T_{trans} - \Delta T)$.

3. Fixing

The initial deformation constraint is released at T_s . If creep or spontaneous recovery has occurred upon unloading, the resulting unrecovered strain upon completion of the fixing step is defined as ε_s .

4. Recovery

The polymer is reheated to above its T_{trans} and recovers back to its original shape, where the resulting strain is recorded as ε_f . If there is irrecoverable deformation during the cycle, the measured strain will be $\varepsilon_f \neq \varepsilon_i$.

Shape Memory Characterizations

For all polymers, the examination based on material, structure and morphology under external factors which include strain, stress, temperature and time, are significant in developing high performance SMPs. There are a few characteristics to be met for a good

SMP whereby the SMP should have a prolonged cycle life, excellent shape fixity and recovery, and acceptable recovery rate [73] .

1. Shape Fixity (R_f)

Shape fixity characterizes the ability of an SMP to fix the strain imparted in the sample during the deformation step after subsequent cooling and unloading. R_f is determined as the ratio of the strain resulting from the fixing step ε_s at the T_s to the strain of the sample upon completion of the deformation step ε_i at T_d . It can be expressed in the literature as:

$$R_f (\%) = \frac{\varepsilon_s}{\varepsilon_i} \times 100 \quad [1]$$

2. Shape Recovery (R_r)

Shape recovery characterizes the ability of a SMP to recover the accumulated strain during the deformation step after subsequent cooling and unloading upon reheating to the rubbery state.

R_r can be defined as the ratio of the difference between the strain resulting from the deformation step (ε_i) and that after completion of the recovery step (ε_f) to the strain resulting from the deformation step (ε_i) [74, 75]. The shape recovery can therefore be expressed by

$$R_r (\%) = \frac{\varepsilon_i - \varepsilon_f}{\varepsilon_i} \times 100 \quad [2]$$

3. Shape Memory Cycle Life

The cycle life of a SMP is defined as the repeatability and durability of its shape memory properties over consecutive shape memory cycles. Thus, the cycle life of a SMP defines the number of consecutive shape memory cycles it will be able to achieve without failure. Here, failure can either represent a noticeable decrease in the shape memory abilities in terms of shape recovery and shape fixity or an actual material failure.

Table 1 shows a summary of a group of SMPs that were examined through a series of thermo-mechanical cycles to determine a material confidence and robustness level that can be qualified for commercial and industrial use.

Table 1. Properties of different commercialized SMPs for industrial use.

Name	Type	T _g (°C)	SMP Performance	Life Cycle
DP5.1 [76]	Epoxy Composites	71	20 Cycles	n/a
5XQ [76]	Epoxy Composites	77	20 Cycles	n/a
BG1.3 [76]	Cyanate Ester	164	20 Cycles	Pass
Commercial SMP Veriflex® [77]	Epoxy Composites	67	19 Cycles	n/a
Veriflex-E [78]	Epoxy	100	7-10 Cycles	n/a
Tecoflex® [79]	Thermoplastic	74	44	n/a

Cycle life is generally tested over 3-5 shape memory cycles. There are few reports that tested for greater cycle numbers: 50 thermomechanical cycles [80], up to 60 mechanical cycles (no change in temperature) [81], and up to 200 SM cycles [82]. They are all

based on low strains deformations that fall within the linear viscoelastic region of the polymer at its T_d .

2.1.4.2. Bending Test

For practical application of SMPs, their shape recovery performance is extremely important and is generally evaluated using a bending test. Bending tests associated with thermal cycles are also able to characterize the shape memory effects in polymers [83-86]. In the flexure test, the measured quantity is the angle of deformed SMP upon bending. Figure 10 shows a typical thermomechanical bending cycling test.

Figure 10. Schematic illustration of setup for shape recovery performance test.

The following coefficient is defined to quantify the recovery ratio of the thermomechanical bending cycle:

$$R_b = \frac{\theta_i - \theta_f}{\theta_i} \quad [3]$$

R_b : recovery ratio from bending;

θ_i : initial angle of deformation;

θ_f : final angle of deformation.

2.1.5. Mechanical Properties

The mechanical properties of SMPs under varying temperature conditions are also important parameters to evaluate the thermal, mechanical and shape memory performance. The relevant tests include uniaxial tension tests, compression tests, three-point bending tests, relaxation tests, creep tests, and nanoscale indentations by atomic force microscopy (AFM). fabricated by traditional moulding methods.

Table 2 compares the thermo-mechanical properties of different types of SMPs fabricated by traditional moulding methods.

Table 2. Thermomechanical properties of SMPs.

SMP Formulation	Type	T_g (°C)	Tensile Modulus (MPa)	Rubbery Modulus (MPa)	Strain to Failure (%)
tBA / PEGDMA [87]	Thermoset	35	10	12	1.0
TMPTMP/TATATO [87]	Urethane based	36	63	17	0.2
Vinyl benzene (Styrene) [88]	Thermoset	43	124	1.15	n/a
IPDUT/IPDI6AE [87]	Thiol-ene	35	55	7	1.0
Veriflex CF62 [89]	Thermoset	62	23	1.24 x 10 ³	3.90

Last but not least, the determination of a polymer being an SMP is independent of the molecular structures and can be otherwise interpreted from its Dynamic Mechanical Analysis (DMA) curve. The characteristics of an SMP under DMA should experience a 2-3 orders of magnitude drop in the elastic modulus when heated and gradually end off with a plateau modulus value. From the molecular dynamics standpoint, the modulus drop is indicative of the significant activation of molecular mobility at the multi-segmental scales. The rubbery plateau, on the other hand, arises from the prohibition of chain slippage at a longer length scale (e.g. the entire polymer chains slip passes one another). Herein, a glass transition or melting transition offers the mechanism for controlling the molecular mobility, whereas the crosslinking is responsible for the prohibition of the long-range chain slippage (thus the rubbery plateau) [57].

2.1.6 Conventional Fabrication Technologies for SMPs

The first discovery of SMPs can be traced back to a US patent in 1941 in which “elastic memory” was mentioned [90]. Despite the long history of SMPs, the processing of SMPs have been through traditional methods which include, *inter alia*, injection moulding [91], blow moulding [92], resin transfer moulding [93] and solid-state foaming [11].

Injection/ Extrusion Moulding

Injection moulding is the most popular mass production method. Injection moulding provides good finish surface and accurate dimension, producing desirable shapes. SMPs are temperature-sensitive materials, in which its viscosity can be very sensitive. SMPs exhibit good flowability in a mould, so it does not require high pressure for injection.

These methods have been widely employed by industries such as SMP Technologies Inc to fabricate their SMPs and reported in many publications [13, 94].

Resin Transfer Moulding (RTM)

The RTM process is a widely accepted fabrication process in which low viscosity resin is pumped under pressure into a closed-mould cavity and the cure cycle starts by heating the mould. This method allows mass production of large, complex shapes and high strength-to-weight products. However, it requires long cycling times whereby one typical cure cycle used for a thermoset resin matrix is 8 hours at 125°C [12] and incurred high tooling costs as core and cavity are necessary for RTM.

Pre-Preg (pre-impregnated) and Autoclave Technology

Prepreg moulding usually prepares its polymer matrix bonded with fibers partially cured and put into cold storage to prevent complete curing. An oven or autoclave is then used for complete curing. The resins are pre-catalysed, giving the materials longer shelf life. However, the method is limited to epoxy, polyester or high temperature resins and the need for autoclaves leads to higher costs, slower operation and restriction in the part sizes [12].

Solid-State Foaming

Solid-state foaming consists of pressing thermosetting resin powders to produce solid tablets, heating the tablets at high temperature to generate both the formation of pores inside the resin and the resin polymerization. Figure 11 illustrates the process flow of solid-state foaming for SMPs. Promising results were reported using solid-state foaming

to fabricate composite SMPs for improvements in shape memory properties, however this is possible only for low weight percentage [95].

Figure 11. Solid state foaming of SMPs.

The above-mentioned techniques for fabricating SMPs are some of the non-limiting examples of conventional methods but they all have common disadvantages. They require high temperature and multi-steps processing with the use of expensive moulds while geometrical complexities of the parts are also restricted by machines' capability. Hence, this brings about another processing technique (discussed in next section) which has attracted significant interest lately due to its unlimited flexibility in terms of the geometric complexity of fabricated parts.

2.2 Additive Manufacturing

2.2.1 Introduction on AM or 3D Printing

Additive Manufacturing (AM) is often used synonymously with the term “3D printing” and they are defined by ASTM International as the process of fabricating objects layer upon layer from 3D model data, through material deposition using a print head, nozzle, or another printer technology [96]. The technology is also known by many names; depending upon the time period and the context, it can be referred to *rapid prototyping*, *layer manufacturing* and *solid freeform fabrication*.

Unlike traditional manufacturing technologies that create parts through subtraction of material from a work piece, AM builds the objects through the successive addition of materials layer-by-layer. Each layer is derived from the virtual cross-section of the part from the slice data of the 3D Computer-Aided Design (CAD) model and each new layer is built upon the top of the preceding built layer. This process of building the part layer-by-layer, mostly from bottom-up, is repeated until the full model is completed.

While there are many ways in which one can classify the numerous AM systems in the market, one of the better ways is to classify RP systems broadly by the initial form of its material, i.e., the material that the prototype or part is built with [14].

Table 3 presents the categorization of all AM systems into (1) liquid-based, (2) powder-based and (3) solid-based.

Table 3. Classification of AM Technologies.

Material Form	AM Technology	Working Principles	Working Materials
Liquid-based	Stereolithography (SLA)	<u>Vat Photo-polymerization</u> An AM process in which liquid photopolymer in a vat is selectively cured by light-activated polymerization	Photopolymers
	PolyJet (PJ) MultiJet (MJ)	<u>Material Jetting</u> An AM process in which droplets of build material are selectively deposited	Photopolymers
	Digital Light Processing (DLP)	<u>Photo-polymerization Projections</u> An AM process in which liquid photopolymer in a vat is cured by light projection from the bottom of the vat	Photopolymers
Powder-based	Selective Laser Sintering (SLS)	<u>Powder Bed Fusion</u> An AM process in which thermal energy selectively fuses regions of a powder bed	Polymer powders Ceramic powders Sand
	Selective Laser Melting (SLM)	<u>Directed Energy Deposition</u> An AM process in which focused thermal energy is used to fuse materials by melting as they are being deposited	Metal powders Ceramic powders
	Three-Dimensional Printing (3DP)	<u>Binder Jetting</u> An AM process in which a liquid bonding agent is selectively deposited to join powder materials	Metal powders Polymer powders Ceramic Sand

Solid-based	Fused Deposition	<u>Material Extrusion</u>	Thermoplastic
	Modelling (FDM)	An AM process in which material is selectively dispensed through a nozzle or orifice	filament/ other materials in thin filament form.

2.2.2 Polymer Based AM

There are basically three main categories of materials that can be used in AM: polymers, ceramics and metals. Of these materials, polymers are most commonly used since they are amongst the cheapest materials that can be used in AM and are the typical content for commercial 3D printers being sold for home use. The main polymers being used in AM are:

- Acrylonitrile butadiene styrene (ABS)-like: most widespread polymer which can most easily be described as the plastic used for making Lego bricks.
- Polylactic acid (PLA): a polymer rising in popularity because of its flexibility and availability in both rigid and soft finishes.
- Polyvinyl alcohol (PVA): a water-soluble synthetic material which acts as support material within AM process.
- Polycarbonate: filament material for extrusion-based 3D printers, offering high heat resistance which can be suitable for lighting applications.

For the direct production of polymer components, polymer-based AM technologies include SLS, PolyJet (PJ), MultiJet (MJ), FDM, SLA and DLP. These systems are evaluated as shown in Table 4 to determine their suitability for development of new SMP materials.

Table 4. Comparative chart of AM technologies utilized for SMPs fabrication.

AM Technology	Manufacturing Process	Advantages	Disadvantages
Selective Laser Sintering (SLS) [97]	Utilizes a high-powered laser to fuse small plastic particles. During the printing process, the platform lowers by a single layer thickness after sintering each layer. The process repeats until the 3D model is completed.	Offers unlimited geometrical possibilities, since no support is required as the build is supported by unsintered material [16]	The product is likely to suffer from shrinkage and warpage due to sintering and cooling. The use of powder as its material produces poor surface finishes [16] which can be detrimental to the thermo-mechanical properties of fabricated SMPs after repeated cyclic tests
PolyJet (PJ) MultiJet (MJ) [35, 41, 98]	The inkjet printer incorporates many nozzles or small jets to apply and cure a layer of photopolymer, layer by layer.	-High dimensional accuracy -Excellent reproduction of thin structures	- The conventional thermoset materials alone do not react to external stimulus, hence the shape memory effects depend principally on the design of the components [42].

			<ul style="list-style-type: none"> - Closed systems that permits only its own proprietary materials
Fused Deposition Modelling (FDM) [37, 99]	<p>Involve the use of thermoplastic materials injected through indexing nozzles onto a platform. The nozzles trace the cross-section pattern for each particular layer with the thermoplastic material hardening prior to the application of the next layer. The process repeats until the build or model is completed</p>	<ul style="list-style-type: none"> - Functional parts - Water-soluble support structure 	<ul style="list-style-type: none"> - Poor surface finish which can produce surface defects - Higher occurrence of delamination due to poorer dimensional precision such that layer thickness are generally more than 100µm [39]
Stereolithography Apparatus (SLA)	<p>Utilizing UV based laser technology to cure layer-upon-layer of photopolymer resin</p>	<ul style="list-style-type: none"> - Excellent surface finishes - Open build parameters - Easily accessible resin vat 	<ul style="list-style-type: none"> - Expensive resins - Tedious manual removal of support structures
Digital Light Processing	<p>Liquid photopolymer in a vat is cured by</p>	<ul style="list-style-type: none"> - Rapid fabrication - Smooth surfaces 	<ul style="list-style-type: none"> - Expensive photo-sensitive resins

(DLP) [19, 100]	light projection from the bottom of the vat	- High resolution - Open system	- No dissolvable support structures
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As of current research and developments in using AM to fabricate SMPs parts, PolyJet and FDM serve as the most widely used systems to demonstrate 4D printing. However, based on the evaluation of each polymer-based AM systems, SLA and DLP can be considered to offer more options for SMP material developments due to their open build parameters that allows unrestricted freedom in interchanging materials and adjusting processing parameters.

2.2.3 4D Printing

3D printing has attracted significant interest lately due to its promising capabilities and liberty in fabrication of complex structures and geometries in a cost efficient way [101]. This unique capability is quite complementary to shape manipulation via the shape memory programming. Thus, combining shape memory properties with 3D printing offers great potential in two aspects: producing SMP devices with relevant complex geometries that are technically challenging for traditional processing methods; more shape variants can be realized for a 3D printed SMP part via shape memory programming. The time-dependent SME offers an additional dimension (i.e., time), leading to the so-called fourth dimensional printing. In principle, 4D printing can be realized in two ways according to whether they are printed as a single material or a combination of multi-materials [102].

