Development of hydrophilic silicone-based ink for the 3D vat photopolymerization printing of biomedical devices

by

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A thesis

presented to the University of Waterloo

in the fulfillment of the

thesis requirement for the degree of

Doctor of Philosophy

in

Chemistry (Nanotechnology)

Waterloo, Ontario, Canada, 2025

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Three-dimensional (3D) printing is a layer-by-layer additive manufacturing technique that continues to gain interest due to its ability to fabricate customized structures at low setup cost and quick turnaround time. In this thesis, advanced ink materials are developed for the fabrication of elastic biomedical devices using vat photopolymerization (VP) printing.

In **Chapter 1**, an overview of various 3D printing techniques is presented, including their respective advantages, disadvantages, and requirements for ink material. Compared to other major 3D printing techniques, VP printing offers high printing accuracy, resolution, and superior surface quality. However, the fabrication of elastic structures using VP printing has long been a challenge due to the high viscosity and tackiness of elastomeric material. A review of various elastic materials and their current applicability in VP printing is also presented. Finally, recent materials and strategies for fabricating biomimetic implants and fluidic devices via VP printing are discussed.

In **Chapter 2**, a VP-printable hydrophilic silicone-based material is developed, using aminosilicone methacryloyl (SilMA) incorporated with acrylamide (AA) and poly(ethylene glycol) dimethacrylate (PEGDMA) as reactive diluents. The incorporation of AA and PEGDMA addresses the issues of high pre-gel viscosity and slow curing rate of SilMA. Furthermore, the formation of a SilMA/AA/PEGDMA interpenetrating network (IPN) upon curing is novel as it differs from the existing acrylate and thiol-ene silicone network. By integrating hydrogel components, the material displayed distinct characteristics compared to conventional silicone, including hydrophilicity and good swelling properties. Additionally, compared to regular hydrogels, the material shows improved strength, elasticity, and durability suitable for the fabrication of biomimetic implants.

Despite its excellent VP printability, the developed material exhibits signs of overcuring, which hinders the printing of ultra-fine features. Hence, in **Chapter 3**, cellulose nanocrystal (CNC) is used to improve printing accuracy and resolution. The use of CNC to tune photocuring depth is novel and, to the best of our knowledge, has not been reported in literature previously. Upon the integration of 1 wt% of CNC, the developed material exhibits a high printing accuracy and resolution down to 100 μm with a near-zero deviation in the X and Y direction. Most importantly, the incorporation of CNC results in a printed fluidic device with excellent surface detail, good fluid processibility, and minimal colour staining.

Yet, with the SilMA-based material, it remains challenging to achieve one-step printing of fluidic devices with embedded channels. Therefore, in **Chapter 4**, ink formulation with siloxane oligomer instead of polymer is developed for an even lower pre-gel viscosity. In this ink formulation, amphiphilic siloxane oligomer (silmer) is complemented with AA and glycidyl methacrylate (GMA). The use of silmer as the primary component in resin formulations is uncommon due to the challenges in dissolving high concentrations of silmer. Herein, a novel approach using a solvent blend is introduced as a critical strategy for formulating the amphiphilic silicone-based ink materials for VP printing. Silmer conformation is solvent-dependent, resulting in tuneable pre-gel viscosity, transparency, and surface properties. Upon ink optimization, a silicone-based fluidic device with embedded channel is successfully produced with VP printing, and the printed device shows excellent capability in synthesizing drug-encapsulated hydrogel beads, demonstrating its feasibility for real-world biomedical applications.

Taken all together, this thesis presents the formulation of VP-printable hydrophilic silicone-based resin material with two different strategies: (1) the addition of reactive diluents and (2) the use of lower-molecular-weight siloxane oligomers; offering new perspectives on

the formulation of hydrophilic elastomeric resin material for VP printing. Furthermore, the successful fabrication of biomimetic scaffold implants and biomedical fluidic devices with VP printing reveals a significantly simpler and more cost-effective method for the fabrication of silicone-based biomedical devices, moving beyond the conventional method of soft-lithography and moulding.

Acknowledgments

I would like to express my sincere gratitude to my supervisor, Prof. Shirley Tang, for providing me with the opportunity to further my studies under her guidance at the University of Waterloo as well as her unwavering support throughout my PhD studies. I have learned how to think critically and push beyond boundaries when encountering with scientific problems.

Besides, I would like to thank my committee members, Prof. John Honek, Prof. Michael K.C. Tam, and Prof. France-Isabelle Auzanneau, for their time, guidance, and valuable suggestions since my seminars, comprehensive exam, committee meetings, and up to my PhD thesis defence. I have gained tremendously through every conversation exchanged during our meetings, which has prompted me to think further about my research. I would also like to thank my external examiner, Prof. Boyang Zhang, for reading my thesis and attending my thesis defence.

Additionally, I would like to thank Prof. Michael K.C. Tam and Prof. Boxin Zhao for providing access to the rheometer and universal tensile tester, and their respective postdocs, Dr. Yebin Lee and Dr. A-Reum Kim, for training me on the equipment. I would also like to thank Prof. Juewen Liu and Prof. Evelyn K.F. Yim, and their respective students, Dr. Kaya Wong and Abigail Conner, for providing me with the cells for biocompatibility testing.

Furthermore, I would like to extend my gratitude to all past and current labmates who have offered kind advice and help throughout my time here: Dr. Sayan Ganguly, Dr. Irfani Ausri, Dr. Pramod Kalambate, Dr. Hossein Golzar, Gillian Guo, Pei Li, and Ethan Piercey. A special thank you to Dr. Sayan Ganguly for all the valuable knowledge and insights on polymer chemistry, and Dr. Irfani Ausri for providing me with advice navigating through my graduate studies here in Waterloo.

Nevertheless, I would like to express gratitude to everyone who has contributed to shaping me into who I am throughout my research journey: Prof. Sadequer Rahman from Monash University for providing me with my first research project during my undergraduate studies; Joyce Ding Yoon Mei for guiding me through my first industrial research experience; Dr. Lim Su Lin, Dr. Kiwi Lim Keuw Wei, Dr. Nicholas Ng Kei Hoa, and Dr. Kow Su Huan for sparking my interest in polymer chemistry and providing me with valuable insights into research in the manufacturing sector; Dr. Claude Cizravi for sharing his research and life experiences during my stay here in Waterloo.

Lastly and most importantly, I would like to thank all my family and friends back home for their unconditional support, with a special dedication to mummy, daddy, and boboss for always entertaining my dumb questions and jokes. Words will never be enough to describe how grateful I am for each and every one of you who have painted my life with rainbows, well, sometimes with thunderstorm, but it was a happy thunderstorm.

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List of Abbreviations

2D = two-dimensional

3D = three-dimensional

AA = acrylamide

ABS = acrylonitrile-butadiene-styrene copolymer

ANR = acrylated natural rubber

BAPO = phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide

BI = blocked isocyanate

BJ = binder jetting

BR = butadiene rubber

CAD = computer-aided design

CR = chloroprene rubber

DIW = direct ink writing

DLP = digital light processing

EPDM = ethylene propylene diene monomer

FDM = fused deposition modelling

FEP = fluorinated ethylene propylene

FFF = filament fused fabrication

GelMA = gelatin methacryloyl

GMA = glycidyl methacrylate

HAMA = hyaluronic acid methacrylate

HDPE = high-density polyethylene

HTV = high-temperature vulcanizing

IgG = immunoglobulin E

IR = polyisoprene / isoprene rubber

LAP = lithium phenyl (2,4,6-trimethylbenzoyl) phosphine

LED = light-emitting diodes

ME = material extrusion

MJ = material jetting

MMP = matrix metalloproteinase

NBR = nitrile butadiene rubber

NGCs = nerve guidance conduits

NR = natural rubber

PAA = polyacrylic acid

PAM = polyacrylamide

PBF = powder bed fusion

PC = polycarbonate

PCL = polycaprolactone

PDMS = polydimethylsiloxane

PEG = poly(ethylene glycol)

PEGDA = poly(ethylene glycol) diacrylate

PEGDMA = poly(ethylene glycol) dimethacrylate

PEGMA = poly(ethylene glycol) methacrylate

pHEMA = poly(hydroxyethyl methacrylate)

PLA = poly(lactic acid)

PLGA = poly(lactide-co-glycolide)

PMMA = poly(methyl methacrylate)

PNIPAM = poly(N-isopropylacrylamide)

PP = polypropylene

PS = polystyrene

PU = polyurethane

PVA = poly(vinyl alcohol)

PVAc = poly(vinyl acetate)

RGD = arginine-glycine-aspartic acid

RTV = room-temperature vulcanizing

RTV-1 = one-component room-temperature vulcanizing

RTV-2 = two-component room-temperature vulcanizing

SBC = styrenic block copolymers

SBR = styrene butadiene rubber

SBS = styrene-butadiene-styrene

SEBS = styrene-ethylene-butadiene-styrene

SIBS = styrene-*block*-isobutylene-*block*-styrene

Silk-GMA = silk fibroin-glycidyl methacrylate

SilMA = aminosilicone methacryloyl

sIPN = semi-interpenetrating network

SLA = stereolithography

SLS = selective laser sintering

STL = standard triangulation language

TPE = thermoplastic elastomers

TPO = diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide

UV = ultraviolet

VP = vat photopolymerization

XNBR = carboxylated nitrile butadiene rubber

XSBR = carboxylated styrene butadiene rubber

Chapter 1 Introduction

1.1 3D Printing

Three-dimensional (3D) printing is an additive manufacturing technique that enables the fabrication of 3D structures in a layer-by-layer manner. [1,2] 3D printing continues to gain interest as an alternative fabrication method due to its capability to directly fabricate complex structures from digital model. The ability of 3D printing to directly fabricate structures presents several advantages over conventional manufacturing techniques, such as moulding, machining, and soft-lithography. [1–6] For instance, with the ability to direct fabricate, 3D printing offers flexibility to introduce immediate design changes until product satisfaction is reached. This is difficult to achieve with conventional manufacturing techniques owing to the need for a new set of moulds upon every structural modification introduced. In parallel to that, the fabrication of moulds is often costly and time-consuming. Hence, without the need for new moulds, 3D printing poses further advantages in enabling product fabrication at a lower setup cost and shorter on-demand fabrication time as opposed to the conventional manufacturing techniques. With the aforementioned advantages, 3D printing is rapidly emerging as a new fabrication tool, especially for rapid prototyping and on-demand manufacturing.

In general, the overall 3D printing process involves the creation of the 3D structure design followed by preparing the file for printing prior to the actual printing of the 3D structure with the 3D printer. [1,2] With the emergence of computer-aided design (CAD), 3D structures can be easily created and modified using computer systems. [1,7] This has significantly contributed to the ease of product fabrication with 3D printing due to the flexibility to produce any 3D structures as per the CAD files. The 3D design in the CAD file is further stored in the standard triangulation language (STL) format to retain the maximum resolution of the designed structure for printing. [8] Specifically, the STL format is a computer language used to describe

the surface of the targeted 3D model with a network of triangles. The network of triangles forms a triangular mesh detailing the surface of the structure modeled, with a smaller triangular size giving a better structural resolution. Owing to the nature of 3D printing, the 3D model in the STL format is further sliced into layers of 2D images. Then, the 2D images are translated into stacking layers by the 3D printer for the printing of a 3D structure.

As we delve further, 3D printing can be further categorized into four major groups based on their printing mechanism, namely the material extrusion (ME), vat photopolymerization (VP), powder bed fusion (PBF), and material (MJ) and binder jetting (BJ). Each of the 3D printing techniques is briefly shown in **Figure 1.1.** Their respective printing mechanisms, advantages, and challenges will be further discussed in detail in the subsequent sections. Besides, the ink formulation criteria for the respective printing technique will be explored as well, with a special focus on polymer material.

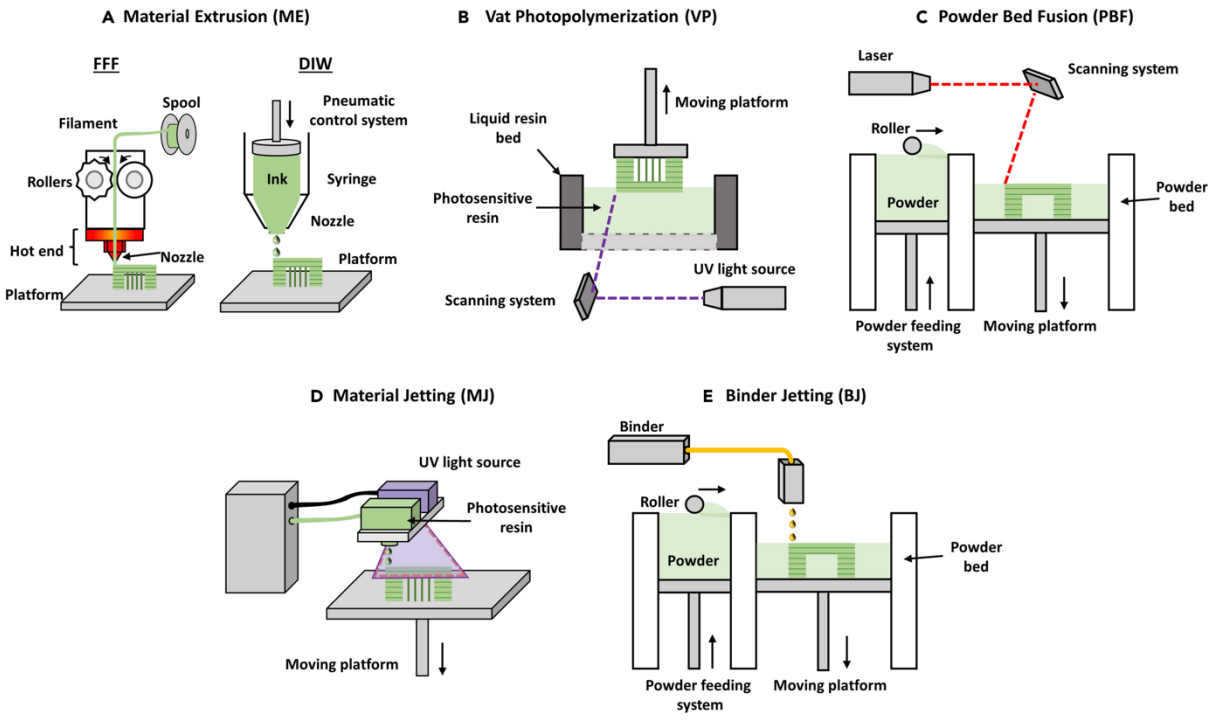


Figure 1.1: The schematic diagrams of different 3D printing techniques. (a) Material extrusion functions by extruding ink material through the nozzle for printing, and can be further

categorized into filament fused fabrication (FFF) when using solid filament and into direct ink writing (DIW) when using viscoelastic ink for deposition. **(b)** Vat photopolymerization (VP) functions by utilizing UV light to form solid polymer from the resin material in the vat via photocuring for printing. **(c)** Powder bed fusion (PBF) functions by melting the powdered material with heat for printing. **(d)** Material jetting (MJ) functions by selectively depositing droplets of ink material for printing. **(e)** Binder jetting (BJ) functions by depositing liquid binder onto the powdered material for printing. Figure is reproduced from Park et al.[2] with permission. Copyright © 2022, Elsevier.

1.1.1 Material Extrusion

ME printing involves the extrusion of a continuous polymer material through the needle nozzle in a layer-by-layer manner for printing[2,9] **(Figure 1.1a)**. The overall printing mechanism for ME printing is relatively simple with only two steps involved for printing. The ink material is first deposited onto the build platform in a continuous manner with the movable needle nozzle tracing the design of the targeted layer structure according to the CAD design. After the deposition of a single layer, the extrusion printhead with the needle nozzle moves up, or the build platform moves down, by one layer thickness to allow the printing of the subsequent layer. The process is repeated until all the layers for the final structure are constructed. The ME printing can be further categorized based on the type of material extruded from the needle nozzle for printing. Specifically, fused filament fabrication (FFF), also known as fused deposition modeling (FDM), involves the extrusion of semi-molten thermoplastic polymers for printing, while direct ink writing (DIW) involves the extrusion of liquid viscoelastic polymer ink material for printing. In FFF, the thin thermoplastic filament is fed into the extrusion printhead from the spool. Then, the filament is heated to an appropriate process temperature to achieve a semi-molten state for its effective extrusion through the needle nozzle for printing

(Figure 1.1a). Conversely, in DIW, the viscoelastic polymer ink material is loaded into a cartridge. Then, the ink is extruded through the needle nozzle at a controlled flow rate by the pneumatic control system for printing **(Figure 1.1a)**.

1.1.1.1 Advantages and Disadvantages

FFF printing is one of the most widely used 3D printing techniques in both home and industrial settings. The popularity of FFF printing is highly contributed by its relatively low cost and simple operation as compared to the other 3D printing techniques.[2,9,10] Besides, FFF printing provides the advantage of simultaneously depositing different polymer filaments through the use of multiple needle nozzle heads during the printing process.[2,9] This offers a significant advantage for the fabrication of multi-material and multicolour structures in a one-step printing process, which is often difficult to achieve with reservoir-based printing techniques. Despite its advantages, FFF printing is typically limited to the use of thermoplastic polymers due to the use of heat as the primary mechanism for melting the polymer filament during extrusion. This is highly attributed to the thermo-reversible properties of thermoplastic polymers in enabling flow upon heating and solidification upon cooling for the printing of solid structures upon material deposition. Additionally, the FFF printing has the disadvantage of frequent needle nozzle clogging, which can disrupt the printing process. In fact, studies have shown that the occurrence of needle nozzle clogging is more pronounced with the filler-reinforced thermoplastic polymer filament due to the increase in resistance for material extrusion as the filler particles agglomerate. [11,12] The clogging of needle nozzle may also be attributed to the insufficient heating of the solid filament as a result of the fast extrusion speed during the printing process, which can be easily resolve by optimizing the printing parameters to suit the thermal properties of the polymer filament. Furthermore, FFF printing is known to have a low printing resolution due to the difficulty in extruding sub-micron-sized filaments. [2,9]

The printing resolution of FFF printing relies heavily on the diameter of the filament extruded through the needle nozzle, which can be further adjusted by varying the needle nozzle diameter, build speed, and processing parameters. However, the reduction in needle nozzle diameter often necessitates a slower build speed and higher air pressure for the successful extrusion of the polymer filament, which is further constrained by the printer's built-in specification on the minimum build speed and maximum air pressure for printing. Moreover, the FFF printed structures typically exhibits poor mechanical properties due to the weak printing layer integration between the printed filaments.[13,14] Several studies have attempted to circumvent this problem by incorporating an additional step to heat the surface of the printed filament with laser or infrared radiation before the deposition of the subsequent filament, as a strategy to encourage the diffusion of polymer chains at the layer interface for better layer integration between the printed filaments.

Similarly, DIW printing provides the advantage of fabricating multi-material or multicolour structures using multiple needle nozzles to simultaneously deposit different ink materials during the printing process.[2,9] Differing from FFF printing, DIW printing can process a wide range of polymer materials as DIW printing does not rely on thermal heating for the extrusion of polymer ink material through the needle nozzle. This further expands the range of material that can be printed by extrusion-based printing techniques. Despite its flexibility with various polymer materials, the use of different materials further increases the complexity of the printing process, as each material often requires distinct curing mechanisms for solidification upon deposition. Typically, the polymer solidification process can be categorized into three different modes based on the respective curing mechanism required by the different polymer types. In the first mode with thermoplastic polymers, solidification occurs through physical processes, such as crystallization and glass transition.[9] As such, the printing process is highly similar to that of FFF printing with no additional processes required for solidification upon

material deposition. On the other hand, in the second mode with thermosetting polymers, solidification occurs through chemical crosslinking reactions, which often require additional heat or light exposure to initiate the process.[9] As a result, the printing chamber requires additional heat or light sources to be installed for the curing of thermal- or photo-sensitive resin material upon its deposition onto the build plate. However, due to the low viscosity of the liquid resin material, the polymer material often lacks structural integrity with signs of filament collapse post-printing. In fact, the phenomenon is more prominent with thermoplastic polymers owing to their relatively slow solidification mechanism based on physical processes as opposed to thermosetting polymers with immediate heat- or light-triggered crosslinking upon layer deposition. In parallel to that, in the third mode, the polymer is deposited directly into the liquid media for zero-gravity printing, where the liquid media provides additional support to the printed filament, as the buoyancy in the liquid media compensates for the gravity of the printed filament upon density matching.[9,15] This necessitates additional modification on the build plate to contain a reservoir for the holding of liquid media for printing. Likewise, DIW printing generally has a lower printing resolution as compared to the other 3D printing techniques, such as MJ and VP printing, due to its limitation in generating sub-micron filaments imposed by the restriction on the minimum needle nozzle diameter required for optimum printability. [2,9]

1.1.1.2 Ink Material

As mentioned above, FFF printing can only process thermoplastic polymer in the form of solid filament for printing, while DIW printing can process a wide range of polymers in the form of liquid resin for printing.[2,9] Regardless, both the solid filament used for FFF printing and the liquid resin material used for DIW printing need to exhibit shear-thinning properties when applied with heat or pressure, respectively, to enable the successful extrusion of polymer material through the needle nozzle for material deposition. Additionally, in the aspect of FFF

printing, the viscosity of the polymer filament upon melting plays a critical role in dictating the structural integrity of the filament upon material deposition. Therefore, both the rheology and viscosity of the thermoplastic polymer filament upon melting need to be precisely controlled to ensure that the polymer filament achieves a sufficiently low viscosity upon heating for extrusion while retaining an optimally high viscosity to maintain the structural integrity of the printed filament prior to cooling upon material deposition. The narrow processing window further restricts the range of thermoplastic polymers that can be processed by FFF printing. Some of the common thermoplastic polymer filaments used for FFF printing include polyamide,[16,17] PC,[18] PLA,[19,20] and ABS.[21] The polymer filament can be further compounded with additional fillers, such as metal,[22,23] glass fiber,[24,25] and carbon fiber,[26,27] for mechanical properties enhancement. Besides, sacrificial material that can be easily removed post-printing can also be deposited simultaneously for the building of complex structures with voids and overhangs. For instance, PVA is a well-known sacrificial material owing to its water-soluble properties, enabling its effective removal by dissolving in water post-printing, leaving a complex printed structure with a smooth finish.[28,29]