2.2.4 Single Thermoplastic Material

One of the most common shape memory single materials used in AM is polylactide (PLA) which serves as the most popular filament among other materials used in FDM [103-105]. PLA can be recognized as a “4D ready” material due to its thermoplastic nature which displays empirical indication of shape memory functionality such that above a specific transition temperature, there is a drastic physical change whereby the polymer softens upon heating to enable molding and reshaping, but solidifies back once it is cooled.

Yang *et al.* [106] also demonstrated the concept of using FDM to print self-tightening PLA surgical staple (as shown in Figure 12) for minimally invasive surgery since PLA exhibits biodegradable characteristics suitable for biomedical applications.

Figure 12. 3D printed PLA staple with self-tightening function using MakerBot Replicator II. (a) The SME in staple; and (b) demonstration of tightening function, before and after heating for shape recovery [106].

Another research group led by Yang *et al.* [99] performed quality evaluation based on influences of nozzle temperature, nozzle scanning speed and part cooling on the FDM-printed parts using thermoplastic polyurethane elastomer (TPU) material. The quality of the printed parts was found to depend largely on the bubble content in the filament

extrusion process which can lead to undesirable void formation. High nozzle temperature and slow scanning speed are also detrimental to the surface roughness that may affect the performance of the SMP parts.

2.2.5 Multi-Thermoset Materials

The latest advancements in multi-materials additive manufacturing have also built a new foundation for the field of 4D printing. With the launch of Stratasys' Connex multi material 3D inkjet printing technology, there are many research that were conducted to explore the wide range of applications for 4D printing.

Skylar Tibbits was the first to introduce the concept of 4D printing by specifically jetting different materials through multiple nozzles in different sections of a designed geometry and by utilizing the water-absorbing or thermal-sensitive properties of the materials, the self-assembly process is activated [31].

Successful attempts were also made by Ge *et al.* using Objet Connex 260 to construct an active composite with SMP fibers embedded in an elastomeric matrix. The orientation of the fibers was spatially controlled in a lamina and laminate architecture with different orientations and volume fractions [107] as illustrated in Figure 13a-h.

Similarly, Yu *et al.* presented components printed by distributing the multi-materials sequentially in a functionally graded manner to exhibit helical and self-interlocking ability [41] (Figure 13i and j). His work has demonstrated the reliability of spontaneous recovery from the multi-material printed parts and the ability of using 3D printers to control the shape recovery in a sequential manner.

Figure 13. 4D-printed laminates of complex shapes. (a) A two-layer laminate with alternating layer of oriented SMP fibers and pure elastomer matrix. The sample went through a process of heating, stretching, cooling before the stress is unloaded and the temporary shape presumes a complex shape according to the architecture. When reheated, the original shape returns to a flat strip. (b) A long rectangular strip in its original shape at room temperature and (c)–(h) show results of this process with differing fiber configurations [107]; (i) Schematic view of the helical and (j) interlocking SMP component [41].

Ge, Qi *et al.* also came up with the fabrication of active origami using multi-material 3D printer that successfully proved the ability of printed structures to self-fold and self-unfold which offers potentials of compacting sizable objects to smaller space-saving parts that remain indefinitely and only be expanded when intended [35]. They were also able to directly print SMP fibers in an elastomeric matrix to enable programmable shape change of the composites [107].

Most of the research in 4D printing utilizes the Polyjet multi-material system to achieve the time-dependent shape memory effect. However, this system requires very high initial costs as the proprietary materials are all expensive thermoset resins [108]. Moreover, the materials alone do not exhibit shape memory properties since the elastomeric material (eg. TangoBlack) are too rubbery while the rigid plastic material (VeroWhite) contains highly cross-linked networks that are mainly glassy and brittle which cannot be reshaped once cured. Hence, a mixture of elastomeric matrix with rigid plastic is mandatory and the spatial arrangements of different materials to be cured heterogeneously by sections play a major role in determining the features of the 4D printed structures.

2.3 Shape Memory Polymer Composites

There are two commonly adopted approaches to improve and expand the applications of SMPs: 1) modify or optimize the molecular structure of the polymer to improve its mechanical, thermal and shape memory properties for the intended application and/or, 2) incorporate functional fillers into the polymer matrix to form multi-phase composites to provide additional property enhancements. The enhancement in thermomechanical behaviour of SMPs through addition of fillers to form SMP composites (SMPCs) has been widely employed for traditional fabrication methods of SMPs but can be challenging for implementation in the 3D printing process.

These reinforced SMPCs are recognised to bear much higher mechanical load while the shape memory effect can be maintained. There are many different types of fillers based on sizes (micro- and nano-), shapes (rod-shaped and spherical-shape) or additional

stimuli effects (electroactive, magnetic-active or water-active), while most of the fillers can significantly improve the elastic modulus and recovery stress of SMPs [49]. This section will look into the various types of fillers used to develop traditionally fabricated SMPCs and a review on the nanocomposites developed through 3D printing processes.

2.3.1 Traditionally Fabricated SMPCs

In the traditional fabrication of SMPCs via moulding, various particle fillers such as carbon black [109], carbon nanotubes (CNTs) [110], exfoliated nanoclay [111] and glass fibers [112] have been widely used to enhance the mechanical properties and shape recovery of SMPs. These particle-filled SMPs usually possess new functions, such as electrical conductivity or magnetic-responsive ability in addition to their shape memory effect. Therefore, this type of SMPCs can also be classified as multi-functional materials.

Carbon black (CB) fillers can be added in the SMPs to introduce electrical conductivity in the polymer matrix which are not intrinsically conductive. With the presence of CB fillers, the conductive polymer compounds can be internally heated when a voltage is applied and the thermally induced shape memory effect can be stimulated indirectly. Le *et al.* [109] studied that the heating stimulated shape memory behaviour is dependent on the dispersion of the CB fillers as well as the electrical resistivity. An extended mixing duration can help to achieve homogenous dispersion of the particles that eventually improves the heating efficiency of the SMPs and increases the electroactive shape memory effect.

Although CB fillers introduce additional electrical conductivity into the SMPs, they are not as effective as other high aspect ratio fillers such as carbon nanotubes (CNTs). CNTs

are one of the most popular candidates for the modification of SMPs [113, 114]. They are known for their intrinsic characteristics such as high strength and modulus, high aspect ratio and electrical conductivity which make them suitable for developing electrically activated SMPs. Shao *et al.* [115] discovered that the CNTs also greatly reduces the electrical resistivity of the SMPs due to formation of a percolated network structure. The percolated network structure that is formed even with high CNTs content helps to improve the degree of shape recovery and fasten the shape recovery process. Jung *et al.* [116] chemically modified the CNTs to achieve crosslinking between the CNTs and SMPs as illustrated in Figure 14, which effectively prevents reaggregation of CNTs within the polymer matrix and results in superior mechanical properties.

Figure 14. A schematic representation of chemical crosslinking between CNT and SMP composites (Jung *et al.* [116]).

The formation of covalent crosslinking with the polymer matrix can also be achieved with the addition of nanosilica particles without any chemical modifications. Zhang *et al.* showed that the nanosilica particles can serve as crosslinking agent due to its abundant surface hydroxyl group in silica that form polymer network with the SMPs which produces high strain and excellent shape memory effect. Gall *et al.* [117] has also observed that the elastic modulus and recovery stress of the epoxy SMP can be greatly

improved even with very low loading of nanosilica particles. Hence, it is interesting and worthy to examine on developing SMPCs with particle fillers that possess the ability to form chemical bonding with the SMP polymer matrix to improve on its shape memory performance.

2.3.2 3D Printing of SMPCs

The integration of nanoparticles into AM materials have been extensively reviewed due to its promising approach to achieve more superior properties. There are a wide variety of nanomaterials, including carbon nanotubes [118], graphene [119] and nanoclay [120] added into AM medium to produce nanocomposites that enhance the mechanical properties of the 3D printed parts. However, there are very few research on the development of composites for 3D printing of SMPCs.

Wei *et al.* [121] introduced iron oxide nanoparticles into a thermo-responsive UV crosslinking PLA-based ink and 4D printed a smart stent. The addition of iron oxide nanoparticles enables the SMP to be internally heated by controlling the magnetic fields. Hence, with the endowed magnetism to the 3D printed structures, 4D printing of SMPCs has been successfully realized with a newly added function in which the 4D active shape transformations can be magnetically guided.

In fact, the development of SMPCs is considerably challenging, especially in liquid resin-based 3D printing technologies such as stereolithography (SL) or digital light projection (DLP) processes due to the incurrence of high viscosity and serious light shielding/scattering. Enhancing the dispersion of the nanofillers is undoubtedly the most fundamental issue for developing any composites, but it is also essential to consider the

nature of the fillers especially in photopolymer resins that cure under UV exposure. In view of using CNTs as nanofillers in SL or DLP systems, CNTs are discovered to be strong UV absorbers and this significantly affected the curing efficiency of the entire components [48]. Hence, meticulous selection on the type of fillers to formulate composite resins for 3D printing processes has to be carried out to successfully fabricate the SMPCs and effectively enhance the shape memory performance.

2.4 Applications

This section highlights and summarizes some of the significant applications of the current 4D printing process as well as future potential applications.

One of the significant demonstrated applications for 4D printing is the realization of soft mechanical actuators. Bakarich *et al.* [122] has developed a new ink that is mechanically robust and thermally actuating for 3D printing of hydrogels. A smart valve for control of water flow was designed to experience 4D printing transformation when in contact with hot water (valve closed) and cold water (valve opened) as shown in Figure 15.

Figure 15. (a) CAD design of the smart valve; (b) Printing process of the hydrogels; (c) Opened valve in cold water; and (d) closed valve in hot water (Bakarich et al. [122]).

In the traditional fabrication of shape memory polymers, the SMPs were widely used in biomedical applications such as stents and surgical sutures as they function as meaningful devices that aid in the expansion of human vessels [6, 123]. Similarly, Ge *et al.* [100] has demonstrated the 4D printing of thermo-responsive cardiovascular stent using micro-stereolithography in which its shape shifting behaviour can be manipulated by varying diameters, heights, number of joints and inter-ligament angles. The use of 4D printing in printing stents efficiently overcome the difficulty of traditional fabrication methods to produce complex geometries with high resolution. Moreover, Wei *et al.* [121] introduced iron oxide particles into a thermo-responsive PLA ink and 4D printed a smart stent, which has successfully realized the printing of SMPCs as well as endowed magnetism to the 3D printed structures that can be remotely actuated and magnetically guided as shown in Figure 16.

Figure 16. Demonstration of 4D printed stent being magnetically actuated (Wei *et al.* [121]).

Other than fabricating intravascular stents for biomedical applications, 4D printing can also be potentially applied in drug delivery systems [124]. The concept was demonstrated by Ge *et al.* [100] that printed multimaterial grippers has the potential to function as microgrippers that can grab and release objects as shown in Figure 17.

Figure 17. 4D printed SMP gripper that enables gripping and releasing of objects when thermally actuated (Ge et al. [100]).

Another significant application in the 4D printing process is the development of origami structures. Ge *et al.* [35] designed and fabricated active hinges by printing SMP fibers in elastomeric matrix that can assemble flat polymer sheets into a box, a pyramid or airplanes as shown in Figure 18. Through this illustration using 4D printing, it establishes a potential concept of printing deployable structures that can change its structural configuration from large volumes or complex assembling processes.

Figure 18. A flat sheet printed with SMP hinges which can transform its shape into a 3D box upon heating (Ge et al. [35]).

Although 4D printing as an end-use manufacturing technology is still in its infancy stage, emerging applications to directly fabricate responsive components have been extensively reported. These include actuators and soft robots [34, 125], medical devices [126, 127], robotic grippers [100] and flexible electronic devices [19]. The current 4D printing applications and potential future applications are summarized in Figure 19.

Figure 19: Applications of the 4D printing process (Momeni et al. [128]).

Based on the literature review on SMPs and current state-of-art for 4D printing, the scientific aspects of 4D printing can be constituted to a fundamental research in materials and designs. Therefore, this work focuses on the development of new smart SMP materials while improving and maximizing the potential applications for 4D printing. The following chapter will introduce the experimental methods used in this study for development of SMPs and SMPCs for stereolithography process.

CHAPTER 3. EXPERIMENTAL TESTS AND SETUPS

A series of experimental tests and setups is introduced in this chapter to develop and characterize the photopolymer SMPs and SMPCs for stereolithography. Figure 20 displays a flow chart of the development and characterization processes, while the detailed experimental methods are further accounted below.

Figure 20. Process flow chart for development and characterizations of SMPs and SMPCs.

3.1 Syntheses of Photopolymer SMPs and SMCs

The materials chosen for the syntheses of the photopolymers are acrylate based so as to meet the criteria of rapid and controlled curing properties. tert-butyl acrylate (tBA) monomer was selected because of its short chain length and small side group which makes it less bulky, allowing for increasing mobility of the molecular chains leading to greater degree of deformation at temperature above its T_g . A crosslinker with a higher thermal transition temperature than tBA has to be added in order to remain thermally stable during thermomechanical changes. This ensures an establishment of a stable network structure and also constitutes to the permanent shape, hence di(ethylene glycol) diacrylate (DEGDA) crosslinker was selected. The molar ratio of tBA to DEGDA is 15:1, which gives a loose crosslinking of the soft and hard segments that ensures rigidity at room temperature, yet sufficiently mobile at temperature above T_g . Different photoinitiators have different working UV wavelength, therefore photoinitiator Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO) was selected to match the laser/ projection wavelength of 405 nm and absorbs the light to cleave and generate radicals. This particular combination produces a SMP with low T_g of 54°C, which is suitable for our targeted low temperature applications that do not require high temperature changes in order to stimulate its recovery. Further details on the synthesis and formulation are provided in Section 4.2.

Commercial tBA monomer were synthesized with DEGDA crosslinker using 0.5 to 5 weight percentage (wt%) of UV photoinitiator Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO). The chemicals were all ordered from Sigma Aldrich and used as received conditions without further purification.

The DEGDA crosslinker were first added dropwise to the tBA monomer, subsequently with the addition of photoinitiators in continuous mixing of the solution using magnetic stirring, followed by planetary centrifugal vacuum mixer (Thinky Mixer, USA) at 1900 rpm until the photoinitiators completely dissolved. The syntheses of the chemicals were performed in an UV-proof environment to minimize pre-photopolymerization. The synthesis process for SMP resin is illustrated in Figure 21.

Figure 21: Synthesis process of SMP resins.