In contrast, in the aspect of DIW printing, the type of ink material that can be used for printing is highly versatile. [2,9] Hence, the requirement for ink materials differs significantly depending on the polymer types and printing modes used. For thermoplastic polymers, the material characteristics required for DIW printing are similar to those for FFF printing, but in the form of a liquid solution rather than a solid filament. Similarly, the thermoplastic polymer will need to possess a suitable processing window for the melting or softening of the semi-crystalline or amorphous polymer upon heat applied for extrusion, followed by crystallization or glass transition upon cooling for material solidification after deposition, respectively. Furthermore, owing to the use of liquid resin material, DIW printing can process a wider range of thermoplastic polymer materials that were previously not available in the form of solid

filament for FFF printing, such as acrylic resins.[30] For thermosetting polymers, the material solidification process often relies on chemical crosslinking upon heat or light curing. [2,9] In parallel to that, thermosetting resin materials are typically formulated with initiator and monomer precursors, enabling the formation of a crosslinked polymer network, which leads to material solidification upon heat or light exposure. Some of the common thermosetting resin materials used for DIW printing include acrylates,[31,32] epoxides,[33–35] silicones,[36,37] and polyurethanes.[38] For printing in liquid, the use of a liquid media as a supporting bath further enables the printing of soft polymer materials, such as hydrogels.[39,40] Besides providing additional support for the printed filament, curing agents, such as initiators or metal salts, are often included in the liquid bath to promote the immediate chemical or ionic crosslinking of the extruded polymer filament upon contact with the liquid media. One common example for printing in liquid includes the printing of sodium alginate hydrogel in a water bath consisting of Ca^{2+} ions for the formation of a solid alginate printed structure upon ionic crosslinking. The water-soluble sodium alginate undergoes cation exchange to form water-insoluble calcium alginate upon contact with the Ca^{2+} ions in the water bath.[9,41]

1.1.2 Vat Photopolymerization

VP printing, also known as stereolithography (SLA) printing, is a light-based printing technique that utilizes a vat to contain the liquid photosensitive resin material for layer-by-layer printing.[2,8,9,42,43] As illustrated in **Figure 1.1b**, the printing begins with the lowering of the build plate into the vat filled with resin material. The build plate is positioned at one printing layer height above the bottom of the vat for the printing of the first layer. Then, the light source selectively exposed the resin material according to the targeted layer pattern from the bottom of the vat, resulting in the formation of a patterned solid layer as the light-exposed area of the resin material solidifies via photopolymerization. Specifically, SLA printing uses a laser source

to cure resin material point-by-point for the printing of a patterned solid layer. Further technological advancement led to the emergence of digital light processing (DLP) printing as a new variant of SLA printing that uses a light projector to cure the entire patterned layer all-at-once. In order to enable the light source to reach the resin material, the bottom of the vat typically consists of a transparent window.[8] The transparent window is commonly constructed with fluorinated ethylene propylene (FEP) film, owing to its good chemical resistance and non-stick properties, which improves its compatibility with a wide range of printing materials and help facilitate the smooth release of the printed layer from the bottom of the vat during the printing process, respectively. After the printing of a solid layer, the build plate moves upwards in the Z-axis direction to separate the printed layer from the FEP film.[2,8,9,42,43] The printing cycle then repeats to print the 3D structure in a layer-by-layer manner, as the build plate lowers into the vat with the previously printed layer positioning at one printing layer height above the bottom of the vat for the printing of the next layer.

1.1.2.1 Advantages and Disadvantages

Owing to the use of photocuring for material solidification, VP printing generally has a faster printing speed and a higher printing resolution than the other 3D printing techniques.[2,8,9,42,43] The printing resolution and printing speed of VP printing can be further refined based on the type of light source and light exposure mechanism used for printing. Specifically, SLA printing is capable of achieving a significantly high printing resolution with the ability to resolve fine features down to 2 μm,[44–46] owing to the use of the laser beam to cure resin material point-by-point.[2,8,9,42,43] However, laser components are often expensive. The need for a built-in laser source for printing further drives up the price of the SLA printer, reducing its affordability for home and industrial use. Additionally, the point-by-point printing mechanism employed by SLA printing results in a relatively slow printing process, as every pixel of the

layer would need to be irradiated sequentially for the printing of a single patterned layer. In conjunction with that, the emergence of DLP printing with the use of the light projector to cure resin material all-at-once offers a cheaper alternative to traditional SLA printing with a faster printing speed. The significant reduction in printer cost is highly attributed to the replacement of the expensive laser components in the traditional SLA printer with the more affordable light-emitting diodes (LED) as the built-in light source for DLP printer. Furthermore, the all-at-once printing mechanism with DLP printing results in a faster printing speed, as all the pixels of the layer are projected in one exposure step for the printing of a single patterned layer. Despite that, it is important to note that the printing resolution of DLP printing is slightly compromised with the use of LED light, as LEDs are less precise than the laser beams used in SLA printing. In general, the process of VP printing is comparatively simple as compared to the other 3D printing techniques, requiring only the pouring of resin material into the vat for printing, thereby eliminating the need for highly skilled trained personnel for printer operation.

Similarly, VP printing has its own disadvantages owing to the use of photocuring as the main mechanism for printing. One prominent disadvantage of VP printing is the need for photosensitive resin material for printing. In addition to that, the resin material needs to be in the form of liquid to be contained within the vat for effective VP printing. Both of these requirements further impose limitations on the variety of materials that can be printed with VP printing. The specific resin material requirement for VP printing will be further discussed in the following section. In parallel with that, VP printing often necessitates additional post-processing processes after printing. This includes the mandatory washing step that helps with the removal of the excess uncured resin material remaining on the surface or in the voids of the printed structure, which would otherwise result in a printed structure with a sticky surface appearance or compromised features, respectively. After washing, the printed structure can be further subjected to UV post-curing as a strategy to further enhance the mechanical properties

as well as the printed layer integration of the printed structure. Despite the slightly laborious process with the additional washing and post-curing steps, the process of structural fabrication via VP printing is still comparatively simple as compared to conventional manufacturing techniques, including soft-lithography and machining. Lastly, the use of a single vat and a stationary build plate further poses difficulties for the printing of multi-material structures with VP printing. Overall, despite its limitations, the high printing accuracy and resolution of VP printing remain an attractive feature for the generation of highly detailed structures, which further contributes to its continuous growth and development in the 3D printing industry.

1.1.2.2 Ink Material

Owing to the printing mechanism, VP printing is typically restricted to liquid photosensitive resin material for printing. Currently, acrylate/methacrylate-based resin remains the most common resin material used for VP printing, and in fact, is one of the most popular commercially available resin materials for VP printing.[47–49] Acrylates are highly preferred due to their rapid curing properties upon photoinitiation, promoting a fast VP printing process.[9,50] However, pure acrylate systems often have very high reactivity, making the printed structure more susceptible to curl distortion as the printed layers are more prone to inhomogeneous shrinkage upon rapid curing. Thus, to minimize curl distortion, methacrylates with a lower reactivity are often blended into the acrylate system, as they help encourage a more homogeneous shrinkage within the printed layers by slowing the overall curing rate of the acrylate system. Despite its excellent strength and hardness, acrylate/methacrylate-based resin typically exhibits a relatively high degree of structural shrinkage and brittleness owing to its high crosslinking density. [9,51] The high crosslinking density of the acrylate/methacrylate-based polymer is highly attributed to the presence of a crosslinking point on every second carbon atom of the main polymer chain as a result of the radical chain-growth polymerization

mechanism. On the other hand, the thiol-ene-based resin material that polymerizes based on the radical step-growth polymerization mechanism presents a crosslinked polymer with a lower degree of shrinkage and brittleness.[9,51–53] This is most likely attributed to the more homogeneous crosslinking and the reduced number of crosslinking points in the main polymer chain within the thiol-ene-based polymer as the thiol group (-SH) reacts with the alkene group (-C=C) in a click reaction upon photoinitiation.[9,51] However, the pure thiol-ene-based polymer is extremely soft and often requires additional monomers with higher strength for mechanical properties enhancement. [54–56] As discussed, there are many factors that need to be considered when designing the resin material with the photoreactive monomers. Further adjustments on the composition and ratio of the photoreactive monomers are necessary to tailor the resin material to the targeted curing properties and desirable final printed material characteristics. Besides, the choice of polymerization mechanism is also crucial as it has an important effect on both the curing properties and final printed material characteristics. Despite the many other variations of VP resin materials, both the acrylate/methacrylate and thiol-ene systems established most of the groundwork for the development of various elastomeric resin materials, including polyurethane[57–61] and silicone, [62–71] which further expands the range of polymer material that can be fabricated with VP printing.

In general, there are two major factors that need to be considered in the aspect of resin material for an effective VP printing process. One of the major factors includes the photocuring properties of the resin material. [8,42,43,72–74] Owing to the use of light to initiate photopolymerization for material solidification, the resin material must possess optimum photocuring properties to effectively generate a solid printed structure with VP printing. Among the resin components, the photoinitiator is especially important, as it plays a vital role in initiating the photopolymerization process upon light exposure, thereby equipping the resin material with photocurability.[43,74,75] Upon light exposure, the photoinitiator absorbs light and

converts the photolytic energy into reactive species, such as free radicals or reactive cations, to initiate the photopolymerization process.[75] To ensure effective fabrication with VP printing, the photoinitiator must exhibit an appropriate light absorption spectrum that overlaps with the wavelength emitted by the built-in light source of VP printer. [43,74,75] However, it is important to note that different light sources emit different wavelengths, and thus, require photoinitiators with corresponding light absorption spectra to accommodate printing with each light source. Fortunately, only a few types of standard built-in light sources (SLA ~395 nm; DLP ~385-450 nm) are used by commercial VP printers. This further narrows the selection of suitable photoinitiators for the formulation of VP-printable resin material. Furthermore, a photoinitiator with high initiation efficiency is preferred for a rapid crosslinking reaction, as this would essentially speed up the overall printing process, resulting in a shorter fabrication time and higher production output. [42] Aside from its chemical structure, the initiation efficiency of the photoinitiator also depends on factors, such as the solvent medium, light intensity, and experimental conditions.[76–78] Therefore, it is essential to ensure that the selected photoinitiator can effectively function with the respective resin material and printing conditions for maximum initiation efficiency. Moreover, the photoinitiator needs to have good solubility with the medium of the formulated resin material.[42] Otherwise, the failure to homogeneously distribute the photoinitiator within the resin material would cause different curing activities at different areas, leading to unequal curing of the printed layer, which subsequently results in poor printing accuracy and resolution. In conjunction with that, after considering the light absorption spectrum, photoinitiator with solvent-compatible properties, such as diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO) and phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO), is commonly used for solvent-based resin. [79,80] As for water-based resin, photoinitiator with aqueous-compatible properties, such as lithium phenyl (2,4,6-trimethylbenzoyl) phosphine (LAP), is used instead.[75,81–83] Besides the photoinitiator, other

additives are often incorporated into the resin material to allow more precise control over its photocuring activity. For instance, radical inhibitors are commonly included to prevent the premature gelation of the resin material before printing,[84] while photoabsorbers are typically incorporated to improve the printing accuracy and resolution of the printed structure. [70,74]

Another major factor to be considered is the viscosity of the resin material. [8,42,43,72–74,85] Typically, VP printing prefers liquid resin material with a low pre-gel viscosity. [85] This is because VP printing depends highly on the flowability of the liquid resin for printing. A low-viscosity resin material would exhibit a better flowability for the effective replenishment of each printing layer during the printing process for a better surface-quality print. Moreover, a low-viscosity resin material generally has better wetting properties to rapidly recoat the bottom of the vat for the printing of next layer. Additionally, the resin material with low pre-gel viscosity would cause less turbulence as the low viscosity enables the resin material to quickly stabilize before the printing of the next layer, minimizing the risk of bubble formation, which would otherwise result in printing defects, as the build plate moves into and out of the vat during the printing process. In conjunction with that, the viscosity of the resin material is recommended to be less than 5 Pa·s for a stable VP printing process.[85,86] However, there may be instances where the viscosity of the choice of resin material exceeds the recommended value. A simple strategy would be to reduce the speed of build-plate moving into and out of the vat to accommodate the printing of high-viscosity resin material. As high-viscosity resin material tends to flow slower as compared to those with low viscosity, a slower build-plate moving speed would be able to accommodate the low liquid flowability of the high-viscosity resin. With a slower build-plate moving speed, more time would be reserved to allow the resin material to flow through the printed voids and fine structures before the printing of the next layer. Despite that, the slowing down of the build-plate moving speed affects the overall printing efficiency of the VP printing process. Instead, several studies have approached to

mechanically modifying the printer vat to accommodate the printing of high-viscosity resin material without reducing the overall printing speed. For example, Wang et al. [65] installed a heating element at the bottom of the printer vat to reduce the viscosity of the viscous resin material with heat during the printing process. With the increase in temperature, the viscosity of the resin material reduces as the polymer mobility increases with heat. [43] Yet, it is essential to note that the increase in polymer mobility as an effect of heating would accelerate the crosslinking reaction of the resin material, which further requires adjustment on the light exposure parameters to accommodate. In another example, Rodriguez et al. [70] modified the printer vat with a rotation bath and a spreader to mechanically spread a thin layer of the viscous resin material for VP printing. This approach to customizing the VP printer for the printing of high-viscosity resin material is innovative. However, the approach to modifying the printer vat with a rotation bath and a spreader is rather sophisticated, and further limits the material versatility that can be processed by the modified VP printer. In another approach, the high-viscosity resin material is diluted with low-viscosity reactive monomers as a strategy to reduce the overall viscosity of the resin material. This is currently one of the common approaches reported by various studies on the development of new resin material for VP printing. [59,60,87–89] However, it is crucial to note that the reactive diluents are part of the crosslinking system, and their respective composition and ratio in the overall resin material would affect the mechanical properties of cured resin material.[87,88]

1.1.3 Powder Bed Fusion

As suggested by the name, PBF is a printing technique involving the use of ink material in the form of powder for the printing of 3D structures. Alternatively, this printing technique is also known as selective laser sintering (SLS) due to its key printing step in utilizing laser radiation for the sintering of powder particles as part of the 3D printing process.[90] In brief, the

printing process for PBF printing involves three major steps, starting with powder deposition, followed by powder solidification, and finally lowering the build platform for the printing of subsequent layers. [2,9,90–92] In the first step, the roller helps with the transfer of powder from the supply platform to the build platform followed by spreading the powder evenly onto the powder bed for deposition (**Figure 1.1c**). In the second step, the powder deposited onto the powder bed is selectively sintered by the laser according to the targeted CAD design from the top of the powder bed. During the sintering process, the thermal energy emitted by the laser radiation results in the local heating of the powder particles, which subsequently leads to the softening, melting, and fusing of the adjacent particles for the formation of a solid layer according to the desired pattern. Finally, in the final step, the build platform is lowered by one layer thickness for the printing of the subsequent layer. These three steps are repeated until all the layers for the final 3D structure are printed.

1.1.3.1 Advantages and Disadvantages

Owing to the nature of the printing process, PBF printing presents a major advantage in enabling the production of complex structures without the need for additional support structures. [2,9,90–92] In the other printing techniques, support structures are usually added to avoid the collapse of the overhang structure during the printing process and will be removed after the printing is done. Even with the addition of support structures, there are still limitations to the degree of structural complexity that can be achieved with the other 3D printing techniques. As for the PBF printing, the presence of loose powder remaining on the build platform eliminates the need for additional support structures. [2,9,90–92] The loose powder surrounding the printed structure during the printing process further functions as the supporting material, which easily enables the fabrication of any overhang structures. Besides, without the need for additional support structures, PBF printing can produce complex structures that are not commonly

achievable with the other printing techniques due to the constraints imposed by the positioning of the additional support structures.

Additionally, owing to the nature of the powdered material, the printed structure usually exhibits a certain level of porosity. [93] The degree of porosity is further dictated by the choice of material, overall particle size distribution, and the printing parameters. There is no clear distinction to which the presence of pores within the structure is regarded as an advantage or disadvantage. In cases where porosity is preferred, the presence of pores adds free volume to the printed structure, facilitating the fabrication of structures requiring either a large surface area or lightweight properties.[92–94] In cases where porosity is not preferred, the presence of pores represents weak points for mechanical loads. [95] Therefore, the porous printed structure is often infiltrated with a secondary polymer material post-printing for mechanical properties enhancement. In fact, the option to infiltrate the porous printed structure with a secondary polymer material is sometimes regarded as a benefit due to the flexibility to fine-tune the material characteristic of the initial printed structure with a secondary material. Moreover, due to the nature of the powdered material, structures fabricated with PBF printing generally exhibit lower resolution and poorer surface quality compared to the other 3D printing techniques, requiring post-processing processes, such as milling or coating, for better surface quality. [96] Even with the smallest possible powder particle size, the PBF printing was revealed to only be able to achieve a minimum resolution in the range of 100 µm.

Furthermore, due to the use of laser-induced heat sintering as the printing principle, PBF printing offers the advantage of processing a wide range of thermoplastic material for printing according to their respective temperature profile. Yet, due to the very same printing principle, PBF printing demonstrates disadvantage in requiring additional powder bed conditioning for an effective laser-induced heat sintering process. Essentially, the powder bed

needs to be maintained at an elevated temperature throughout the printing cycle to facilitate the building process. [2,9,90–92] This is because the amount of heat required for powder sintering can be effectively lowered with an overall higher temperature, which subsequently reduces the laser exposure time for sintering and leads to an overall faster building process. However, when printing with semi-crystalline polymer, it is important to always keep the temperature to be a few degrees lower than the melting temperature of the powdered material to avoid the melting of the powdered material before subjecting it to powder sintering. Although it is usually not a concern with the elevated temperature, it is also important to keep the temperature of the powder bed above the crystallization temperature of the powdered material to enhance the resistance of the semi-printed structure toward layered curl distortion. The layered curl distortion is often a result of the asynchronous crystallization of the solidified layers before the printing of all layers. Thus, with a powder bed temperature above the crystallization temperature, the crystallization process within the solidified layers can be effectively delayed, promoting a synchronous cooling of all layers in the final printed structure post-printing. Moving on, the continuous heating of the powder bed often accelerates the oxidative degradation of the powdered material, which causes a change in the melting properties and affects the printing performance of the powdered material. This leads to the second conditioning required by the powder bed chamber. The powder bed chamber would need to be filled with inert gas to further hinder the oxidative degradation of the powdered material. The need for additional printing conditioning remains one of the major drawbacks of PBF printing as it introduces additional considerations for the re-optimization of printing parameters upon the use of new printing materials. Despite the numerous disadvantages, it is believed that both the ability to fabricate complex structures and to process a wide range of materials is the primary reason for the continuous use of PBF printing in the additive manufacturing sector.

1.1.3.2 Ink Material

It is true that PBF printing allows the processing of a wide range of materials as long as they are supplied in the form of powder for printing. However, due to the stringent requirements for powdered material development, there is only a limited number of commercially available polymer-based powdered materials for PBF printing.[97] Besides, due to the printing mechanism of laser-induced heat sintering, most of the polymer-based powdered materials are thermoplastic in nature, with very few examples using two-component thermosets. Currently, polyamides remain the most popular choice of material for PBF printing, holding more than 90 % of the market share.[98] In hopes of maximizing the potential of PBF printing, researchers have continued to expand the scope of material available for PBF printing. Yet, other semi-crystalline polymers, including HDPE and PP[99], and amorphous polymers, including PS[100], PMMA[101], and PC[102], were revealed to demonstrate a lower mechanical strength than their moulded counterparts due to the high porosity present in the printed structure. Despite that, researchers believe that these alternative materials present great potential to overtake polyamide in the future if further improved due to their comparatively lower production cost as opposed to polyamide.[103–105] Moving on, the exploration of TPE further expands the scope of PBF printing for elastomeric material. Interestingly, the production of TPE powder is hampered by the very same desirable properties that initiate its development for PBF printing. The elastomeric properties of TPE provide the material with impact resistance, posing further challenges for powder production due to its inability to easily induce fractures for material breakage during the cryogenic milling process.[106] Further investigation on the effective method for high-quality elastomer powder production is necessary for its future commercialization.

Regardless of the type of material, the powdered material must possess specific characteristics to suit its application for PBF printing. First of all, the powdered material would need to show a certain level of flowability and compactibility for an effective powder deposition process.[107–109] The flowability of the powdered material was revealed to be highly influenced by the shape of the powdered particle. Specifically, spherical-shaped powder particles derived from dispersion polymerization present a better flowability than the irregular-shaped powder particles derived from cryogenic milling.[99] Besides manipulating the shape of the powder particles, additional anti-static agents are often included to further improve the flowability of the powder particles.[110] In terms of compactibility, powder particles with a high packing efficiency typically generate a printed structure with high density, which further translates to good mechanical properties due to the lesser free volume in the final printed structure.[99] However, this might not be true for irregular-shaped powder particles as a high compactibility can compromise its flowability.[105] Therefore, both factors need to be considered simultaneously with respect to the shape of the powder particle for the best results.