For the synthesis of SMPCs with nanosilica particles, nanosilica suspensions in acrylate monomer was employed to covalently bind the nanofillers with the acrylate based photopolymer. Versatile dispersion of colloidal silica in acrylate monomers (NANOCRYL A 223) was purchased from Evonik Industries. The silica phase consists of surface-modified, synthetic SiO₂ spheres of 20 nm size with a high SiO₂ content of 50 wt%. As for the content of nanosilica particles in the SMP resin, the amounts are indicated according to the weight percentage of 1, 2.5, 5, 10 and 15 with respect to tBA, DEGDA and photoinitiators. Nanosilica suspensions was mixed thoroughly into the photopolymer resin by magnetic stirring for 30 mins and followed by using a planetary centrifugal vacuum mixer (Thinky Mixer, USA) for another 15 minutes. Ultrasonication

(S&M Vibracell 500W 20kHz Ultrasonic Processor) at 40% amplitude was applied for 30 minutes with 5 seconds pulse interval to further disperse the nanosilica particles in the photopolymer. The process of synthesis for SMPC resin is illustrated in Figure 22.

Figure 22: Synthesis process of SMPC resins.

3.2 Fabrication of SMPs via Stereolithography Process

3.2.1 Stereolithography Process

The stereolithography (SLA) process can be divided into two major categories – projection and scanning type. In the projection type SLA process, a digital light projection (DLP) or LED is utilized to project a whole cross-sectional area of mask projection on the resin surface. On the other hand, scanning type SLA process uses a UV laser beam to scan and cure the surface of the resin layer by layer [129]. The curing depth and width of printed parts can be controlled by adjusting the exposure time or laser scanning speed respectively. To summarize, the main difference between the two system is primarily the source of UV, which is either a projector or laser beam.

The key strength of stereolithography is its ability to rapidly direct focus radiation of appropriate power and wavelength onto the surface of the liquid resin. 3D objects from

computer-aided design (CAD) models are ‘sliced’ into 2D cross sections for photo curing that takes place layer-by-layer. The conventional top-down laser stereolithography starts with an excess of liquid resin and laser cures from the top onto the resin surface. However, in this project, a modified bottom-up scanning SLA (DigitalWax System 029X, Italy) as shown in Figure 23, was utilized and it works with the same mechanism as bottom-up projection SLA (ASIGA PLUS 39, USA) where its build platform is immersed into the resin on a transparent base and the resin is cured from below.

The bottom-up configuration also uses fewer amounts of resins, which makes it more economically efficient in developing SMP resins for stereolithography processes. Photoinitiation was induced by a UV solid state laser for scanning SLA/ UV exposure for projection SLA at a fixed wavelength of 405 nm. After each layer is cured and attached onto the platform, the z-positioning elevator rises to detach from the bottom surface and allows the resin to flow in and the process repeats until the 3D object is completely built. The temperature of the printing environment was kept at below the transition temperature of the SMP to prevent the printed SMP from being too soft and gel-like since SMPs are thermally sensitive.

Figure 23: Schematic of bottom-up scanning/ projection type SLA.

3.2.2 Optimization of Processing Parameters

The experimental interest here is to determine the laser threshold scanning speed (for scanning SLA) or exposure time (for projection SLA) and achieve dimensional accuracy by minimizing excess curing width. This can be achieved by carrying out the curing depth studies to get insights on the effects of the different resin compositions on the layer thickness of the printed samples. The curing depth determines the minimum layer thickness suitable for stereolithography fabrication and curing time per layer to optimize the processing parameters. The curing depth of the printed parts must be larger than the layer thickness so as to ensure good adherence to the previous cured layer. This will also minimise the chances of delamination between each layer since there is a slight overlap of curing between the previous cured layer and the next layer.

A 0.5 mL amount of prepared resins was pipetted onto the quartz slide and placed above the projector lens or laser beam as shown in Figure 24. The DLP projector has a light intensity of 20 mW/cm^2 , while that of the laser scanning SLA is around 40 mW/cm^2 . Rows of square array (5 x 5 mm) were projected for a specific time ranging from 0.5 to 50 seconds (Figure 25) and similar set up for scanning speeds ranging from minimum value of 100 to maximum value of 1360 mms^{-1} . The hatch spacing for the laser scanning type stereolithography process was kept at 0.06 mm. The exposed square array formed thin square layers on the quartz slide, while the remaining uncured resin was washed away with *Iso*-propanol (IPA). The curing depths thus correspond to the surface height of the thin square layers and were measured using a stylus profilometer (Taylor Hobson Talysurf Series 2, UK) as shown in Figure 26. The stylus tip moved forth and back to take an average of the surface heights to account for the curing depths. A total of 3 samples were measured for each curing time, however only the lowest curing depth

values were recorded. The purpose is to ensure that the layer thickness set on the printing system is always smaller than the lowest curing depth achievable. By plotting the curing depths of each composition against the exposure time/ scanning speed, the curing characteristics of the SMP/ SMPC resins can be analysed and the optimized parameters were obtained.

Figure 24. Experimental setup for curing depth studies of DLP and SLA.

Figure 25. Curing depth test illustrating cured resin array from 0.5 to 10 s.

Figure 26. Measurement of curing depth of a sample using stylus profilometer.

3.2.3 Post-Processing of SLA SMPs

With the optimized laser parameters and resin concentrations, a batch of specimens with specific dimensions for thermal, mechanical and thermomechanical tests were printed via the two different stereolithography processes. After the printing process, the specimens were removed off the platform and flushed with isopropyl alcohol (IPA) to wash off any unreacted photopolymers. They were then placed in a UV oven (CMET UV-600HL, Japan) for post-curing of 10 minutes, ensuring that the specimens were all fully polymerized.

The SLA-printed parts were ensured to have smooth surfaces before they were used for testing. Surface roughness of the parts were not measured as they have insignificant effects of the part performance since SLA process is also recognized for its high resolution and excellent surface finished parts among all other AM techniques [47]. This ensures that the printed SMPs are of better quality with lesser surface defects to avoid defect-induced failure during repeated thermomechanical cycling.

3.3 Thermal Analysis of SLA SMPs

3.3.1 Thermogravimetric Analysis

A thermogravimetric analysis (TGA) was carried out on TA Instruments TGA Q500 equipment (USA) to find out the polymer decomposition temperatures. The TGA results obtained can be used to anticipate the degradation temperatures of each sample, which were used as the upper limits of the deformation temperature for subsequent thermomechanical cyclic tests. The samples with a mass of approximately 10mg each were placed in a platinum pan and heated up in the furnace from room temperature to 600°C at a heating rate of 10°C min⁻¹.

3.3.2 Dynamic Mechanical Analysis

Given that the shape memory effect of thermoset SMPs is dependent on the glass transition temperature (T_g) in which the material is rigid below the T_g and become rubbery when above it, the T_g and viscoelasticity of the SMPs were determined using Dynamic Mechanical Analysis (TA Instruments DMA Q800, USA). Samples printed in the shape of rectangular bars with dimensions of 17.5 mm x 11.9 mm x 1.20 mm were placed onto the DMA single cantilever clamping fixture under a dynamic load of 1 Hz with amplitude set at 15 μ m. The samples were heated from 20°C to temperatures well above the T_g at a heating rate of 3°C min⁻¹. The T_g can be evaluated as a maximum of the loss factor $\tan \delta$ and storage modulus in both the glassy and rubbery state were analysed from the DMA results.

3.3.3 Thermomechanical Analysis

To determine the onset of softening in the SMP in which it starts to change from glassy to rubbery state, its thermomechanical properties were analysed using

Thermomechanical Analysis (TA Instruments TMA Q400, USA). The sample with a thickness of 0.65 mm was placed on the quartz stage holder surrounded by a furnace and a quartz penetration probe rested on top of the sample with a small force of 0.02N. The sample was cooled down to -20°C before heated up to 80°C at a heating rate of 5°C min⁻¹. TGA measures the linear or volumetric changes in the dimensions of a sample as a function of temperature when it is cooled or heated in a controlled atmosphere. A thermocouple placed next to the sample detects the softening temperature when there is a sudden drop in the dimensions of the sample.

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

Under Chapter 6 on SMPCs, the chemical interaction of the nanosilica with the SMP was analysed using FTIR Analysis (Thermo Scientific™ Nicolet™ iS™10 FT-IR) accomplished through the Attenuated Total Reflectance (ATR) mode. By interpreting the infrared absorption spectrum, chemical bonds can be identified. FTIR is also used to examine the difference in the network structure during synthesis of an SMP. The ATR-FTIR spectra were taken over 4000 to 500 cm⁻¹ range at a resolution of 4 cm⁻¹.

3.5 Mechanical Properties

3.5.1 Tensile Tests

Tensile tests were performed using tensile machine (Instron 5548 Micro Tester, USA) equipped with a thermostatic chamber to determine the mechanical properties of the SLA-printed dumbbell-shaped specimens. The tensile tests were conducted in accordance with the standard test method for micro-tensile based on ISO 527-1:1996 standards at both room temperature and above T_g. The tests were run at a crosshead speed of 1 mm min⁻¹. For experimental runs above the T_g, the samples were placed

inside the chamber to reach an equilibrium temperature (10°C above its T_g) before the tests were carried out.

3.6 Electron Microscopy

To determine if there are presence of agglomeration, ultra-thin samples of cured SiO_2 -SMP were characterized by transmission electron microscopy (TEM; JEOL 2010 UHR, Japan).

3.7 Shape Memory Characterizations

3.7.1 Thermomechanical Cyclic Tests

Thermomechanical cycle experiments were performed with dynamic mechanical analysis (TA Instruments DMA Q800, USA) in single cantilever mode to characterize the shape memory behaviour of SLA SMP printed parts.

Prior to deformation, step 1 involves heating the DMA samples ($17.5 \times 11.9 \times 1.20 \text{ mm}$) to above their T_g at a rate of $3^{\circ}\text{C}/\text{min}$ and equilibrated for 15 minutes. In step 2, samples were deformed by applying a moderately increasing static force at a constant rate of $0.1 \text{ N}/\text{min}$ to a designated strain (ε_i). In step 3, the samples were cooled at a rate of $3^{\circ}\text{C}/\text{min}$ to 25°C to fix the deformation. In step 4, the force exerted on the samples was unloaded to a preloaded force of 0.001 N at a rate of $0.3 \text{ N}/\text{min}$. Upon unloading, part of the strain was instantaneously recovered and the unloading strain (ε_u) was recorded. The shape fixity ratio (R_f) that determines the ability of the SMP to fix the mechanical deformation can be calculated from Equation [4]:

$$R_f(\%) = \frac{\varepsilon_u}{\varepsilon_i} \times 100 \quad [4]$$

In the final step, the samples were reheated to above their T_g at a rate of $3^\circ\text{C}/\text{min}$ and held isothermal for 10 minutes to recover any residual strain. The final strain (ε_f) was measured and the shape recovery ratio (R_r) that quantifies the ability of the material to memorize its permanent shape and is a measure of how much applied strain is recovered upon reheating can be derived in Equation [5].

$$R_r(\%) = \frac{\varepsilon_i - \varepsilon_f}{\varepsilon_i} \times 100 \quad [5]$$

Figure 27 illustrates the experimental setup for the thermomechanical cyclic tests using DMA. The test was repeated from step 2 over multiple cycles until the samples are fractured to determine its cycle life.

Figure 27. Experimental setup for thermomechanical cyclic tests.

CHAPTER 4. SYNTHESIS AND CURING

CHARACTERISTICS OF SMPS IN PROJECTION AND LASER STEREOLITHOGRAPHY PROCESS

4.1 Introduction

Stereolithography process can be divided into two major categories – projection and scanning type. Although the principles of both processes are similar, the effects of process parameters to cure the SMP material can be quite different. The light in the projection type SL process and that of the scanning type can be of different energy densities due to different control parameters such as exposure time and scanning speed, which will correspond to varying degree of polymerization. Therefore, it is essential to determine the critical energy density by the UV projector or laser to sufficiently form a solid network.

Another curing behaviour to look into is the analysis of the curing depth which predicts the spatial accuracy of the printing process. The depth of cure determines the minimum layer thickness of the printed model and therefore the total printing time required [130]. The current theoretical model for prediction of curing depth is mainly based on the Beer-Lamber equation:

$$C_d = D_p \ln \frac{E}{E_c} \quad [6]$$

where C_d is the curing depth that is measured based on the thickness of a cured resin being scanned or exposed by UV, D_p is the resin penetration depth, E is the exposure

energy density on the resin surface and E_c is the critical or threshold exposure energy density of the resin to initiate polymerization, below which polymerization cannot occur.

In this chapter, the effects of process parameters and curing behaviour in terms of curing depths of the SMPs with varying concentration of photoinitiators and crosslinkers using a projection type and laser scanning type stereolithography process were studied. The study of curing depths in photopolymerization is an important aspect of the curing process, because it affects the final dimensions of the cured sample. Vertical resolution is dependent on the light penetration depth, which can be controlled by addition of suitable photoinitiators to the photopolymer resin. It is worth noting that the main time-consuming step in SLA is not the laser-scanning itself, but the deposition of the new layer of photocurable material. Here, the viscosity of the material plays an important role. Very often nonreactive additives or solvent and sometimes preheating must be used to decrease the viscosity of the photopolymer resin. Viscosity and wetting behaviour of the resin onto the solidified part are both of critical importance here. However, in the case of the developed SMP using tBA and DEGDA mixture, the developed resin comprises of low molecular weight monomers that have very low viscosity, close to that of liquid water. Hence, viscosity of the developed resin has little effects on the printing process. The rheological properties of resins for SLA process is more critical only when developing resins of high molecular weight as the viscosity can be too large that results in long settling time during printing. Another case where viscosity is an important characteristic is when the resins contain high solid loadings that will affect the wetting behavior during printing.

These results provide a clear basis for optimizing the cure of these systems by controlling not only the depth of cure but minimizing shrinkage as well. By understanding the curing behaviour and using the model for calculation of the critical energy density and threshold penetration depth attainable, this allows new SMP materials to be successfully printable using any types of UV based 3D printing systems.

4.2 Synthesis and Resin Formulation

Commercial tert-butyl acrylate (tBA) monomer were mixed with di(ethylene glycol) diacrylate (DEGDA) crosslinker, and UV photoinitiator Phenylbis (2,4,6-trimethylbenzoyl) phosphine oxide (BAPO). The tBA-*co*-DEGDA networks were synthesized by free radical polymerization using the bottom-up stereolithography process and Figure 28 illustrates one of the possible chemical structures of the crosslinking between tBA and DEGDA.

Figure 28: Chemical structure of UV crosslinked tBA-*co*-DEGDA network.

The synthesis of the polymers is based on a thermally induced one-way dual-component with phase switching mechanism. In SMP, two distinctive features have to be met: one is the hard segment (netpoints) consisting of covalent bonds or intermolecular interactions that defines the permanent shape and the other is the soft segment (switching segment) that is made up of chains, enabling fixation of a temporary shape [32, 102]. The acrylate based tBA monomer is introduced as the soft segment since tBA forms shorter chains which are less bulky, hence increasing mobility of the molecular chains for easier deformation when the material changes from rigid plastic in room temperature to soft rubber at temperature above its glass transition temperature (T_g). DEGDA crosslinker acts as the netpoints, ensuring that a network structure is established within the SMP. Its higher thermal transition temperature also provides thermal stability in the network structure to withstand the thermomechanical conditions encountered in the shape memory process without breakage, hence defining itself as the hard segment in the SMP that constitutes the permanent shape.