Secondly, owing to the printing mechanism of laser-induced heat sintering, the powdered material will need to demonstrate sufficient laser radiation adsorption[110,111] and appropriate sintering behaviour for the effective solidification of powder particles upon laser irradiation.[112] In conjunction with that, it is critical to understand the thermal properties of the polymer in order to better select a suitable polymer with appropriate sintering behaviour matching the temperature range offered by the respective PBF printer. In the aspect of semi-crystalline polymers, the polymer melts to form a viscous flow as the temperature rises above the melting temperature and further cools to form crystals when the temperature drops below the crystallization temperature. Hence, a sufficient processing window between the melting and crystallization temperature is vital for an effective control of the powder solidification process. [2,9,90–92] As for the amorphous polymer, the polymer softens gradually, transitioning

from the glassy state to viscous flow, when the temperature rises above the glass-transition temperature. [113,114] Unfortunately, the glass-transition temperature is the only temperature point responsible for the drastic change in the amorphous polymer state from the glassy to the viscous flow state. This results in a significantly narrow processing window for an effective control on the powder solidification process, which also poses as a factor for the slower development of amorphous polymer for PBF printing in comparison to semi-crystalline polymers.

Lastly, the powdered material will need to exhibit adequate thermal stability throughout the printing process for constant product quality. As the printing parameters remain constant throughout the printing cycle, a change in powder thermal characteristics during the printing process would significantly devastate both the powder printability and printed structure quality. In parallel to that, commercial PBF powders are often treated with stabilizing agents and antioxidants as a strategy to strengthen their stability towards thermal aging.[110]

1.1.4 Material and Binder jetting

Both MJ and BJ are grouped under the same umbrella of jetting-based printing techniques owing to their use of the same printhead technology for printing. These two jetting-based printing techniques are further classified according to the functionality of the material jetted for structural fabrication. For instance, in MJ printing, the printhead nozzles deposit "material", such as photosensitive resin, for the direct printing of the final solid structure during the printing process. Specifically, droplets of resin material are selectively deposited onto the build platform in a layer-by-layer manner followed by UV flash-curing upon each fresh droplet deposited, and the process is repeated until the printing is done[115] **(Figure 1.1d)**. Conversely, in BJ printing, the printhead nozzles deposit "binder", such as liquid adhesive or solvents, onto the powder bed substrate for the printing of solid particles, as the powder fuses upon chemical reaction initiated by the binder. In fact, the printing mechanism of BJ is highly similar to PBF

with the repetitive printing cycle starting with powder deposition, followed by selective powder solidification, and finally the lowering of the build platform for the printing of the next layer[116,117] **(Figure 1.1e)**. The only difference that sets both BJ and PBF printing apart is the curing mechanism employed by the respective printing technique, where BJ fuses powder chemically upon binder deposition while PBF fuses powder thermally upon exposure to laser radiation.

1.1.4.1 Advantages and Disadvantages

Owing to the mechanism of jetting for resin material deposition, MJ printing presents a high printing accuracy and resolution, with the ability to resolve fine features down to 16 μm, and a significantly faster printing speed (2800-4000 cm^3/h) than the other 3D printing techniques (ME: 50-150 mm/h; VP: 20-36 mm/h).[118] This enables MJ printing to easily fabricate high-quality structures within a short fabrication time. Besides, owing to the use of a multi-nozzle printhead, MJ printing further presents a prominent advantage for the printing of different ink materials simultaneously in a one-step printing process.[118,119] This allows the direct printing of a single 3D structure consisting of multiple materials for different colours or material characteristics, which is often difficult to achieve with the other 3D printing techniques involving only a single reservoir for a single ink material, such as VP and PBF printing.[119] Yet, due to the very same advantages, the MJ printer is often expensive, which lowers its affordability and heightens the overall cost of product fabrication. Additionally, due to the use of piezoelectric or thermal printhead for ink material jetting, MJ presents a narrow processing window for ink material, demanding stringent requirements on both the rheology and surface tension of the ink material for an effective printing process.[119–121] The need for specific ink material characteristics further imposes a limit on the range of material that can be processed by the MJ printing.[119,121] Furthermore, owing to the nature of MJ printing in

depositing both building and support material simultaneously, the printing of structures with overhangs and voids is less economical than the other 3D printing methods due to the dense support structures.[115] Moreover, the process of UV flash-curing upon each droplet deposited results in a printed structure with high brittleness, which is attributed to the high crosslinking density within the polymer network of the printed structure, rendering it unsuitable for structural applications.[122] Overall, despite the benefit of high printing resolution and multi-material printing, MJ printing presents major disadvantages in terms of cost (for both the printer and the use of excessive support material), ink material variety (limited by the stringent requirement on the ink material characteristics), and mechanical properties (high brittleness due to excessive UV curing).

In the aspect of BJ printing, the slightly different printing mechanism of BJ, as opposed to PBF printing, renders it with a few advantages over PBF printing.[9,116,117] With the use of a multi-nozzle printhead instead of a laser source for printing, BJ printing presents an overall lower printer cost for purchasing and maintenance as compared to PBF printing. However, owing to the use of the same printhead technology, the cost for BJ is somewhat similar to MJ, which is still higher compared to the other 3D printing techniques, such as ME and VP printing. Besides that, similar to MJ printing, the use of a multi-nozzle printhead presents a huge advantage for the printing of multicolour structure with its ability to simultaneously dispense binder with different colours onto the powder bed substrate, which is not at all possible with PBF printing. Additionally, with solution binding as the key mechanism for powder particle fusion, BJ printing eliminates the need to select suitable ink materials based on their heat-sintering behaviour, which successfully widens the range of powdered materials that can be used for the fabrication of 3D structures. This includes extremely low-cost powder, such as plaster and starch, which can be effectively printed upon solution binding with an aqueous binder. Yet, it is important to note that BJ printing generally has a lower printing resolution

than PBF printing, as the droplet size of the binder dispensed from the needle nozzle in BJ printing is far bigger than the laser spot size irradiated in PBF printing. Despite the differences, the printed structures fabricated with BJ printing exhibit highly similar material characteristics as those fabricated with PBF printing owing to the use of powdered material. This includes drawbacks such as high porosity and poor surface quality, requiring additional post-processing processes for further mechanical and surface properties enhancement. In general, despite the several advantages over PBF printing, the printed structure fabricated with BJ printing still presents the typical structural characteristics of high porosity and poor surface quality owing to the use of powdered material for printing.

1.1.4.2 Ink Material

In MJ printing, both the building and support material are deposited simultaneously for the fabrication of the final structure. [115] The support material is deposited to support the building material in regions of overhangs or voids of the final printed structure, and will be further removed post-printing. Regardless, both the building and support material will need to possess a set of criteria to be successfully jetted from the needle nozzle for printing. As briefly mentioned above, both the rheology and surface tension remain the key parameters in dictating the printability of the ink material with MJ printing. As the printer progresses to deposit ink material for printing, the polymer ink material must have shear-thinning behaviour to enable the ink material to fluidize and flow through the needle nozzle when applied with pressure for ink material deposition. [120] In parallel to that, the polymer ink material must possess a suitably low viscosity for the deposition of droplets through the printing nozzle. Specifically, the viscosity of the polymer ink material needs to be precisely controlled within the range of 20 to 40 mPa·s for successful droplet formation.[121] Besides, it is also crucial for the ink material to possess optimal surface tension properties for the formation of droplets from the continuous

liquid ink material. Upon jetting, the ink material needs to possess quick modulus recovery to uphold the structural integrity of the printed structure. [120] Furthermore, due to the mechanism of UV flash-curing upon droplet deposition, the ink material must be able to cure rapidly upon UV exposure. In conjunction to that, acrylate-based resin is commonly used as the building material for MJ printing owing to their relatively low pre-gel viscosity and rapid curing properties.[123] Conversely, the epoxy-based resin, that is also a common photosensitive resin material, does not suit the application for MJ printing due to its relatively slower curing rate upon UV exposure. As for the support material, the material will need to possess special material characteristics to enable post-printing removal according to their respective removal process without affecting the building material. For instances, water-soluble monomers or polymers, consisting of mainly non-reactive PEG, is commonly used as the support material for MJ printing, and in fact, is the initial commercially available ink material for support material developed along with MJ printing by the company Objet Geometries Ltd. (now acquired by Stratasys).[123] With the water-soluble properties, the support material can be easily removed with water upon soaking after printing. Further research has continued to introduce new support material for MJ printing. This includes bicarbonates that can be removed upon mild acid,[119] wax that can be removed upon mild heating [119], and PNIPAM-based gel that can be removed as it flows upon cooling, [124] post-printing.

As for BJ printing, owing to the deposition of binder onto the powder bed substrate for printing, the material characteristics for both the binder material and powdered material need to be considered for an effective printing process. Generally, the powder particles would need to meet certain criteria similar to that of PBF printing for an effective powder deposition process. However, due to the non-thermal printing mechanism, both the heat-sintering behaviour and thermal stability would not need to be considered when selecting the powdered material for BJ printing. Similarly, the binder material would need to exhibit low viscosity and

shear-thinning properties for an effective droplet deposition process. The binder material can be further differentiated into the reactive and non-reactive binder, depending on the specific solvent-powder binding mechanism employed by the BJ printing.[125] For reactive binder, the binder material often consists of reactive resins, such as polymer solution, that is capable of forming a strong film holding the powder particles together upon drying, as part of the powder solidification process for structural printing.[126,127] This essentially allows the printing of any powdered particle as the binding power relies solely on the reactive resin in the binder material. Conversely, for non-reactive binder, the binder material does not contain any reactive material and only contains solvent or solvent mixture, that is capable of swelling the polymeric powder particle for fusion via polymer interdiffusion and entanglement upon contact.[125] In fact, the absence of reactive resin was revealed to benefit the printing process as it eliminates the risk of needle clogging for a more efficient printing process.[9] Particularly, the non-reactive binder can effectively process a wide range of materials when used with an appropriate solvent selected based on the respective chemical characteristics of the powdered material. For instance, the use of an aqueous ink would enable the printing of water-soluble polymers, such as starch,[128] maltodextrin,[129,130] and PVA.[131–133] Yet, it is important to note that the printed structure fabricated with aqueous ink is not water-resistant, and needs to be infiltrated with resins, like cyanoacrylate, epoxy, and polyurethane, post-printing to prevent the disintegration of the printed structure when exposed to moisture.[9,134] On the other hand, the use of a non-aqueous ink would enable the printing of hydrophobic polymers, such as PLA and PLGA.[135] However, special precautions would need to be taken when printing with non-aqueous ink consisting of organic solvents as they often emit toxic vapors.

1.1.5 Summary

As discussed above, each of the 3D printing techniques has its own pros and cons depending on their respective printing mechanisms and ink material used **(Table 1.1)**. Hence, the selection of a suitable 3D printing technique for structural fabrication depends highly on the targeted properties and application of the printed product. Owing to my main goal to fabricate printed structures with fine features, the 3D printing technique will need to have a high printing resolution for the generation of delicate printed structures with high surface quality. In conjunction with that, both the VP and MJ printing with a high printing resolution down to the micron scale appear to be the best fit for the fabrication of delicate structures. However, when considering the range of material that can be processed with the respective printing methods, VP printing with the ability to process a wider range of material further emerged as the better choice of 3D printing method to proceed with for this project. As mentioned in **Chapter 1.1.2**, there are new variations of the VP printing technique developed since the establishment of SLA printing. Owing to the significantly lower printer cost and faster printing speed, I further proceed with DLP printing for ink material development for this project. It is true that DLP printing has a slightly compromised printing resolution as opposed to SLA printing. However, this is not a huge problem as ultra-fine structural features below 10 μm are often not needed for the full functionality of the structural product. Hence, the printability of the developed ink material with DLP printing serves as good evidence for its feasibility to be fabricated with different variations of VP printing. To generalize, the term VP printing is used to represent all the possible VP printing methods, including DLP printing, in the following sections.

Table 1.1: A summarized overview on the printing and ink material characteristic for the different 3D printing techniques.

3D printing technique		Printing principle	Minimum resolution	Ink material	Advantages	Disadvantages
Material extrusion (ME)	Filament fused fabrication (FFF)	Extrusion of solid filament through the heated needle nozzle [2,9]	Depends on nozzle diameter size; 100-300 µm[44–46,136]	Thermoplastic polymer[16–21,28,29]	Low-cost printer; [2,9,10] Simple printing process; [2,9,10] Multi-material printing.	Limited to thermoplastic material; [2,9] Low printing resolution; [2,9] Poor printing layer integration; [13,14] Needle nozzle clogging. [2,11,12]
	Direct ink writing (DIW)	Pressurized extrusion of liquid viscoelastic ink [2,9]	Depends on nozzle diameter size; 100-300 µm[44–46,136]	Any polymer solution[30–40,137–140]	Multi-material printing; [2,9] Can process a wide range of material; [2,9]	More complex printing process; [2,9] Low printing resolution; [2,9] Poor structural integrity post-printing. [2,9]
Vat photopolymerization (VP)	Stereolithography (SLA)	UV curing of liquid photocurable resin material [2,8,9,42,43]	Depends on light source; 2-10 µm[44–46]	Acrylate-, [47–49] Methacrylate-, [47–49] Epoxy-, [89,141] Silicone-, [62–71] Polyurethane-based resin[57–61]	Fast printing speed; [2,9] High resolution; [2,9] Simple printing process. [2,9]	Expensive printer; [2,9] Slower printing speed than DLP; [2,9] Single material printing; [2,9] Limited to photosensitive resin material; [2,9] Post-printing processes. [2,9]
	Digital light processing (DLP)		Depends on light source; 10-50 µm[45,46]		Lower cost than SLA; [2,9] Fast printing speed; [2,9] High resolution; [2,9] Simple printing process. [2,9]	Single material printing; [2,9] Limited to photosensitive resin material; [2,9] Post-printing processes. [2,9]

Table 1.1 continued: A summarized overview on the printing and ink material characteristics for the different 3D printing techniques.

3D printing technique		Printing principle	Minimum resolution	Ink material	Advantages	Disadvantages
Powder bed fusion (PBF)	Selective light sintering (SLS)	Laser-induced heat sintering of powder particles [2,9,90–92]	Depends on powder particle size; 50-200 µm[45,46]	Thermoplastic polymer[98–106,142]	Can process a wide range of material; [2,9,90–92] Capable of generating complex structure; [2,9,90–92] Lightweight structure. [92–94]	Required ink material to be in powder form; [2,9,90–92] Low printing resolution; [96] Poor surface quality; [96] High porosity; [95,96] Weak mechanical properties. [95]
Material jetting (MJ)		Jetting of liquid photocurable resin followed by UV curing [115]	Depends on droplet size;[45] 16-100 µm[44–46,118,136]	*Building material:* Acrylate-; Methacrylate-based resin[123] *Support material:* Water-soluble monomers/ polymers (PEG);[119] Bicarbonate; [119] Wax; [119] PNIPAM[124]	High resolution; [118] Fast printing speed; [118] Multi-material printing. [118,119]	Expensive printer; [118] Can only process a limited range of material; [119–121] Less economic (dense support material); [115] Not suitable for structural application (highly brittle). [122]
Binder jetting (BJ)		Jetting of liquid adhesive onto powder bed substrate [116,117]	Depends on droplet size and powder particle size; 200 µm[2,45]	*Reactive-binder:* polymer solution [125–127] *Non-reactive binder:* solvent or solvent mixture [125] *Powder bed substrate:* polymer powder [128–133,135]	Lower cost than PBF; [9,116,117] Can process a wider range of material than PBF; [9,116,117] Multicolour printing. [9,116,117] Lightweight structure. [92–94]	Expensive printer; [118] Required substrate ink material to be in powder form; [9,116,117] Lower printing resolution than PBF; [9,116,117] Poor surface quality; [9,116,117] High porosity; [9,116,117] Weak mechanical properties. [95]

1.2 Elastic Material

Over the years, elastomers have been widely used for the fabrication of various biomedical products that require elasticity and flexibility for better functionality and comfort. This includes general medical care products, wearable medical devices, prosthetic devices, transdermal patches, and body implants. [143,144] Recently, elastomers further gained attention in the biomedical field due to their highly compatible mechanical properties with soft tissues for the fabrication of biomimetic implants.[120,144–146] Besides, the elastic properties of elastomers further drive the development of microfluidic devices due to its better capability to withstand high fluid pressure and its capability to enable the fabrication of elastic components, including valves and pumps.[147,148] By definition, elastomer is a viscoelastic polymer with the ability to quickly recover from deformation with minimal hysteresis. [149] This is highly attributed to the nature of elastomer consisting of long polymer chains with low crosslinking density, which enables the sliding and stretching of the long polymer chains to achieve a high elongation when applied with stress and recover quickly upon stress removal. [150,151] This contributes to the relatively low elastic modulus and high yield strength of elastomers as compared to the other polymer materials.[152,153] In general, elastomers can be further classified into two major categories based on their respective crosslinking mechanism, with the chemically crosslinked elastomers termed thermosetting elastomers and the physically crosslinked elastomers termed thermoplastic elastomers. Typically, thermosetting elastomer is composed of a network of crosslinked polymer chains that are held together by irreversible strong covalent bonds, which often results in a strong polymer but with low reprocessibility due to the presence of irreversible crosslinking between the polymer chains. Conversely, thermoplastic elastomer consists of entangled polymer chains held together by reversible weak van der Waals forces, which are capable of untangling upon stress applied and re-entangling upon stress removal, favoring fabrication processes requiring remoulding and reshaping. It is important to note that most of

the elastomers are lightly crosslinked thermosetting elastomers with only very few examples of thermoplastic elastomers.

Besides mechanical properties, to cater to biomedical applications, the elastomers need to demonstrate good biocompatible properties without causing any adverse physiological reactions, including cytotoxic, carcinogenic, allergenic, mutagenic, pyrogenic, and teratogenic symptoms, upon contact with biological fluids or tissues to be classified as biomedical grade product for safe use with biological systems.[143] In the aspect of 3D printing, the elastomers need to exhibit excellent printability with low viscosity and optimum photocurability to be fabricated with VP printing. To date, there are very few biocompatible elastomers with suitable 3D printability, especially for VP printing. [144,145] The lack of suitable elastomeric resin material for VP printing is highly attributed to the high viscosity and the lack of photocuring properties in conventional elastomers. Furthermore, the high tackiness and stickiness of elastomers pose further challenges for their fabrication with VP printing owing to their high tendency to adhere to the bottom of the vat as compared to rigid polymers, leading to printing failure as the elastomeric printed layers detach from the printed structure following the lifting of the build plate out of the vat after the printing of a patterned layer. Also, the soft elastic nature of certain elastomeric materials further limits the fabrication of overhang structures with VP printing. This is because the supporting material fabricated with the soft elastomeric material often lacks structural integrity and strength to uphold the overhang structure, resulting in printing failure as the overhang structure collapses. Moreover, most of the elastomeric resin materials can only be solubilized with organic solvent, and thus, are formulated as solvent-based resin material. The presence of toxic solvent further adds on to the cytotoxicity of the printed material, making it unsuitable for biomedical applications.

On the other hand, despite its elastic properties, hydrogels are categorized as a separate category from elastomers based on their ability to absorb and retain a large amount of water (more than 10 % by definition).[154,155] Unlike elastomers, hydrogels exhibit exceptional water swelling properties due to their hydrophilic nature. Moreover, their mechanical properties, including elasticity, are strongly influenced by water content. Upon crosslinking, hydrogels exhibit favourable mechanical properties (e.g., softness and flexibility) and physicochemical properties (e.g., swelling and permeability), enabling them to closely mimic the characteristics of soft tissues. Along with their tissue-specific properties, the excellent biocompatibility of hydrogels further enhances their broad application in both implantable (e.g., tissue scaffolds and implants) and non-implantable biomedical devices (e.g., skin patches and wound dressings).[154–159] However, it is worth noting that the mechanical properties of hydrogels are generally inferior to those of elastomers, which has been a concern in the fabrication of biomedical devices that require high strength and elasticity.[4,155] Hydrogels can be further categorized into several groups based on their source (i.e., natural or synthetic), polymer structure (i.e., amorphous or semicrystalline), polymer network (i.e., homo-, copolymeric, or IPN), crosslinking mechanism (i.e., physical or chemical), surface charge (i.e., cationic, anionic, etc.), responsiveness (i.e., chemical, physical, or biochemical), and degradability (i.e., degradable or non-degradable).[154] For simplicity, only the source and crosslinking mechanism will be considered when categorizing the hydrogel material in the following section. In terms of source, natural hydrogels are typically derived from biologically sourced polysaccharides (e.g., alginate, cellulose) and proteins (e.g., gelatin, collagen), while synthetic hydrogels are generally formed through the polymerization of synthetic monomers (e.g., vinyl alcohol, acrylamide, ethylene glycol). As such, natural hydrogels generally offer better biocompatibility than their synthetic counterparts, while synthetic hydrogels are favoured for their reproducibility and consistency in batch quality. As for the crosslinking mechanism, the

chemically crosslinked hydrogels would exhibit characteristics similar to that of thermosetting elastomers owing to the formation of irreversible covalent bonds, while the physically crosslinked hydrogels would resemble the properties of thermoplastic elastomers owing to the formation of reversible bonds, such as ionic and hydrogen bonding, within the hydrogel matrix. Moving on, in the aspect of fabrication with 3D VP printing, hydrogel material pretty much shows fewer difficulties as compared to elastomers. This is due to the availability of a wide range of low-viscosity hydrogel precursors for selection, which favors the formulation of hydrogel resin material with good flowability for VP printing. Also, the ability to easily introduce or modify hydrogel precursors with photosensitive molecules further elevates the potential of hydrogel material to be fabricated with VP printing. The only concern with the formulation of hydrogel resin material for biomedical device fabrication via VP printing would be the presence of photoinitiators and synthetic monomer precursors, which can be toxic and potentially require additional washing or leaching processes to improve the biocompatibility of the printed structure. [80]

In this section, the different types of common elastic material, including elastomers and hydrogels, for biomedical applications and their current status and development for fabrication with VP printing will be reviewed prior to the selection of a suitable elastomeric resin material for this project. The discussion will also take into account the biocompatibility of the elastic material, especially their respective photocurable derivatives, to better understand their suitability for biomedical applications.