The tBA-co-DEGDA network forms an acrylate-based photocurable system which polymerizes through free radical mechanism using BAPO photoinitiators. It is necessary to introduce the photosensitive initiators to kick off the photo-polymerization upon exposure to UV as the monomers do not generate sufficient initiating species for polymerization. The rate of polymerization for radical curable acrylates is distinctively fast and precise due to its high reactivity and also strong crosslinked polymers are generated only in the illuminated areas, thus the localised polymerization produces high resolution parts [131], especially with the use of stereolithography which gives controlled curing so that any complex or thin features can be printed precisely and accurately with no excess curing width. Unlike cationic polymerization which is

common in epoxy-based monomers, acrylate-based systems are more stable due to sensitivity towards atmospheric oxygen and absence of post-polymerization which is a phenomenon where polymerization still proceeds even in the dark without UV exposure [132]. The choice of the acrylate-based tBA-*co*-DEGDA system with its unique features satisfies the requirements of stereolithography process to fabricate each cross-sectional layer within seconds. However, high shrinkage is usually experienced during fabrication due to shorter chain length [133-135]. Hence, in this chapter, the curing behaviour with varying concentration of crosslinkers and photoinitiators using a projection type and laser scanning type stereolithography process were studied and characterized.

4.3 Results and Discussion

4.3.1 Theoretical Model for Energy Density

Based on the Beer-Lamber's equation, the curing depths are dependent on the energy density of the UV projection or laser beam. For projection type sterolithography process, the energy density is in terms of a cross-sectional area which is related to the intensity of the UV light and exposure duration as shown in Equation [7]:

$$E_p = I \times t \quad [7]$$

where E_p is the effective energy density by projection, I is the intensity of the UV light which is fixed at 40 mW/cm² and t is the UV exposure time.

For the laser scanning type stereolithography process, the laser beam irradiation follows a Gaussian distribution and is directed onto the photopolymer surface by scanning line by line to create a desired cross-section. Although the scanning path of the laser beam

is highly dependent on the cross-sectional shape of the structure, in this work the most common path in conventional stereolithography which uses a scan parallel to only one direction is assumed. Figure 29 shows the schematic diagram of the laser scanning beam and the scanned area.

Figure 29. Schematic diagram of laser scanning beam where d is the laser spot size and h_s is the hatching space.

The energy density of a single laser scanned line is a function of the laser power P , laser spot size d , and laser scanning speed v_s which is illustrated in the equation as follows [136]:

$$E_{line} = \frac{P}{d \times v_s} \quad [8]$$

To make comparison with the energy density by projection, energy density in terms of scanned area instead of scanned line is examined. For a scanned area, the hatching spaces h_s in between each scanned line are taken into consideration. The effective area that is cured by the laser scanning is only a fraction of the entire area with a ratio of d to h_s , whereby the effective energy density for a scanned area is derived as:

$$E_{area} = E_{line} \times \frac{d}{h_s} = \left(\frac{P}{d \times v_s} \right) \left(\frac{d}{h_s} \right) = \frac{P}{v_s \times h_s} \quad [9]$$

where E_{area} is the effective energy density by laser for a scanned area which becomes regardless of laser spot size, P is the laser power fixed at 86 mW, v_s is the scanning speed and h_s is the hatch spacing. In this study, the process parameters for curing depths of specimens by both projection and laser type SL process were listed in Table 5 and

Table 6. A total of 6 samples were measured, however only the lowest curing depth values were recorded. The purpose is to ensure that the layer thickness set on the printing system is always smaller than the lowest curing depth achievable.

Table 5. Process parameters setting for projection type stereolithography process.

Exposure time t [s]	Intensity I [mW/m²]	Energy Density E_p [J/m²]	Curing Depth C_d [μm]
1	40	400	0
2	40	800	1.25
4	40	1600	23.57
6	40	2400	24.44
8	40	3200	42.4
10	40	4000	41.41
20	40	8000	60.71
30	40	12000	151.4
40	40	16000	150.9

Table 6. Process parameters setting for laser scanning type stereolithography process.

Laser scanning speed v_s [mm/s]	Power P_L [mW]	Hatching space h_s [mm]	Energy Density E_{area} [J/m ²]	Curing Depth C_d [μm]
100	86	0.060	14333	23.21
200	86	0.060	7167	22.96
300	86	0.060	4778	21.71
400	86	0.060	3583	21.08
500	86	0.060	2867	20.61
750	86	0.060	1433	18.53
1000	86	0.060	716.7	17.87
2000	86	0.060	477.8	12.13
3000	86	0.060	358.3	16.62
4000	86	0.060	286.7	10.64

4.3.2 Curing Characteristics

SMPs of the same compositions were used for both the projection and laser scanning type, but different curing behaviours are observed. Figure 30 depicts the relationship between the curing depths as a function of energy density. At the same energy density, it is shown that the projection type SL process obtains a larger curing depth than the laser scanning type. This is due to the difference in intensity from both the systems. The projection type SL process is of a much lower light intensity, hence it requires longer exposure time in order to achieve the same energy density exposed on the resin by the laser scanning type. The prolonged exposure duration eventually results in deeper light penetration through the resin, forming a thicker cured layer as compared to the laser scanning type.

Figure 30. Curing depth as a function of energy density for projection-type and laser-scanning-type SL process.

Figure 30 also illustrates that the curing depths for the SLA processes start to plateau despite increasing energy density. This is because energy density is increased by extending the exposure time and lowering laser scanning speeds, however the intensities of the light source remain fixed. Upon initiation of polymerization, the formation of cured resin will scatter or block further penetration of light through the resin, causing the intensity ratios absorbed by the resin to decrease exponentially as the percentage of cure increases. This is in alignment with Fuh *et al.* [134] who revealed that the intensity ratios experience a sudden decrease upon polymerization instead of gradually decreasing when curing increases. Therefore, the curing depths are maximized after reaching a critical point when the light intensity is completely blocked off.

4.3.3 Abnormal Shrinkage Phenomenon

The curing behaviours of the SMP are observed to differ when the curing is performed via projection of an entire area or by scanning line by line. In a projection type stereolithography process, a shrinkage phenomenon in the lateral direction was observed from curing depth samples with increasing UV exposure duration as shown in Figure 31. This is attributed to the entire cross sectional area being cured concurrently, hence the energy density per unit time for a large cross section is much more as compared to that of a laser type stereolithography process [134]. The large energy density per unit time given by the projection type results in inhomogeneous curing of the samples and causes a shrinkage phenomenon to occur. Another reason is because when the energy density becomes larger due to prolonged UV exposure time, this will cause accumulation of heat in the exposed area and the exposed region will be slightly warmed up. As polymerization is a highly exothermic process, heat is released by the resin during photo-polymerization [137]. Moreover, a higher energy density also infers that there is higher degree of monomer-to-polymer conversion which has a fundamental influence on shrinkage stress due to development of polymerization contraction [138]. The intensity of the projection type stereolithography process is also non-uniform where the intensity is more concentrated in the middle [139]. Since the SMP material is highly temperature-sensitive, the sample starts to soften and leads to shrinkage in the lateral direction.

Figure 31. Shrinkage phenomenon in the lateral direction observed from curing depth samples with increasing UV exposure duration by projection type SL process.

4.3.4 Threshold Energy Density

According to the Beer-Lambert's equation and Figure 30, the critical or threshold energy density (E_c) and attainable penetration depth (D_p) can be determined for the developed SMP materials to avoid over dosage of energy density. The SMP resin requires a threshold energy density of 1350 J/m^2 with a resin penetration depth of 17.86 μm . Generally, E_c and D_p are two constants of the resin, hence given any UV based 3D printing systems, as long as the energy density is above 1350 J/m^2 , the developed SMP material can be cured and printed. The penetration depth of resin determines that the minimum layer thickness of the printer to be set below 17.86 μm in order to prevent any formation of voids between layers, ensuring a slight overlap curing and interlayer adhesion, hence preventing internal voids formation which could act as stress concentration points. This penetration depth is significantly close to the lower limits of conventional layer thicknesses between 16 μm and 150 μm , thus ensuring high printing resolution in the z-axis.

To further evaluate the dimensional accuracy of the printed samples based on the threshold energy density, the samples were cured at varying energy densities (for both projection and laser scanning SLA) with a layer thickness of 50 μm to form specimens size of 17.5 mm $\times$ 11.9 mm $\times$ 2 mm. The dimensional accuracy of the printed samples in terms of minimized excess curing width in x and y directions were measured using digital caliper as shown in Figure 32. When the samples were cured under high energy density (i.e. the laser is set at very low speed/ the UV exposure time is kept very long), there is loss in dimensional accuracy caused by presence of excess curing width due to overcuring. The excess curing width of the specimens decreased exponentially as the energy density is lowered (increasing laser scanning speed/ decreasing exposure time). To keep the deviation of dimensional accuracy within 100 μm , the threshold energy density is determined as 1350 J/m^2 which is in agreement with the energy density required for minimum curing depth.

Figure 32: Excess curing width in x and y directions as a function of energy density.

4.3.5 Curing Depths with Varying Photoinitiator Concentrations

The curing depths of polymerization are strongly governed by not only the penetration of incident light by the UV source, but also the photoinitiator concentration which is explained by Jacobs' Equation [10] and [11]:

$$C_d = D_p \ln \left(\frac{E_{\max}}{E_c} \right) \quad [10]$$

$$D_p \propto \frac{2}{2.303 \propto [PI]} \quad [11]$$

where C_d is the curing depth, D_p is the depth of penetration, $E_{\max}$ is the energy dose per area, E_c represents a critical energy dosage and $[PI]$ stands for concentration of photoinitiators [130]. The curing depth determines the minimum layer thickness suitable for stereolithography fabrication and curing time per layer to optimize the printing process. The curing depth of the printed parts must be larger than the layer thickness so as to ensure good adherence to the previous cured layer. This will also minimise the chances of delamination between each layer since there is a slight overlap of curing between the previous cured layer and the next layer which is illustrated in Figure 33.

Figure 33. Schematic illustration of overlap curing between layers.

Upon specifying the threshold energy density for the SMP to be cured, SMPs with varying concentrations of photoinitiators at 0.5, 1, 2, 4 and 5 wt% were prepared to evaluate the effects of photoinitiator concentrations on the curing behaviour. Table 7 shows the thickness of the samples as a measure of curing depths for SMPs with photoinitiator concentrations of 0.5, 1, 2, 4 and 5 wt%. The curing depths measured for 0.5 and 1 wt% photoinitiator concentrations were fluctuating slightly above and below 10 μm . Dramatic shrinkage was observed in the printed parts due to the low curing depths. This phenomenon can be explained due to the low concentration of photoinitiators which reduces the generation of free radicals, hence a loosely crosslinked polymer is being formed, leading to a large amount of shrinkage [130]. Therefore, photoinitiator concentrations of 0.5 and 1 wt% were not considered for formulation of the SMPs. The increase in the concentration of the photoinitiators yields a deeper curing depth, because the photon absorption becomes greater and the initiation of free radicals occurs more localized, thus producing a tightly cross-linked polymer that undergoes little shrinkage [130]. The measurements of the curing depths could be seen from Table 7 and the lowest curing depths achievable for 2, 4 and 5 wt% photoinitiator concentration are 28.10 μm , 35.45 μm and 38.85 μm respectively. To ensure that the

parts are fabricated without any presence of voids in between layers, the layer thickness of the stereolithography process is set to be 25 μm , whereby tBA-co-DEGDA system with 2 wt% photoinitiator mixtures will be used for all stereolithography fabrication of test specimens. Given that the layer thickness is smaller than the minimum curing depth attained by the 2 wt% photoinitiator concentration, there will be a slight overlap curing between layers, hence preventing internal voids formation which could act as stress concentration points.

Table 7: Curing depths (C_d) measured with respects to different photoinitiator concentrations.

Photoinitiator Concentration [wt%]	Lowest C_d [μm]	Highest C_d [μm]
0.5	< 10	< 10
1		
2	28.10	30.33
4	35.45	36.92
5	38.85	39.93

4.3.6 Curing Depths with Varying Crosslinker Concentrations

Besides the influence of photoinitiator concentrations on curing depths in the stereolithography process, there are also other parameters found to affect the curing behaviour, such as light intensity, components of the resin and concentration of inhibitor. Here, the curing depths are observed to differ with a change in crosslinker concentrations in the SMP compositions. Figure 34 shows the curing depth behaviour of 10, 20, 30 and 40wt% DEGDA crosslinker concentrations against increasing energy density.

Figure 34. Curing depth of varying DEGDA crosslinker concentrations as a function of energy density.

The DEGDA crosslinkers within the SMP network serves the purpose of forming crosslinks with the monomer so as to fix the permanent shape of the SMP. With increasing concentration of crosslinkers, the curing depths of the SMP are observed to increase. The reason is due to photon propagation through the resin is graded instead of being discretized, the penetration depth can reach up to the point at which the degree of cross-linking and polymerization is sufficient to form a solid network [140, 141]. Hence, with increment in the content of DEGDA crosslinking agent from 10 to 40 wt%, there is higher degree of crosslinking, allowing larger curing depths to be reached at a faster rate even at low energy density.

4.4 Summary

In this chapter, a study on the curing behaviour of shape memory polymers using stereolithography process by projection and laser scanning type methods was performed. It is discovered that the principles of both the stereolithography process might be similar, but the curing depths obtained from the projection type are much higher than that of the laser scanning type with the same energy density due to prolonged exposure time. This eventually leads to the occurrence of an abnormal shrinkage phenomenon in the SMP samples printed via projection type due to accumulation of heat from concurrent curing. From the experimental analysis, the threshold energy density of the developed SMP resin was found to be 1350 J/m^2 with a resin penetration depth of $17.86 \text{ }\mu\text{m}$. To avoid shrinkage during printing due to low curing depth and ensure strong adhesion between layers, the optimal photoinitiator concentration is determined as 2 wt% while the layer thickness is set at $25 \text{ }\mu\text{m}$ for all subsequent stereolithography fabrication of test specimens. The variations in resin compositions by increasing crosslinker concentrations has shown to increase the curing depths at a faster rate even at low energy density. However, the increase in curing depths also denotes that there is higher degree of crosslinking within the SMP network which adversely affect the shape memory properties which is discussed in the next section. In this summary, this section has shown the methodology in obtaining the critical energy density and threshold penetration depth of the SMP material that allows newly developed SMP materials to be cured and printed by any UV based 3D printing systems.