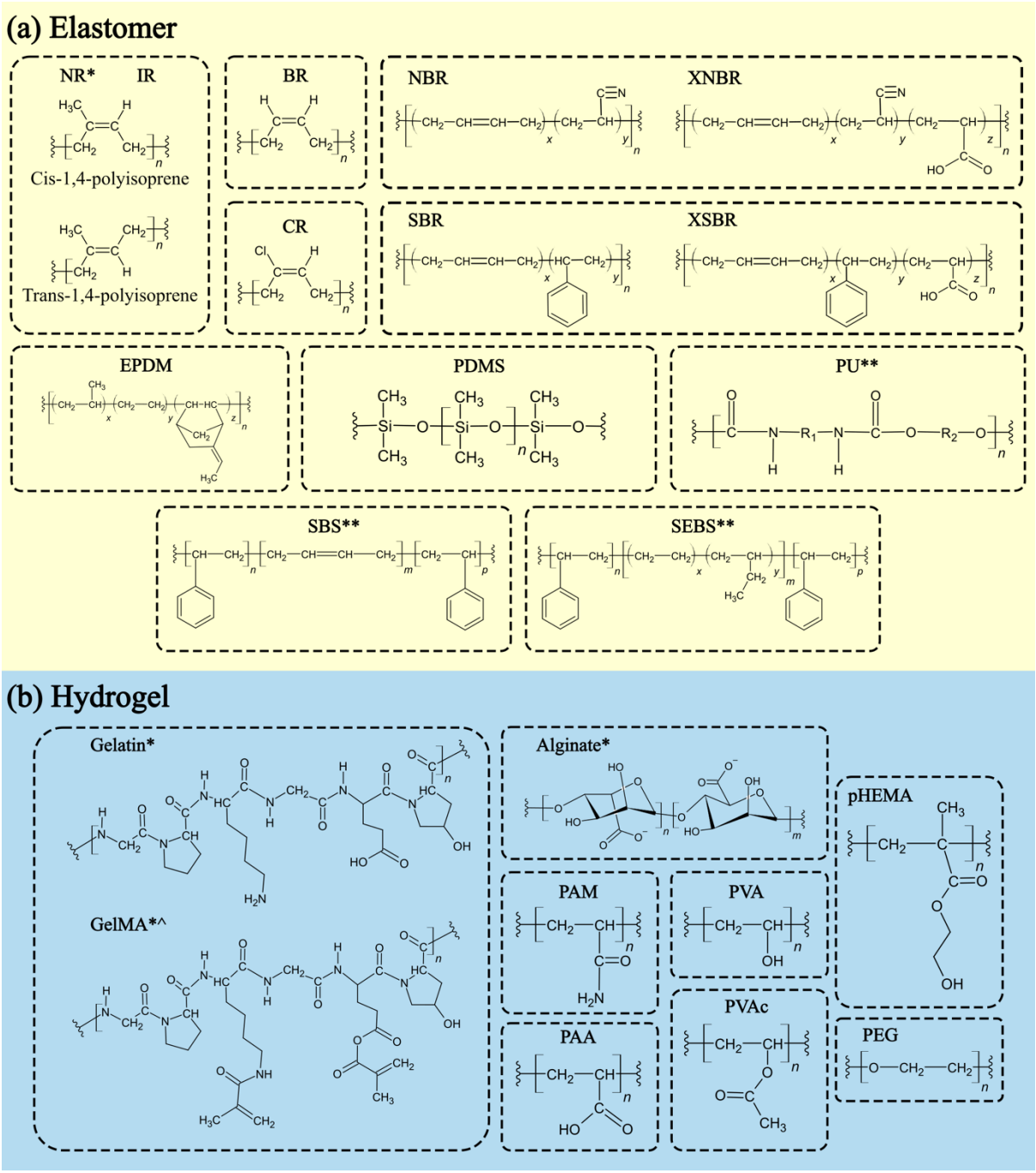


Figure 1.2: The chemical structure of the common elastomers and hydrogels used for biomedical applications. (a) The chemical structure of elastomers, such as natural rubber (NR), isoprene rubber (IR), butadiene rubber (BR), chloroprene rubber (CR), nitrile butadiene rubber (NBR), carboxylated nitrile butadiene rubber (XNBR), styrene butadiene rubber (SBR), carboxylated styrene butadiene rubber (XSBR), ethylene propylene diene monomer (EPDM), polydimethylsiloxane (PDMS), polyurethane (PU), styrene-butadiene-styrene (SBS), and

styrene-ethylene-butadiene-styrene (SEBS). **(b)** The chemical structure of hydrogel, such as gelatin, gelatin methacryloyl (GelMA), alginate, polyacrylamide (PAM), polyacrylic acid (PAA), poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc), poly(hydroxyethyl methacrylate) (pHEMA), and poly(ethylene glycol) (PEG). *derived from natural source; **thermoplastic; ^after modification. All the chemical structures are illustrated with Chemsketch.

1.2.1 Natural Rubber

Natural rubber (NR) is a green renewable elastomeric polymer consisting of mainly cis-1,4-poyisoprene derived from the *Hevea Brasiliense* tree, usually in the form of latex. [160–164] The excellent elasticity and biocompatibility of NR further promote its wide use in a variety of general medical care products, such as medical gloves, catheters, and intravenous tubes. Typically, the NR latex is a colloidal suspension consisting of 30 to 40 % rubber content, 50 to 60 % of water, and 5 to 6 % of non-rubber components, including proteins and lipids. In parallel with that, the appearance of NR latex is non-transparent and usually in a milky white colour even after coagulation and curing. As the NR latex is harvested from a natural source, the composition of the NR latex can vary according to the tree source, soil condition, and seasonal effects, resulting in a lack of consistency in terms of batch quality. Besides, the presence of allergenic proteins in the NR increases the risk for Type I allergy in certain individuals, as it triggers the release of immunoglobulin E (IgE) antibodies as a response to the allergenic latex protein and causes immediate allergy symptoms upon contact with NR latex products.[165–167] This further accelerates the development of synthetic rubbers as a non-allergenic alternative to NR. Additionally, it is important to note that raw NR latex often lacks strength and fails to recover after deformation, necessitating further crosslinking to strengthen the NR matrix upon curing.[168–171] Conventionally, NR is crosslinked via sulfur vulcanization

in the presence of accelerators and high heat (60 – 200 ºC). The vulcanization process begins with the formation of an activator-accelerator complex that facilitates the introduction of sulfur bridges as crosslinks between the allyl group (-CH=CH-CH_2-) of the NR polymer chains. The type of sulfidic crosslink in the NR matrix can be further controlled by varying the amount of sulfur to accelerator ratio, which enables the tuning of mechanical properties depending on the type of sulfidic crosslink introduced in the NR matrix. For instance, an NR matrix consisting of a higher amount of monosulfidic and disulfidic bonds with a shorter sulfur chain length will be stiffer than those consisting of more polysulfidic bonds with a longer sulfur chain length. However, the use of accelerators further introduces another risk for Type IV allergy, where the sensitized individual develops symptoms of contact dermatitis upon continuous exposure to NR latex products. [165–167] This is commonly attributed to the presence of accelerator residues in the NR latex product as a consequence of improper or insufficient leaching during the production process.[172] Despite ongoing efforts to develop alternative vulcanization process, accelerated-sulfur vulcanization remains the most cost-efficient crosslinking method for the manufacturing of NR products owing to the low price and high abundance of elemental sulfur, making it difficult to be replaced entirely in the rubber industry. [168–171] Overall, in spite of the excellent elasticity and good biocompatibility of NR, the presence of allergens that can trigger severe and unpredictable allergy reactions in some individuals further urges for its full replacement in the biomedical field.

In another aspect, NR has a long history as a photocurable material in the adhesive and coating industry.[173–175] The NR material is made photocurable with the introduction of photosensitive molecules into the NR polymer chain. In brief, the NR polymer chain is first epoxidized to modify the unsaturated carbon bond with epoxide groups to serve as the anchor point for further chemical modification.[174–178]Then, the epoxidized NR is reacted with photosensitive molecules for the introduction of photoreactive functional groups into the NR

polymer chain. Commonly, the epoxidized NR is reacted with acrylic acid to introduce the highly photoreactive acrylate moieties into the NR polymer chain via ring-opening acrylation for the formation of acrylated NR (ANR), which is capable of rapid photocuring upon UV light exposure. Despite the well-established chemical modification mechanism for the development of photocurable NR-based material, there are not many studies reporting on the fabrication of NR products with VP printing. Apart from the high viscosity, it is unsure if the lack of investigation is due to the high tackiness and stickiness of NR-based material that further prevents its effective fabrication with VP printing.[172,179] Not until very recently, in 2021 and 2023, Tessanan et al. [177,178] demonstrated the blending of ANR into acrylate-based commercial resin for structural fabrication via VP printing. However, the ANR content included in the commercial resin by Tessanan et al is extremely low, with only a maximum of 3 wt%, which barely qualifies as the printing of NR material as the commercial resin remains the major composition. Tessanan et al. revealed that the further addition of ANR beyond 3 wt% would significantly increase the viscosity of the resin material, causing difficulties in fabricating with VP printing. In another approach, Srisawadi and team[180–183] reported on the VP printing of NR-based sensing devices with pre-vulcanized NR back in 2020. Interestingly, the reported VP-printable NR material contains no photoinitiator, photosensitive molecules, or monomers. Instead, carbon materials, such as carbon black and graphite, which can absorb heat, are incorporated as heat processing aids to promote a temperature surge upon laser irradiation, enabling the curing of the pre-vulcanized NR material as it coagulates with heat. It is clear that the VP-printable NR material developed by Srisawadi and team is inspired by the conventional curing system of NR involving heat to accelerate the formation of sulfur crosslinking within the NR matrix. However, continued reliance on heat for curing fails to harness the benefits of light irradiation for faster crosslinking and eliminating the need for toxic chemicals involved in sulfur vulcanization. On a side note, it is important to mention that the VP-printable NR-

based resin materials reported by both research teams are not intended for biomedical applications and, therefore, lack information on their biocompatibility.[177,178,180–183]