CHAPTER 5. TAILORING SHAPE MEMORY PROPERTIES

5.1 Introduction

Previously, the curing behavior and determination of processing parameters for the newly developed SMPs have been successfully demonstrated. The printability of the SMPs were validated to meet the requirements of the stereolithography process. This new material development in stereolithography process not only addresses the issue of limited commercial availability of SMP materials for 4D printing, but also overcomes the restrictions of the closed system of a Polyjet printer to freely tune the thermomechanical properties of 4D printed parts beyond its available digital materials. The ability to control the shape memory behavior by changing material compositions presents a huge advancement for 4D printing technology to extend to a wider spectrum of applications.

Furthermore, while shape memory properties in terms of shape fixity and shape recovery were highly reported in literature review, the thermomechanical degradation in terms of shape memory cycle life was rarely investigated. The thermomechanical degradation which determines the durability of the SMPs is an important characteristic on establishing whether the polymers can meet the needs of industrial applications where robustness of the shape memory performance over multiple cycles is critical. Therefore, in this chapter, the characterizations and analysis of tailoring shape memory properties were carried out and the durability of the 4D printed structures was also evaluated.

5.2 Results and Discussion

5.2.1 Thermal Analysis of SLA SMPs

Figure 35 shows the DSC curves of the SMPs with concentrations of crosslinker from 10 to 50 wt%. No endothermic peak was observed, indicating that the printed parts were fully cured, ensuring that the polymerization process is completed. Moreover, only one single step on each curve was observed, showing the SMPs are amorphous copolymers exhibiting T_g .

Figure 35. DSC results showing amorphous nature of SMPs.

The optimal T_g was determined by the temperature at which the relaxation peak of the $\tan \delta$ curves of DMA occurred, as shown in Figure 36. The T_g for the SMP with 10 wt%

of crosslinker was 53.9°C, and with every 10 wt% of additional crosslinker, an increment of approximately 5°C in T_g was observed. The peak height decreased and the peak shifted towards higher temperatures with increasing concentration of crosslinker. The increment in temperatures is because more energy is required to regain the chain mobility for more crosslinked polymers [142]. Meanwhile, it can be observed that the SMPs experienced a large change in storage modulus for more than 2 orders of magnitude below and above its T_g . A criteria for a good SMP has been established in the literature review, such that a large and sharp change in storage modulus is necessary when the SMP changes from glassy to rubbery state [142, 143], hence the SMPs here possess excellent shape memory behaviour. The peak heights corresponding to the storage modulus also determines the molecular mobility of the polymers. The curves were observed to flatten with increasing DEGDA content, showing that flexibility of the SLA SMPs reduces with additional crosslinkers. Therefore, by controlling the material compositions, the flexibility of the tBA-co-DEGDA network enables tunable thermomechanical properties such as T_g and storage modulus.

Figure 36. Peaks of $\text{Tan } \delta$ curves denoting the T_g of SMPs with varying crosslinker concentrations.

5.2.2 Thermomechanical Analysis

Thermomechanical analysis (TMA) is conducted to determine the onset of temperature at which the SMP starts to soften and become rubbery. Figure 37 shows that there is a dramatic drop in the thickness of the SMP sample when it reaches 45.3°C. At temperature below this, there is slight increase in the thickness due to thermal expansion of the part. However, when the temperature passes above 45.3°C, the thickness is reduced largely from -1.22 μm to -8.41 μm . This point at which the SMP encounters a large dimensional change is defined as the softening temperature which occurs at 45.3°C. As T_g is characterized as a range of temperatures over which this glass transition occurs, the softening temperature indicates the onset of transition in the SMP, which is approximately 10°C below its T_g of 53.9°C.

Figure 37: TMA results of SLA SMP to determine softening temperature.

5.2.3 Mechanical Properties

Mechanical properties in terms of tensile strength in glassy state and elongation in rubbery state are the most critical properties for programming the SMPs. The two properties dictate the capability of shape fixity and recovery, which are two important values for determining the functionality of the SMPs. Figure 38 shows the stress-strain curves of the SMP with 10 wt% of DEGDA crosslinkers and 2 wt% of PI below and above T_g .

At temperatures below T_g (room temperature 25°C), the SMP exhibited a tensile strength of 20.2 MPa with a low elongation of 8.79%. An elastic modulus of 230 MPa demonstrates the stiffness of the SMP in its glassy state at room temperature. At temperatures above T_g (65°C), the tensile strength dropped to 0.30 MPa and the elastic

modulus reduced to 1.66 MPa where the specimens become rubbery. The elongation was observed to achieve a larger percentage of 18.2%, which is approximately more than twice the breaking strain of 8.79 ± 0.95 % at room temperature. This is attributed to the SMPs tested at room temperature experiencing necking due to localized deformation and induced a fracture at low elongation. However, at temperature above T_g , the heating activates the molecular mobility which allows the molecules to stretch and align easily in the direction of the tensile pull, thus resulting in larger elongation at break. As observed from Figure 38, when the SMPs are tested below T_g , the parts underwent brittle fracture and failed catastrophically. When tested above T_g , the parts underwent plastic deformation for a longer elongation with observable necking. This big difference in elongation indicates that the SMPs printed can meet the requirements of large deformation during the deploying process and are suitable for shape memory applications [142].

Figure 38: Stress-strain plots for SLA SMPs at temperatures below and above T_g .

The tensile strength of the SLA SMP was significantly comparable to the industrial thermoset SMP such as Veriflex [89]. Notably, the elongation was observed to be 82% higher than Veriflex shown in Table 8. The higher elongation in the rubbery state achieved by the SMPs printed via stereolithography process is desirable for durable practical application of SMPs since it significantly reduces the likelihood of thermoset SMPs having brittle fractures at very low strain [89, 144]. The versatility of the SLA SMPs that allows it to be largely deformed and elongated at temperatures above its T_g , increases the possibility for wider scope of applications such as dynamic configurable parts, inexpensive and reusable customized moulds, that are more highly achievable via 3D printing as compared to conventional manufacturing. At the same time, the ability to use 3D printing for SMP increases the geometry freedom and reduces design constraints for the fabrication of complex parts. The mechanical properties achieved based on the SLA SMPs can be comparable with commercial thermoset SMPs and one of which is as shown in Table 8 as comparison.

Table 8: Comparison between SLA SMPs and commercial thermoset Veriflex SMP.

Properties	SLA SMPs		Veriflex VF62^[89] (thermoset commercial SMP)	
Glass Transition Temp T_g [°C]	53.96		62	
	At $T < T_g$	At $T > T_g$	At $T < T_g$	At $T > T_g$
Ultimate Tensile Strength, σ [MPa]	20.20 $\pm$ 2.21	0.30 $\pm$ 0.05	23	1.0
Elastic Modulus, E [MPa]	230 $\pm$ 41	1.66 $\pm$ 0.10	1240	0.2
Elongation, ϵ [%]	8.79 $\pm$ 0.95	18.2 $\pm$ 0.34	3.9	10.0

5.2.4 Shape Memory Properties

In this section, we demonstrated that the variations in concentration of the DEGDA crosslinkers not only influence the thermal properties of the SLA SMP, but also affect the shape memory properties. The shape fixity and shape recovery properties are critical in defining the suitability of the materials for shape memory applications. The shape memory properties of the printed SMPs are studied by undergoing thermomechanical cyclic tests using DMA single cantilever mode by applying strains below and above its breaking strain. This is to investigate the effects of strains on the cycle life of the SMPs, while the shape fixity and shape recovery ratio can be readily determined by using Equations [4] and [5].

Analysis of A Single Shape Memory Cycle

To analyse the shape memory properties, a single shape memory cycle as shown in Figure 39 was chosen to explain the curve characteristics. The SMP was heated in the DMA furnace up to a temperature above its T_g ($T = 65^\circ\text{C}$) and a deformation force is exerted to give an approximated strain of 11.09% (ϵ_{load}) on the SMP. However, there is a slight elastic spring back causing a drop in the shape fixity. This is due to a retraction force of the network to recoil upon removal of the loaded force after cooling to 35°C (below its T_g). The ϵ recorded after the spring back is around 9.69%, which gives a shape fixity (R_f) of only 87.4%. Subsequently, to measure the shape recovery property, the furnace is reheated while the speed of recovery is measured to be 1.75 %/min and as illustrated by the strain vs time curve, the strain returns to 0% which indicates that there is full shape recovery for the SMP.

Figure 39: Thermomechanical cycle of SLA SMPs.

Effects of Strain Loading on Shape Fixity

Two essential aspects of SMPs are their ability to fix a temporary shape (fixity) and to subsequently recover to its original shape by an external stimulus (recovery). A comparison between the fixity ratio of the SMPs under different strain loadings is as shown in Figure 40 to determine the effects of strain loadings on the SMPs. An approximately 10% strain (which is below its breaking strain of 18.2%) was imposed on the SMP when it was heated to above its T_g . However, upon removal of the load force after cooling to below its T_g , there is a slight elastic spring back causing a drop in the shape fixity. The ϵ recorded is below 10%, which gives R_f of only 85% but there is a rising trend in the fixity up to 92% after 6 thermomechanical cycles. The fixity then further drops to about 86% at the 7th cycle and stays relatively constant for the subsequent cycles. The phenomenon can be explained such that at the incipient stage, the shape fixity is lower in ratio as the release of constrained force is followed by

restrictive force due to heavy friction among molecules to retain the temporary shape hence generating spring back by the SMP. After the 7th cycles, the repeated movement of the cross-linked structures during repeated cycles reduced the friction among the molecules. Molecular chain mobility become easier and the molecules are locked in deformed chain conformation, which results in smaller spring back, thus giving better shape fixity ratio. The fixity remains relatively constant for subsequent cycles, indicating that repeated thermal mechanical cycles helps to reduce entanglement of the amorphous polymer network and improve on the ability to retain its temporary shape.

On the other hand, applying higher strain on the SMPs has significant effect on the fixity ratio. When the strain loading is doubled to approximately 20% (which is above its breaking strain of 18.2%), there is a huge elastic spring back which leads to a fixity of only 69%. The deformation introduced is relatively large such that it results in an entropic change in the polymer chains, in which the cooling stage should serve as a kinetic trap to store this entropic energy and only release the energy during reheating for recovery. However, the energy state in the SMPs were too high due to the large deformation imposed on the permanent shape together with the initial restrictive friction among molecules, hence the cooling of SMPs is unable to fully trap the entropic energy which results in some loss of energy that causes the huge spring back. The friction among molecules are reduced after repeated cycles, therefore fixity ratio rises to 86% but still unable to fully “memorize” the deformed shape.

Figure 40. Effects of strain loadings of 10% and 20% on fixity over repeated cycles.

Effects of Strain Loading on Shape Recovery

Figure 41 shows the shape recovery properties over several cycles until the SMPs failed to recover. For SMPs under a strain loading of 10% strain (which is below its breaking strain of 18.2%), the SMPs could fully recover to its original permanent shape for 14 thermomechanical cycles. However, the netpoints which are responsible for defining the permanent shape, becomes less stable from the 15th cycle onwards due to thermomechanical conditions and fatigue encountered in the shape recovery process. Therefore, the SMPs were unable to fully recover starting from the 15th cycle. Nevertheless the recovery ratio ranges between 97 and 99%, hence the SMPs can be considered as excellent shape memory material because it meets the requirements of shape memory ratio being more than 90% [145].

On the contrary, the SMPs under a strain loading of 20% (which is above its breaking strain of 18.2%) did not recover completely since the first cycle. The SMPs were only able to recover at most 95% of its original shape but could withstand up to 10 thermomechanical cycles. This denotes that the deformation force imposed might be too large such that it causes slippage in the polymer chains that lead to macroscopic deformation instead of entropic change [5]. Hence, full 100% recovery was not possible, which indicates that a strain loading higher than the breaking strain of the printed SMP will significantly reduce its shape memory performance.

Figure 41. Effects of strain loadings of 10% and 20% on recovery over repeated cycles.

Effects of Crosslinker Concentrations on Shape Memory Properties

Figure 42 presents the shape fixity curves of the SLA SMPs with concentrations of DEGDA crosslinkers ranging from 10 – 50 wt%. The SLA SMPs keep a high shape fixity of more than 85% when the amount of crosslinkers is 30 wt% or less within the tBA-co-DEGDA network. In the first cycle, the SLA SMPs with 10, 20 and 30 wt% crosslinker achieved a considerably high shape fixity of 84.9%, 95.2% and 93.9% respectively. The shape fixity of SMP with 10 wt% crosslinkers gradually improves after several cycles due to the repeated movement through multiple cycles, hence reducing the friction among the molecules which enables relaxation of the entangled amorphous polymer network [102]. Hence, molecular chain mobility becomes easier and the molecules can be locked in deformed chain conformation, giving higher shape fixity close to 90% for subsequent cycles. The increment of the crosslinker concentration within the polymer network also increases the rigidity of the SMP and thus improves the ability of retaining the temporary shape at the incipient stage.

Figure 42. Effects of increasing concentrations of DEGDA crosslinkers on shape fixity properties of the SLA SMPs over repeated thermomechanical cycles.

However, the SLA SMPs with higher concentration of crosslinkers exhibit a shorter cycle life and they fractured after 8 cycles (20 wt%) and 6 cycles (30 wt%) on average. This has been attributed to the low molecular weight ratio of tBA monomer within the network, indicating that the polymer chains have lower ability to coil. The amount of tBA monomer functions as a softening agent which is imperative for the SMP to undergo inelastic strain deformations without chain slippage (permanent deformation), thus contributing to its ability to recover to its original shape. The presence of a very small amount of chemical crosslinking could potentially be another factor that determines whether the SMP has high shape memory performance^[76] and long lasting cycle life [146]. The results shown in Figure 42 indicate that in a SMP system with the same

monomer and crosslinker, the SMP of higher crosslinker concentration gives a higher shape fixity at the beginning while the SMP of lower crosslinker concentration is more favorable, giving a longer cycle life with comparatively high shape fixity.

The chemical composition of the SLA SMPs is also one of the factors affecting the shape recovery properties as shown in Figure 43. The ability to recover to its original shape is highly dependent on the concentration of the crosslinkers within the SMP network. The SMP with the lowest amount of crosslinkers has 100% shape recovery in the initial 14 thermo-mechanical cycles, while the subsequent cycles maintained stability within a high shape recovery range of 97 – 99%. Therefore, SMP with a lower concentration of crosslinkers results in a more loosely crosslinked covalent network that prevents catastrophic damage during shape deformation, hence achieving a more robust SLA SMPs with excellent shape recovery properties and longer cycle life achieved. Based on the average of 6 samples, the SLA SMPs with 10 wt% crosslinkers concentration exhibit an outstanding durability of 22 cycle life, which meets the criteria for commercial SMPs that are examined through a series of at least 20 thermo-mechanical cycles [76] to be qualified for its material confidence and robustness level. The shape memory performance of the SMPs undergoing repeated thermomechanical cycles is illustrated as shown in Figure 44.

Figure 43. Effects of increasing concentrations of DEGDA crosslinkers on shape recovery properties of the SLA SMPs over repeated thermomechanical cycles.

Figure 44: Full thermomechanical cyclic tests of SLA SMPs.

The full thermomechanical cycles that the SMPs were tested as a function of temperature under a strain of approximately 11.09% until failure by fracture. The SMPs could go through repeated folding and unfolding cyclic tests for up to 22 cycles. The shape memory performance of the SLA SMPs can also be presented in 3D diagrams as shown in Figure 45a and b. The 3D representations of the thermomechanical cycles clearly illustrate the various deformation-fixing-recovering stages that the SMPs underwent and depict whether the SMPs recover completely by looping back to its original strain value. This proved that the SLA SMPs possess excellent shape recovery and fixity properties which can be comparative to the typical thermoset SMPs as shown in Figure 46.

Figure 45: Thermomechanical cyclic tests of a) SMPs under free strain recovery of 10% and b) SMPs under free strain recovery of 20%.

Figure 46 shows a comparison of the shape recovery properties between our developed SLA SMPs and other thermoset SMPs fabricated using conventional methods such as injection molding and casting. The data presented was from the SLA SMP with 10 wt% DEGDA crosslinkers and 2% PI, while the typical thermoset SMPs were sourced based on various well-known SMP companies [76, 142] as well as several highly cited papers [144, 147-149]. Figure 46 highlights that the performance of our developed SLA SMPs under the applied loading of 10% and 20% strain exhibit highly comparative shape recovery properties as benchmarked against other thermoset SMPs of industrial grade. This significantly means that the SLA SMP can be a potential substitute for conventionally manufactured SMP with an additional unique feature of being 3D printed, thus having great flexibility in design for new product development. Moreover,

the high recoverable strain and the ability to control shape memory behavior of the SLA SMP by tuning to specific compositions are some of the added advantages over their metallic counterparts - shape memory alloys (SMAs).

Figure 46. Shape recovery properties of SLA SMPs as compared to typical thermoset SMPs.

5.3 Demonstration of SLA SMPs

Figure 47 demonstrates the stereolithography fabrication process of a Buckminsterfullerene (or C60 bucky-ball) which has a diameter of 45 mm, with each strut of 12.5 mm long and a diameter of 3 mm. The printing process involves polymerization of the photopolymer layer-by-layer, based on its cross section. The design is self-supported and the shape allows us to test the properties of the shape memory polymer.

Figure 47. Overview of the processes involved in the design and fabrication of bucky-ball by stereolithography

Figure 48 shows deformation and recovery process of the bucky-ball. A series of photographs illustrates the shape recovery process of SMPs printed via stereolithography process sequentially from left to right. Figure 48a) A complex structure in a permanent shape of a C60 bucky-ball was printed using a bottom-up laser scanning SLA. Figure 48b-c) The SMP ball was placed in hot water at a temperature above its T_g (65°C), then it was opened manually and cooled down to a temperature below its T_g (27°C) to form a temporary flat structure. The deformation from the enclosed shape into a fully opened, flat structure significantly demonstrated the ability of the SMP to withstand high strain. Figure 48d-h) The flattened structure was once again placed into the hot water for recovery to its original shape, and the entire recovery process was completed in 11 s. The fabrication of a C60 bucky-ball can be a challenge by conventional methods via casting or simple molds because of the intricate struts that

are designed in 3D. Other 4D printed structures using stereolithography process were also illustrated in Figure 49 and Figure 50 to demonstrate their shape memory behaviour. This work has demonstrated the ability to fabricate parts of complex geometries with fast shape recovery rate within seconds in one simple step of printing.

Figure 48. SLA SMP Buckminsterfullerene (or C60 bucky-ball) in printing (Figure 48a), unfolded after printing (Figure 48b-c), and recovered its original bucky-ball shape by soaking at 65°C of water (Figure 48c-h).

Figure 49. Shape memory structure printed via 3D projection type stereolithography process. (I-II) A 'W'-shaped SMP was printed using ASIGA DLP, (III) The printed part was placed inside hot water where the temperature of the water acts as the thermal stimulus, (IV) the structure was fixed in its deformed state at room temperature, (V-VI) The original shape was recovered upon reheating.

Figure 50. Shape memory structure printed via 3D laser scanning type stereolithography process. (I) A complex SMP bucky ball was printed using DWS 029X. (II-IV) The SMP was heated up via thermal conduction in hot water and temporarily deformed and cooled down. (V-VIII) shows the shape recovery process when the SMP was reheated.

5.4 Summary

In this chapter, the developed tBA-*co*-DEGDA networks were reported to provide high tailorability of thermomechanical properties of the printed SMPs. Several characterizations were carried out to demonstrate that the tailorable glass transition temperatures, high recoverable strain and shape memory behavior of the SLA SMPs can be controlled by changing the concentrations of crosslinkers. The T_g of the SMPs were found to increase approximately 5°C for every 10 wt% increase in the crosslinker concentrations. In terms of mechanical properties, the SLA SMPs also exhibited 82% higher elongation in its rubbery state than conventionally manufactured industrial grade thermoset SMPs, which demonstrated the ability of the SLA SMP to withstand high strain deformation. Not only does the chemical compositions affect the thermal and mechanical properties of the printed parts, it also affects the shape memory properties of the SMPs. With more crosslinkers within the polymer network, the rigidity of the SMP increases and improves the shape fixity but significantly deteriorates the shape recovery ability as the SMP becomes easily fractured under high deformation. SMPs with 10 wt% DEGDA crosslinker and 2 wt% photoinitiators exhibited the best shape memory performance with 100% full recovery and stability of the shape memory properties over the first 14 thermomechanical cycles. An outstanding durability of 22 cycles was demonstrated to show its prolonged shape memory cycle life. The robustness of this material addresses the fundamental issue of fast mechanical degradation observed in multi-material printed parts during repeated thermomechanical cycling. Moreover, the printed SMPs exhibited highly comparative shape recovery properties as benchmarked against other thermoset SMPs of industrial grade.

CHAPTER 6. SHAPE MEMORY POLYMER COMPOSITES CROSSLINKED WITH NANOSILICA

6.1 Introduction

Previous chapters have established that the developed SMPs for stereolithography processes demonstrated significant improvements in achieving fast curing rate, higher shape fixity, shape recovery, and prolonged shape memory cycle life as compared to industrial thermoset SMPs that are conventionally fabricated. Nevertheless, high strength polymers often exhibit low elongation at break [150]. This holds true as well for the commonly 4D printed parts using Polyjet printing. The active motion of the Polyjet 4D printed parts were restrained to only 30% of the linear stretch [43], printed digital materials were also found to break at 10 - 25% [151] and thermo-mechanical durability were identified as one of the limitations [44]. This drawback has largely restricted the applications of 4D printing to perform as engineering materials.

Moreover, most 3D printing technologies operate at under 10 mm/hour, and have a maximum deposition rate of under 50 cm³/hr [46]. There is a concern that these machines do not provide good Return on Investment (ROI) because of the fabrication speed. The speed-limiting process for polymer printing systems is resin curing. Most commercially available machines print at speeds between 1.3 mm/hr (Polyjet) and 30 mm/hr (digital light processing SLA), where a macroscopic object several centimetres in height can take hours to construct. For additive manufacturing to be viable in mass production, print speeds must increase by at least an order of magnitude while maintaining excellent part accuracy.

To enhance the performance of 4D printed SMPs, nanofillers can be introduced to the polymer matrix to form shape memory polymer composites (SMPCs). In the conventional fabrication of SMPCs via moulding, various fillers (nano or microscopic) such as exfoliated nanoclay [111], glass fibers [112] and carbon black (CB) [109] have been widely used to improve the mechanical performance and shape recovery stress of SMPs. The fillers not only have reinforcement effect in improving the mechanical performance, but also enable new functions. Carbon nanotubes (CNTs) are one of the most popular candidates for the modification of SMPs [113, 114]. In addition to the extraordinary mechanical properties that they offer, their electrical conductivity also enables the SMPCs to achieve electroactive shape memory effect (SME). On the other hand, nanosilica (SiO_2) particles are another attractive fillers that have chemical interaction with the SMP chains, allowing the SiO_2 -SMP to exhibit excellent mechanical strength, high strain and enhanced shape memory properties [150]. Despite the improvement in properties, the moulding fabrication methods of SMPCs require extremely long polymerization time which leads to an eventual non-homogenous dispersion of nanosilica particles due to agglomeration at the bottom of the mould [152]. Therefore, the homogeneity and reduction of fabrication time can be improved by using AM techniques to fabricate the SMPCs layer by layer. Although the addition of fillers in AM have been extensively reviewed, this approach is still challenging for liquid resin-based 3D printing technologies such as stereolithography (SLA) or digital light projection (DLP) processes due to the incurrence of high viscosity and serious light shielding/scattering. Enhancing the dispersion of the nanofillers is undoubtedly the most fundamental issue for developing any composites, but it is also essential to consider the nature of the fillers especially in photopolymer resins that cure under UV exposure. In view of using CNTs as nanofillers in SLA or DLP systems, CNTs are discovered to be

strong UV absorbers and this significantly affected the curing efficiency of the entire components [48]. The genesis not only involves a selection of filler material and preparation of well-dispersed nanofiller photopolymer resin with good flowability and curing characteristics, enhancement in shape memory properties is also an important criterion for fabricating SMPCs using stereolithography processes.

In this section, further exploration on the successfully developed tBA-*co*-DEGDA 4D-printable SMP [44] were performed by incorporating nanosilica particles for stereolithography printing techniques. Nanosilica particles have very high specific surface area and are widely used in polymer industry and surface coating. However, to the extent of our knowledge, there is still no available SiO₂-SMP resins for liquid based printing technologies. One possible reason is the poor dispersion of most nanosilica particles in photopolymers. Owing to the poor compatibility between the organic polymer matrix and inorganic fillers, inhomogeneous composites may result due to aggregation of the nanosilica particles [153]. In the present work, we developed a well-dispersed SiO₂-SMP photopolymer resin in which the material properties for a high performance SMPCs are related to the concentrations of nanosilica particles. The curing characteristics of the SiO₂-SMP were also investigated, which revealed the multifunctionalities of the nanosilica particles. This study evaluates the influence of nanosilica particles on the properties of SMPCs through stereolithography printing techniques while the long-term objective is to use nanosilica for developing tailorable higher performance SMP materials for 4D printing.

6.2 Results and Discussion

6.2.1 Enhancement in Curing Characteristics

In the stereolithography printing technique, several factors such as light intensity, exposure time, monomer functionality, photoinitiator and photoabsorber concentrations can affect the curing characteristics [154]. The integral effect of all these parameters can be represented by the curing depth, which provides critical information such as the minimum layer thickness and curing time per layer to optimize the printing process. The kinetics of curing depth in photopolymerization system have been studied extensively over the years [130]. In understanding the curing depth dependence on photoinitiator and light absorber concentration, Zissi *et al.* proposed the following equation [155].

$$C_d = \frac{1}{\alpha_i c_i + \alpha_a c_a} \ln \left(\frac{t}{t_0} \right) \quad [12]$$

Where C_d is the curing depth, α_i is the absorption coefficient of the photoinitiator, c_i is the concentration of photoinitiator, α_a is the absorption coefficient of the photoabsorber, c_a is the concentration of photoabsorber, t is the exposure time and t_0 is the resin threshold time required to start the polymerization. However, due to the absence of photoabsorbers and inclusion of nanosilica particles, the participation of the nanosilica in the photopolymerization process [156] should be considered and thus Equation [12] should be revised into the following equation:

$$C_d = \frac{1}{\alpha_i c_i + \alpha_f c_f} \ln \left(\frac{t}{t_0} \right) \quad [13]$$

Where α_f is the absorption coefficient of the nanosilica fillers and c_f is the concentration of nanosilica fillers.

Figure 51 shows the curing depths of the SMP resins of the same photoinitiator concentration, with and without the addition of nanosilica particles. A logarithmic increase in curing depths with an increase in the exposure time can be observed for all compositions and the experimental data are congruent with the theoretical cure model by Beer Lambert's law [157]. Notably, the curing profiles of the SiO₂-SMP attain higher curing depths at a faster rate in comparison with the neat SMP. The addition of 1 wt% nanosilica particles improves the curing depth significantly in a very short time by forming a cured layer of 54.2 μm in just 0.7 s, while the neat SMP only achieved 12.5 μm after curing for 2 s. The fast polymerization rate of the SiO₂-SMP could be attributed to the nanosilica particles acting as heterogeneous nucleation sites [158] for polymerization as shown in Figure 52. It has been known that certain fillers such as natural fibers have nucleation ability and provide a large number of compact nucleation sites on their surfaces [159]. Similarly, the surfaces of the nanosilica particles serve as pre-existing surfaces that allow the polymerization path to start with, hence reducing the free energy barrier required to create a new surface [160]. The presence of nanosilica

with high specific surface area provides remarkably more nucleation sites for polymerization which greatly shorten the curing time for the SiO₂-SMP resin.

Figure 51. Curing depth studies of SMP resin with and without nanosilica particles.

Despite the enhancement in curing characteristics with nanosilica particles, it is observed that the initial curing depths are lower for SMPs with higher nanosilica concentration as shown in the side image of Figure 51. The initial curing depths of 1, 2.5, 5 and 10 wt% nanosilica are 54.2, 46.1, 31.5 and 23.66 μm , in which the experimental results are in alignment with predictions of Eq (13). The nanosilica particles are highly transparent due to their small size and low aspect ratio, hence the nanoparticles are expected to have negligible effect on the resin viscosity but the addition of nanoparticles changes the refractive index of the mixture. With a high concentration of nanosilica in the mixture, there is a large mismatch in the initial refractive index between the SMP ($n = 1.41$) and nanosilica ($n = 1.5$). The larger the difference in the refractive indices of the polymer matrix and the filler particles, the larger the occurrence of light scattering which causes the light intensity through the resin

to attenuate exponentially [161]. Meanwhile, the curing depth of nanocomposites is inversely proportional to the square difference of refractive index between the premix and the nanoparticles [162]. Hence, due to the initial refractive index of the monomer mixture being much lesser than that of the nanosilica, there is a domination of light scattering at the initial stage of curing at 0.7 s. This causes a delay in reaching the maximum light transmission, hence giving a lower curing depth at initial curing for SMPs with increasing amount of nanosilica particles.

On the other hand, increasing the exposure time allows the refractive index of the resin to approximate to that of the nanosilica during polymerization. The refractive indices are known to increase when monomers are cured to form polymers [163]. As the difference between the refractive index of the SMP and nanosilica reduces with increasing exposure time, the effect of light scattering diminishes and is expected to be prevailed by the nucleation effect of the nanosilica to cure further into the resin. To effectively improve the curing characteristics of SMPs, lower concentration of nanosilica should be considered due to their strong nucleation ability dominating over the effect of light scattering, hence forming higher curing depth within an extremely short exposure time.

Figure 52. Schematic diagram of nanosilica particles acting as nucleation sites for initial polymerization.

6.2.2 SiO₂-SMP Formation

The FTIR spectra in Figure 53 confirms the presence of tBA-*co*-DEGDA polymer binding with the nanosilica. The C-O stretching vibrations between 1000 and 1075 cm⁻¹ and C=O vibration at 1732 cm⁻¹ are characteristics of the tBA-*co*-DEGDA polymer. With an addition of 1 wt% nanosilica, the SiO₂-SMP spectra shows a shift and an increase in the peak intensity of the absorbance band towards 1100 cm⁻¹, which is attributed to the stretching vibration *Si-O-C* group, a signature that validates the successful bonding between the acrylate polymer group and the silanol groups in nanosilica. Further increment in the nanosilica concentration to 5 wt% shows the formation of a new peak at 1080 cm⁻¹, which belongs to the stretching *Si-O-Si* group. The presence of the *Si-O-Si* bond indicates that there is excess nanosilica particles which cannot form crosslinkages with the acrylate polymer group. This also explains why further increment of nanosilica does not improve but aggravate the shape memory properties as discussed in the next section. Meanwhile, further addition of nanosilica leads to a shift in the peaks which causes the *Si-O-Si* and *Si-O-C* peaks to overlap and form wider absorbance bands. The chemical interaction between the polymer group and

nanosilica indicates that the nanosilica particles not only act as reinforcing fillers, but also participate as multifunctional cross-links.

Figure 53. FTIR spectra of (a) SMP without addition of SiO_2 ; (b) SMP with addition of SiO_2 in different concentrations.

6.2.3 Thermal Analysis of SiO_2 -SMP

Figure 54 shows the effects of the nanosilica concentrations on the T_g and the modulus in the rubbery state G' of the SiO_2 -SMP printed samples. The T_g in Figure 54 can be evaluated as the maximum of the loss factor $\tan \delta$, where we observe that an addition of 1 wt% nanosilica particles into the neat SMP gradually increases the T_g from 53.96 to 56.23°C. This slight increase is attributed to the restrictions of nanosilica particles on the molecular motions of tBA-co-DEGDA chains. However, the incorporation of higher nanosilica concentrations of 2.5 and 5 wt% reflects a shift of the peaks to the left, indicating a decrease in the T_g values to 47.59 and 37.77°C respectively. This phenomenon has been reported by various research groups that the decrease in T_g with

increasing particle loadings is due to the plasticizing effect of the nanosilica particles in the acrylate domains [164, 165]. The localized chain mobility has been enhanced from the repulsive particle interactions, hence forming regions of free volume to reduce their T_g s. However, at even higher nanosilica content of 10 and 15 wt%, the T_g values rise again to 44.11 and 62.56°C as the motion of polymer chains becomes heavily inhibited by the nanosilica domains [153]. The high T_g indicates a wide transition from its glassy state at room temperature to rubbery state at above T_g , which limits the ability of a SMP since it gives rise to a slower recovery at heating [50].

Figure 54. Loss factor $\tan \delta$ of SiO_2 -SMP printed parts as a function of temperature.

The presence of nanosilica particles also increases the crosslinking of the SMP network as validated by the FTIR spectra. This enhances the chain stiffness which leads to a

higher modulus in the rubbery state G' as shown in Figure 55, where the storage modulus that determines the molecular mobility of the network increases from 641.97 MPa (neat SMP) to 2562 MPa (SMP with 1 wt% nanosilica). These observations also provided implications for the increased T_g . At slightly higher amount of nanosilica particles (2.5 and 5 wt%), the plasticizing effect dominates and the formation of more flexible chains gives rise to a simultaneous effect on the network structure where there is a drop in the modulus (to 715.73 and 293.38 MPa respectively) and decrease in T_g . This is however, true only at a low and medium nanosilica amount as further increment in nanosilica concentrations (10 and 15 wt%) increases the modulus in the rubbery state (to 482.96 and 1135.37 MPa) since the network chains become immobilized by interaction with nanosilica domains, hence indicating structural confinement of the chains from the increased crosslinking. Therefore, optimization of the nanosilica content is thus necessary to avoid having very high T_g with a widening of the glass transition.

Figure 55. Storage modulus of SiO₂-SMP printed parts as a function of temperature.

6.2.4 Mechanical Properties

The effects of nanosilica particles on the mechanical properties of SiO₂-SMP printed dog-bone samples were examined at below T_g (i.e. at room temperature 25°C) and above T_g to consider the material behaviour at deformation which is closely related to the shape memory properties. Figure 56 shows the comparison of mechanical properties between SMPs with and without nanosilica particles. The overall mechanical properties significantly increased with the addition of nanosilica. The elongations at break and Young's modulus were remarkably improved by the presence of nanosilica, though the improvement in tensile strength was less pronounced.

Figure 56. Comparison of mechanical properties of neat SMP and SiO₂-SMP printed parts at room temperature and at above T_g in terms of tensile strength.

In Figure 56, the tensile strength at room temperature decreased as the nanoparticles were introduced into the brittle matrix. However, at elevated temperature, the tensile strength of the SiO₂-SMP in rubbery state were improved 2.4 to 3.6 times the corresponding values of the neat SMP as the much higher specific surface area of the nanosilica can promote stress transfer from the matrix to nanoparticles [166]. The reinforcement effects of the nanosilica particles on the SiO₂-SMP also enhances the extensibility of the parts as illustrated in Figure 57, where elongation at break for low nanosilica content (1, 2.5 and 5 wt%) at rubbery state can reach 85.2%, 44.7% and 27.7%

as compared to the neat SMP that can only elongate till a maximum of 18.2%. The incorporation of nanosilica particles brings about higher elongation at break only at low nanosilica content since it is evident that the SiO₂-SMP starts to become brittle when nanosilica concentration are higher considering the corresponding SMPCs with 10 wt% and 15 wt% concentration break at $\approx$ 10% elongation. Hence, the nanosilica content should be kept low to allow for higher deformability during the shape memory process.

Figure 57. Comparison of mechanical properties of neat SMP and SiO₂-SMP printed parts at room temperature and at above T_g in terms of elongation.

The addition of nanosilica particles consistently increases the stiffness as illustrated in Figure 58. The Young's modulus of SiO₂-SMPs with increased loading at room temperature were improved from at least 240% to 600% higher than that of the control sample without nanosilica. At elevated temperature, the Young's modulus only showed improvement when the nanosilica concentration is 2.5 wt% and above. The moduli of the SMP containing nanosilica particles agrees with many models that are used to predict the moduli of such nanocomposites systems [167, 168]. In particular, the

Halpin-Tsai model [169] is used to predict the modulus, E , of the SMPC containing nanosilica as a function of the modulus, E_0 , of the SMP without nanosilica addition, and of the modulus of the particles, E_p . The modulus of the SMPC, E , is given by:

$$E = \frac{1 + \zeta \eta V_f}{1 - \eta V_f} E_0 \quad [14]$$

Where ζ is the shape factor, V_f is the volume fraction of particles, and η is given by:

$$\eta = \left(\frac{E_p}{E_0} - 1 \right) / \left(\frac{E_p}{E_0} + \zeta \right) \quad [15]$$

The shape factor $\zeta = 2w/t$ is used, where w/t is the aspect ratio of the particles. Given that the nanosilica particles are spherical which is observed from TEM images discussed later, the aspect ratio is unity, hence $\zeta = 2$. When the nanosilica concentration is very low at 1 wt%, the effect of nanosilica on the Young's modulus of the SiO₂-SMP becomes significantly reduced. Based on the experimental data in Figure 58, the optimal nanosilica concentration is identified as 2.5 wt% which gives satisfactory enhancement in terms of mechanical properties in the rubbery state.

Figure 58. Comparison of mechanical properties of neat SMP and SiO₂-SMP printed parts at room temperature and at above T_g in terms of Young's modulus.

6.2.5 Dispersion of Nanosilica Particles

The significant reinforcement by nanosilica particles may be attributed to its excellent dispersion. Macroscopic uniformity of the nanosilica in the mixture can be seen from Figure 59a while TEM images in Figure 59b indicates that the SiO₂ particles are spherical, reasonably uniform in size, and have an average diameter close to the manufacturer's reported mean value of 20 nm. It is well established that the dispersion state of nanoparticles is a crucial factor in determining the final properties of nanocomposites. Possessing high surface energy, the nanosilica particles tend to form agglomerates or clusters in the polymer matrix, consequently resulting in property degradations. From Figure 59, aggregated nanosilica was not readily apparent in the TEM images, suggesting its excellent dispersion within the SMP. Moreover, the optical transparency is also well maintained to enable high curing characteristics of the SiO₂-SMP due to the small reduction of light transmission by the well-dispersed nanosilica particles.

Figure 59: (a) Macroscopic uniformity of nanosilica in developed resin; (b) TEM images of 2.5 wt% SiO₂-SMP.

6.2.6 Shape Memory Properties

To examine the shape memory performance of the SiO₂-SMP, cyclic thermomechanical tests by varying nanosilica concentrations were performed using DMA in the single cantilever mode. The 3D representation of the thermomechanical cycles is shown in Figure 60.

Figure 60. 3D representation of thermomechanical cyclic tests.

The results in terms of shape fixity ratio (R_f) and shape recovery ratio (R_r) for SMPs with 0, 1, 2.5 and 5 wt% nanosilica concentration under different applied strains of 10, 20 and 30% are presented in Figure 61 and Figure 62. SiO₂-SMP with 10 and 15 wt% nanosilica concentration do not exhibit shape memory properties as the addition of

nanosilica has formed high crosslinking within the polymer matrix, making it brittle and unable to withstand high deformation for shape recovery. On the other hand, SMPs with 5 wt% nanosilica were fractured at 20%, while 1 wt % nanosilica and the neat SMP were fractured at 30% applied strain, hence results were eliminated from the chart.

With respects to shape deformation under 10% applied strain, Figure 61 shows that all SiO₂-SMP exhibit higher shape fixity ratio as compared to the SMP without nanosilica, in particular the SMPs with 2.5 wt% and 5 wt% nanosilica having 100% shape fixity after the strain has been unloaded. Even at larger strain loading of 20%, the SiO₂-SMPs demonstrated higher shape fixity ($\approx 87\%$) than the corresponding shape fixity of the neat SMP ($\approx 69\%$), while the addition of 2.5 wt% nanosilica concentration demonstrates excellent shape fixity of 94.89% under 30% applied strain. The significant improvement in shape fixity is due to the triple effects of the nanosilica particles as reinforcing fillers, multifunctional crosslinkers and stress relaxation retarder [170]. The nanosilica introduced additional crosslinking networks into the polymer chains which hinders the retraction force of the network to recoil upon removal of the loaded strain, hence allowing the SMP to effectively freezes the deformation and gives higher fixity. However, the effect of multifunctional chemical crosslinks does not increase with further addition of nanosilica concentration of 5 wt% and above. The crosslinking density cannot increase further due to a misbalance between the reactive groups of the polymer and the nanoparticles, whereby this phenomenon has also been justified by the FTIR results. The additional nanoparticles only function as reinforcement which augment rigidity and stiffness. Hence, it is established that the influence of nanosilica particles as multifunctional crosslinkers is evident at low nanosilica content up to 2.5 wt%.

Figure 61. Shape fixity ratio (R_f) of SiO_2 -SMP under varying applied strains.

By contrast, the shape fixity is improved at the expense of the shape recovery as illustrated in Figure 62 which shows a slight decrease in shape recovery ratio to 90-97% with increasing concentration of nanosilica particles. This is attributed by a reduction in the retraction force stored during fixation to drive the strain recovery upon release of stress in the rubbery state. Nonetheless, the SiO_2 -SMPs with 2.5 wt% nanosilica content still exhibit excellent shape memory performance as compared to the neat SMP when subjected to 10 thermo-mechanical cycles at a 20% applied strain as shown in Figure 63. The presence of nanosilica has proven to give better shape fixity of 87.61% at the initial cycle to that of the SMP without nanosilica which only achieve 68.87% fixity ratio. The fixity improves after several cycles due to relaxation of the entangled amorphous polymer network and enables the SiO_2 -SMP to obtain 100% fixity after the 7th cycle, while the neat SMP loses its shape memory properties after the 5th cycle. On the other hand, the shape recovery properties of the SiO_2 -SMP (91%) may be lower than

that of the neat SMP ($\approx 95.7\%$), but the multifunctional crosslink nature of the nanosilica maintained the shape recovery ratio within a high range of 87-90% over 9 thermomechanical cycles. Moreover, the incorporation of nanosilica into the SMP network has significantly doubled the shape memory life cycle of the SiO_2 -SMP as compared to the neat SMP.

Figure 62. Shape recovery ratio (R_r) of SiO_2 -SMP under varying applied strains.

Figure 63. Comparison of shape memory cycles in terms of shape fixity (R_f) and shape recovery (R_r) of SMPs with 0 wt% and 2.5 wt% nanosilica content under 20% applied strain.

6.3 Demonstration of SLA SMPCs

Figure 64 demonstrates the projection stereolithography fabrication of 2 complex features using the developed SMPCs. The entire fabrication process of a flower (76mm in height) was completed in 27mins, which means its printing speed is about 2.8 mm/min $\approx$ 168 mm/hr. The fabrication speed is improved 5.6 times faster than a conventional DLP that fabricates at 30 mm/hr. Figure 65 illustrates the shape recovery process of a SMPC thermally simulated under a hot air gun. The recovery process took a total of 12 s for a complete recovery.

Figure 64a) Printing process of SMPCs on DLP; b and c) Fabrication of complex structures.

Figure 65. Shape recovery process of SMPCs under hot air stimulation.

6.4 Summary

In this section, we explored on the development of a new SMPC incorporated with nanosilica particles for stereolithography printing process and evaluated the roles of the nanosilica in influencing the SMP properties. Curing depth studies showed that polymerization nucleation enhancing activity of the nanosilica particles on the polymer matrix remarkably accelerated the polymerization rates. The curing time of each layer was greatly reduced to 0.7 s, which effectively shorten the total printing time and overcome the issue of long polymerization with traditional moulding methods. Besides

acting as nucleation sites for polymerization, the nanosilica particles were also discovered to function as crosslinking agents. The chemical interaction between the nanosilica and the polymer network was validated through FTIR test, showing that the nanosilica not only reinforces the polymer matrix, but also forms multifunctional crosslinks that improve the mechanical and shape memory properties of the SiO₂-SMPs. Tensile tests revealed its high mechanical properties with 2.4 to 3.6 times higher in tensile strength, while elongation at break in rubbery state reaches 85.2% as compared to the 18.2% elongation for neat SMP. Young's modulus of SiO₂-SMPs with increased loading at room temperature were improved from at least 240% to 600% higher than that of the control sample without nanosilica. The significant reinforcement in properties is highly attributed to the excellent dispersion of the nanosilica as seen from the minimal aggregation in the microscopy images. To further elucidate the thermomechanical properties of the SiO₂-SMPs, multiple thermomechanical cycle tests were performed. The SiO₂-SMPs exhibited outstanding shape memory performance with 100% shape fixity, 90-97% shape recovery and more importantly, the shape memory life cycle was doubled as compared to the neat SMPs. Because of the high curing characteristics, excellent dispersion, improved mechanical and shape memory properties, this approach seems promising for future fabrication of advanced reinforced composites. The incorporation of nanosilica particles into SMP for 4D printing serves to provide better understandings on the effects of nanosilica particles in both the development and fabrication of SiO₂-SMP resin for stereolithography, while the enhanced performance attributed to the multifunctional abilities of nanosilica particles provide a promising opportunity for the development of new 4D printing materials.

CHAPTER 7. CONCLUSION

In this work, a new photopolymer resin of tBA-*co*-DEGDA network with shape memory properties was successfully developed and printable by stereolithography process. Synthesis of the SLA SMPs is based on a thermally induced dual-component phase switching mechanism. The choice of tBA as monomer acts as the soft component of the SMP to allow large deformation, while the DEGDA crosslinker serves as the hard component that remain thermally stable to define the permanent shape directly printed from the stereolithography process. The tBA-*co*-DEGDA network thus forms a photocurable acrylate-based system that demonstrates fast and controlled curing with excellent shape memory properties in a single print.

During the optimization process for printing the SLA SMPs, the curing characteristics and behaviour of the SMPs fabricated via projection type and laser scanning type stereolithography process were analysed. The curing depths obtained from the projection type are much higher than that of the laser scanning type with the same energy density due to prolonged exposure time. Moreover, since projection type stereolithography involves concurrent curing of a larger area, the likelihood of shrinkage phenomenon occurring in projection type due to heat and stress accumulation is higher than in laser scanning type. Through the curing depth studies, the critical energy density to form a cured layer was found to be 1350 J/m^2 with a resin penetration depth of $17.86 \text{ }\mu\text{m}$. The significance of finding out the critical energy density and threshold penetration depth provides a clear basis for optimizing the curing of new SMP materials in stereolithography process. Furthermore, by understanding the curing behaviour, the developed SMP materials can be compatible and printable on any types of UV based 3D

printing systems. This also addresses the research needs in understanding the interaction between the process parameters of the 3D printing system and material properties.

Besides the development of a new SMP material for stereolithography process, by controlling the material compositions of the SMPs, the shape memory properties of the SMPs can be tailored. A series of tBA-*co*-DEGDA resins with varying concentrations of DEGDA crosslinkers were prepared to investigate on the influence of crosslinking on thermal, mechanical and shape memory properties. The SMPs showed well separated transition temperatures varied from 54.9 °C to 74.1 °C and exhibited excellent shape memory behaviour with high shape recovery from 90 to 100%. The mechanical properties were also significantly improved with 82% higher elongation in its rubbery state than industrial thermoset SMPs that were conventionally fabricated via moulding processes. Furthermore, while most of the studies so far targeted on enhancing the shape fixity and recovery properties of 4D printed parts, the mechanical degradation and durability during thermo-mechanical cycling were identified as fundamental issues for commercialization. In recognition of this drawback and the issue of repeatability and consistency in printed parts, this work successfully developed printable SMPs that are more robust with outstanding prolonged cycle life of at least 20 shape memory cycles as compared to current 4D printed parts.

Further enhancement in the developments of the SMPs via stereolithography process were explored by incorporating nanosilica fillers into the polymer matrix to form SMPCs. A well-dispersed SiO₂-SMP photopolymer resin was developed and the roles of the nanosilica in influencing the SMP properties were evaluated. One of the most significant findings is the highly accelerated polymerization rate of the SMPs attributed

to the nanosilica particles acting as heterogeneous nucleation sites. The presence of the nanosilica was found to alter the energy barrier for initiating the polymerization process, hence the curing time of each layer was greatly reduced to 0.7 s, which effectively shorten the total printing time and overcome the issue of long polymerization with traditional moulding methods. Through the optimization process to improve the mechanical properties, the optimal concentration of nanosilica particles was determined to be 2.5 wt%, giving satisfactory enhancement in terms of mechanical properties where elongation at break in rubbery state reaches 85.2% as compared to the 18.2% elongation for neat SMP. The influence of nanosilica as multifunctional crosslinkers has effectively improved the fixity property of the SMPCs but only evident at low nanosilica concentration up to 2.5 wt%. The incorporation of nanosilica into the SMP network has also resulted in high shape recovery ability and significantly doubled the shape memory life cycle of the SiO₂-SMP under higher strain loading as compared to the neat SMP.

This work has demonstrated the ability to develop and fabricate SMPs parts using stereolithography process, which not only overcome the limitations in geometric complexity that are technically challenging to fabricate using contemporary manufacturing techniques, but the novelty also lies in expanding new class of smart and responsive materials for 3D printing. The results achieved are intended to provide better understandings in 3D printing of SMPs, such that it is essential to note that this approach of process optimization and material evaluation is effective and generally applicable for new material development in the stereolithography process, while these novel SMPs and SMPCs developed also significantly advances the 3D printing technology for more robust applications.

CHAPTER 8. FUTURE WORK & RECOMMENDATIONS

8.1 Study on the Thermal Responses of SMPs

8.1.1 Effects of Recovery Temperatures

In 4D printing in which ‘time’ serves as the additional dimension, a fundamental desire is the ability in having a controlled thermal response. The preceding discussion in this work has demonstrated that the tailorable glass transition temperatures, high recoverable strain and shape memory behavior of the SLA SMPs can be controlled by changing the material compositions of the polymer networks. Although the change in properties is usually elicited through variations in the intrinsic materials, greater emphasis on influences of external factors on the thermal responses of the SMPs can be considered to further improve the shape memory performance.

Thermal response of a SMP enables the switch between a temporary shape and the permanent shape by absorbing thermal energy which essentially affects the actuation rate of the SMP. Some important material properties such as glass transition temperatures, mechanical properties and recovery rate can be used for actuation, but the actuation rate can also be controlled by the recovery temperatures. The actuation rate which corresponds to the shape recovery rate is a function of recovery temperature. Hence, the shape memory behavior including free recovery at different programming temperatures could be a subject of future study to provide an underlying understanding on the effects of the programming temperatures on thermal responses of the printed SMPs.

8.1.2 Effects of Heating/ Cooling Rates

Similarly, it is hypothesized that the controlled heating/ cooling rates also have effects on the shape recovery and shape fixity of the SMPs. In this work, slow heating/ cooling rate of 3°C/min was utilized to keep the system close to a quasi-equilibrium thermal state where heat conduction rate is assumed to be quick due to the small thermal mass of the printed samples. The thermal response of the SMPs is mainly attributed to the material effects and heat transfer effects can be omitted in the process. However, at different heating/ cooling rates, the effects of heat transfer become significant and the stress/strain-temperature curves should be evaluated.

Different cooling rates can lead to different temperatures at which the molecular chains of the SMPs are locked in deformed chain conformation and the stress reaches zero with a fixed temporary shape. Meanwhile, different heating rates also means that different temperatures have to be reached to induce a complete shape recovery. Therefore, the behaviour of stress-strain curves with respects to heating and cooling rates on the printed SMPs can be further examined.

8.2 Study on Shape and Topology Variations

Most studies on 4D printing make use of smart materials or stimuli-responsive shape memory polymers to achieve its time-dependent shape memory effect [107, 171]. It can be said that the approach is highly material dependent. The fact that there is still limited range of printable materials, the material-dependent approach does not allow freedom in the choice of materials beyond the realm of available resins. Moreover, for 4D printing of single material, there is a lack of sequential control in the shape recovery process [108]. All components of the printed structure will response simultaneously

once a stimulus is applied. Therefore, a new study approach for 4D printing can be adopted to direct the focus more towards the designs of the printed structures, eliminating the dependence of materials.

The design-based approach for 4D printing takes into consideration the geometric shape and topology effects on the thermal response of the SMP material. The geometrical and topological designs can be in terms of variations in material thickness, diameter or height which might result in differences in the stiffness and heat transfer within the same material while the time required to reach its T_g to activate the thermal responses for shape recovery will also differ. Hence, future work can venture into analysing the shape and topology variations to achieve configuration changes in the printed SMPs.

8.3 Multi-Shape Memory Polymers

This current work and many recent progresses in 4D printing technology develop only ‘one-way’ SMPs which implies that the shape recovery is irreversible. The shape change during the recovery process can only follow the path from temporary shape to the permanent shape, but not vice versa. A new trend is arising to design more complex SMPs with two-way or more shape memory effects, which can also be known as multi-SMPs. A multi-SMP can be defined as a SMP that is programmed to exhibit more than 1 shape in the recovery process and the shapes can be altered in a reversible manner. It is known that the fundamental enabling mechanism for a multi-SMP is quite similar to that of a dual-SMP in this work, in which a network structure is also required for memorizing the permanent shape. However, a broad thermal transition range with at least 2 or more distinct transition temperatures is mandatory to have multi-steps programming instead of one-step for multi-shape memory effects.

Owing to the development of tailorable tBA-co-DEGDA photocurable resins, the SMPs possess a wide range of glass transition temperatures. The additional distinct transitions would theoretically acquire additional temporary shapes, hence realizing the possibility in developing tunable multi-SMPs. Moreover, the development of multi-SMPs also gives an added benefit of creating functionally graded SMPs when the materials of varying glass transition temperatures are spatially distributed in a gradient fashion. Although some multi-SMPs have already been developed using the conventional manufacturing methods through moulding processes, it is worthy to take advantage of the freedom of design in the 3D printing technology to fabricate multi-SMPs or functionally graded SMPs. Modeling of shape or even micro-structural gradients for filler distributions using CAD software offers the capability of designing and editing micro structures or irregular shapes with ease. Hence, exploration into developing multi-SMPs offers the 4D printing technology to come up with new and exciting application concepts in the near future.

8.4 Potential Applications

The formulated resin shows a glass transition temperature around 53.96°C which is considered to be in the low temperature range, hence the fabricated SMPs can undergo low temperature deformation and find potentials in low temperature range applications such as self-tightening sutures and stents or dental applications, although specific biocompatibility tests have yet to be performed. One potential application would be to fabricate dental aligners which allow adjustment of the teeth as an alternative to braces (as depicted in Figure 66). Moreover, the mechanical property of the developed material (yield strength: 20.2 MPa) is not close, yet not too far from the commercial

thermoplastic teeth aligners [172] widely available in the market as shown in the Table 9. The robustness of the formulated SMPs which gives the fabricated part ability to withstand repeated cycles, allow the dental aligners to be reused multiple times at different stages of the teeth adjustment, making it economically efficient.

Figure 66: Dental aligners fabricated from the developed SMP photocurable resin

Table 9. Properties of four commercial orthodontic aligner materials [172].

Brand Name	Firm	Material*	Thickness, mm
F22 Aligner	Sweden & Martina (Due Carrare, Padova, Italy)	TPU	0.75
Duran	SCHEU (Iserlohn, Germany)	PET-G	0.75
Erkoloc-Pro	Erkodent (Pfalzgrafenweiler, Germany)	PET-G/TPU	1
Durasoft	SCHEU (Iserlohn, Germany)	TPU/PC	1.2

* TPU indicates thermoplastic polyurethane; PET-G, polyethylene terephthalate glycol-modified; and PC, polycarbonate.

Name	Thickness, mm	Yield Load, N	Yield Strength σ , MPa	Deformation ϵ	Stiffness K, MPa
F22 Aligner	0.75	30.51	81.36	0.049896	2.7
Duran	0.75	28.89	77.04	0.035928	2.9
Erkoloc-Pro	1.0	21.02	31.53	0.0672	0.6
Durasoft	1.2	26.47	27.57	0.0730368	0.6

CHAPTER 9. PUBLICATIONS

PCT PATENT

“Formulation of Photopolymers for Resin Based 3D Printing to Fabricate Shape Memory Polymers”. Inventors: **Y. Y. C. Choong**, S. Maleksaeedi, P.-C. Su, H. Eng.

Filing of PCT Patent (National phase) by Nanyang Technological University (NTU) on 27 April 2017. NTU Ref: PAT/011/16/17/PCT.

Technical disclosure accorded and filed by Agency for Science, Technology and Research (A*STAR) and Nanyang Technological University (NTU) on 27 April 2016 Singapore. Patent Application no.:10201603355Q.

- **Y. Y. C. Choong**, S. Maleksaeedi, H. Eng, P.-C. Su “Ultrafast 4D Printing of Nanosilica-filled Composites with Robust Thermomechanical Properties” (New TD submitted to NTUitive).
- **Y. Y. C. Choong**, S. Maleksaeedi, H. Eng, P.-C. Su, J. Wei, “4D Printing of High Performance Shape Memory Polymer using Stereolithography”, *Materials and Design*, Apr 2017, doi:10.1016/j.matdes.2017.04.049.
- **Y. Y. C. Choong**, S. Maleksaeedi, H. Eng, P.-C. Su, J. Wei “Curing Characteristics of Shape Memory Polymers in 3D Projection and Laser Stereolithography”, *Virtual and Physical Prototyping*, Special Issue-4D Printing, Nov 2016, doi: 10.1080/17452759.2016.1254845.
- **Y. Y. C. Choong**, S. Maleksaeedi, H. Eng, P.-C. Su “Nanosilica boosts 4D printed shape memory polymers with high curing speed and performance” (Manuscript ready for submission once TD approved).

- H. Eng, S. Maleksaeedi, S. Yu, **Y. Y. C. Choong**, F. E. Wiria, R. E. Kheng, J. Wei, P. -C. Su, H. P. Tham, “Development of CNTs-filled photopolymer for projection stereolithography”, Rapid Prototyping Journal, Mar 2016, doi:10.1108/RPJ-10-2015-0148
- H. Eng, S. Maleksaeedi, S. Yu, **Y.Y.C. Choong**, F.E. Wiria, C.L.C. Tan, P., “3D Stereolithography of Polymer Composites Reinforced with Orientated Nanoclay”. The International Conference on Materials for Advanced Technologies, Materials Research Society, Singapore, 2017.
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- **Y.Y.C. Choong**, S. Maleksaeedi, H. Eng, P.-C. Su, J. Wei, 2016. “Curing Behaviour and Characteristics of Shape Memory Polymers by UV Based 3D Printing”. Proceedings of the 2nd International Conference on Progress in Additive Manufacturing, 2016. C. K. Chua, Y. W. Yeong, M. J. Tan and E. Liu, Singapore: 349-354.
- **Y.Y.C. Choong**, S. Maleksaeedi, F. E. Wiria, P.-C. Su, 2014. “An Overview of Manufacturing Polymer-Based Functionally Graded Materials using 3D Stereolithography Process”. Proceedings of the 1st International Conference on Progress in Additive Manufacturing, 2014. C. K. Chua, Y. W. Yeong, M. J. Tan and E. Liu, Singapore: 333-338.

CHAPTER 10. REFERENCES

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