1.2.2 Synthetic Rubber

1.2.2.1 Isoprene Rubber

Isoprene rubber (IR), also known as polyisoprene, is a synthetic analogue to NR synthesized with isoprene monomers via solution polymerization.[184,185] Owing to its synthesis process, IR generally has a purer chemical composition and better batch uniformity than its natural counterpart. Furthermore, the absence of proteins in IR eliminates the risk of Type I allergy in sensitized individuals, which is a major disadvantage for NR-based products. Despite the advantages, IR was revealed to have poorer mechanical properties as opposed to NR.[186,187] This is thought to be largely due to the presence of other isomeric forms of polyisoprene, in addition to cis-1,4-polyisoprene, including trans-1,4-, 1,2-, and 3,4-polyisoprene in the IR synthesized via solution polymerization.[184–187] As such, researchers continued to explore alternative synthetic routes for the synthesis of IR with over 90 % of cis-1,4-polyisoprene, aiming to match the mechanical properties of NR with 99.9 % of cis-1,4-polyisoprene. Not until the 1950s, IR with as high as 98 % of cis-1,4-polyisoprene was produced with the emergence of Ziegler-Natta stereospecific catalysts that can strictly control the stereochemistry of the monomer and enable the synthesis of polymer with a high proportion of preferential stereoisomer.[188] In spite of the high proportion of cis-1,4-polyisoprene achieved, IR still failed to match the strength and elasticity of NR.[184–187,189] Kawahara et al. [186,187,189,190] further revealed that the mechanical properties of NR are also affected by the presence of other non-rubber components in NR, such as proteins and lipids. The non-rubber components in NR were found to play a role in dictating the arrangement of cis-1,4-polyisoprene polymers in the NR matrix, thereby resulting in an island-nanomatrix structure that provides the NR with enhanced

mechanical properties. Hence, the poorer mechanical properties of IR compared to NR were attributed to the lack of non-rubber components that facilitates the arrangement of cis-1,4-polyisoprene polymers into an island-nanomatrix structure for enhanced mechanical properties. In order to cope with that, IR is often incorporated with nanometer-sized reinforcing material for mechanical properties enhancement. [184,185] However, there is still a gap between the mechanical properties of the IR nanocomposites when compared to the unfilled NR. Further investigation is required to improvise the current IR material in the market to fully mimic the mechanical properties of NR. Similar to NR, IR is conventionally crosslinked through the sulfur vulcanization process, which further introduces the risk for Type IV allergy in sensitized individuals upon continuous exposure. All in all, despite its slightly poorer mechanical properties, IR remains an important elastomer replacing NR in certain medical products where the risk of protein allergic reaction outweighs the need for superior mechanical properties.

Likewise, there are not many studies reporting on the VP printing of IR-based material. In 2020, Strohmeier et al. [191] reported on the VP printing of methacrylated IR incorporated with divinyl ethers as reactive diluents for viscosity reduction and thiol crosslinker for the formation of a photocrosslinkable polymer network via thiol-ene click chemistry upon light exposure. However, the photoreactive IR material was revealed to have significantly lower tensile stress (~0.32 to 0.90 MPa) and strain (~42 to 54 %)[191] as compared to the conventional IR (stress: ~25 to 30 MPa; strain: ~300 to 900 %).[192] It is believed that the poor mechanical properties of the photoreactive IR material result from the low molecular weight of the methacrylated IR and the lack of physical entanglements within the thiol-ene IR polymer network.[191] Besides, Strohmeier et al. revealed that the IR-based resin material has a very sticky consistency, even with the addition of divinyl ethers, resulting in an extremely poor flowability that further restricts its fabrication with VP printing. This led them to conclude that this might be the reason for the lack of IR-based material reported for VP printing as opposed to syringe-based printing

techniques. Despite the lack of biocompatibility data, it is worth noting that Strohmeier et al. highlighted the potential cytotoxicity of methacrylates and subsequently worked to reduce the methacrylate functional groups in the IR-based material. Similarly, in 2024, Wen et al. from the Long research group[193] reported the VP printing of IR-based material upon the incorporation of reactive diluents. Surprisingly, Wen et al. revealed success in achieving tensile strain as high as 682 % with their version of IR-based resin material. Inspired by the nature of colloidal dispersion in NR, Wen et al. presented a strategy to form a hydrogel scaffold with the water-soluble reactive monomers, surrounding the high-molecular-weight IR polymeric particles dispersed within the IR/hydrogel matrix, upon light exposure **(Figure 1.3)**. Subsequently, the IR/hydrogel printed structure was post-processed at 65 ºC under reduced pressure to remove water and to facilitate the coalescence of IR particles with the hydrogel scaffold, forming an elastomeric semi-interpenetrating network (sIPN). The presence of high-molecular-weight IR and physical entanglement within the IR/hydrogel matrix further resolves the previous issue reported by Strohmeier et al. on their version of photoreactive IR material with low tensile strain. However, it is important to note that the tensile stress of the IR/hydrogel resin material developed by Wen et al. remains relatively low (~0.08 to 2.02 MPa) compared to conventional IR, indicating the need for further improvements to match the mechanical properties of conventional IR material. Additionally, it is vital to recognize that the IR/hydrogel resin material requires an additional heating process after printing, which further complicates the fabrication process. Moreover, the printed structure would experience a substantial amount of isotropic shrinkage (~15 %) upon heating, leading to deviations in structural geometries.

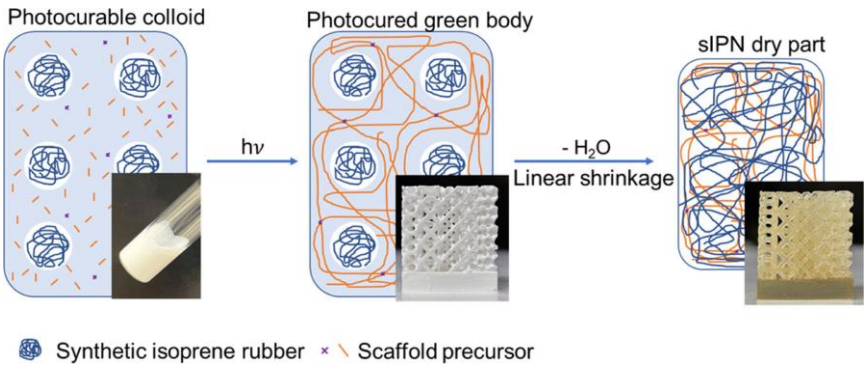


Figure 1.3: The formation of a semi interpenetrating network of IR/hydrogel polymer matrix. The photocurable colloid consists of a mixture of colloidal synthetic IR and hydrogel scaffold precursor that can formed a photocured hydrogel green body upon light exposure during the printing process, followed by thermal post-processing to facilitate the entanglement of IR polymer upon water removal. The figure is reproduced from Wen et al.[193] with permission. Copyright © 2024, American Chemical Society.

1.2.2.2 Other Diene Rubbers

Other synthetic diene rubbers, including butadiene rubber, or polybutadiene (BR), chloroprene rubber, or polychloroprene (CR), ethylene-propylene-diene monomer (EPDM), styrene-butadiene rubber (SBR), and nitrile butadiene rubber (NBR), are also commonly used for the fabrication of general medical care products (e.g. medical gloves, tubes, etc.), non-implantable medical devices (e.g. prosthetic devices, leg straps, etc.), and medical device parts (e.g. seals, gaskets, etc.).[143,194–196] Each of these rubbers has its own unique features that contribute to their use in the biomedical industry.[197] For instance, BR offers better low-temperature flexibility than NR at a lower cost and is often blended to improve the low-temperature properties, resilience, and abrasion or wear resistance of the other rubbers.[197,198] However, it is important to note that BR presents several disadvantages, such as poor tensile strength, tear resistance, and tack, when used solely. On the other hand, CR displays a higher resistance towards oxidative degradation than NR and excellent flame resistance due to the

presence of chlorine atom but shows poor low-temperature properties, rendering it unsuitable for biomedical applications requiring ultra-low temperatures.[192,197,199] Similarly, the acrylonitrile in NBR and styrene in SBR provide the respective rubber with enhanced chemical and oil resistance,[197,200–202] and improved strength and durability,[192,197,198] accordingly, but comes at the disadvantages of poorer ozone resistance and low-temperature properties than NR for both rubbers. [192,197,198,200–202] It is interesting to note that both NBR and SBR have their own enhanced versions with carboxyl groups incorporated into their rubber polymer backbone. Owing to the presence of carboxyl groups, both carboxylated NBR (XNBR) and SBR (XSBR) feature better compatibility with polar fillers for a more homogeneous filler dispersion within the rubber matrix than their non-carboxylated counterpart, [203–205] and can undergo ionic crosslinking for enhanced mechanical properties with improved reprocessibility.[206–210] Finally, EPDM, with a highly saturated non-polar hydrocarbon backbone, offers unique characteristics, such as excellent ozone resistance that benefits its sterilization with UV rays, and superior compatibility with polar solvents at elevated temperatures that enables its use with hot polar fluids. Likewise, the advantages provided by the saturated non-polar hydrocarbon backbone in EPDM would also result in disadvantages, such as poor resistance towards oils and non-polar solvents.[143,192,197,198] The presence of a variety of different synthetic diene rubbers further enables the fabrication of elastomeric devices with unique features that are best suited for their respective biomedical application.

There are not many studies reporting on the VP printing of the described diene rubbers. Indeed, there are several studies discussed on the potential to photocure BR, NBR, and SBR, as the butadiene unit in the respective rubber polymer backbone reacts with the thiol crosslinker in the presence of photoinitiator to form a crosslinked polymer network via thiol-ene crosslinking.[211–215] However, the VP printing of BR material was not reported until 2019 by Scott et al.[216] Building upon the concept of thiol-ene crosslinking, Scott et al. revealed the

successful VP printing of acrylated BR oligomer with dual crosslinking mechanism. Upon UV exposure, the acrylate end groups of the acrylated BR oligomer can react with each other via chain-growth polymerization to form a linear polymer network. Simultaneously, the acrylate end groups of the acrylated BR oligomer can also react with the thiol group of the dithiol crosslinker via thiol-ene step growth coupling for the formation of polymer branching. This results in a crosslinked BR polymer network consisting of both thiol-ene and acrylate crosslinking upon photoinitiation. In 2023, Moore et al. [217] demonstrated a more straightforward photocrosslinking mechanism based only on thiol-ene crosslinking for the formulation of a photocurable BR material with thiol crosslinker for VP printing. Moore et al. revealed that the thiol crosslinker prefers reaction with 1,2-vinyl, followed by 1,4-cis, over the 1,4-trans moiety of BR, and showed the strategy to manipulate the crosslinking density of the photocurable BR material for mechanical properties optimization by controlling the ratio of thiol crosslinker against the amount of vinyl and cis moiety present in the BR polymer backbone. In another approach, in 2020, Scott et al.[218] adopted the same strategy as Wen et al., [193] from the same research group (mentioned in **Section 1.2.2.1** on the VP printing of IR), to form a hydrogel scaffold surrounding the SBR latex particles with the formulation of SBR/hydrogel colloidal resin material, consisting of low pre-gel viscosity and excellent photocurability, for the VP printing of highly elastic SBR-based material. They further investigated the removal of the hydrogel scaffold after photocuring in 2022 [219] and the integration of silica nanoparticle filler into the SBR/hydrogel colloidal latex resin material for mechanical properties enhancement in 2024. [220] In addition to SBR, in the very same year in 2024, they proceed to investigate the feasibility of EPDM/hydrogel colloidal resin material for fabrication with VP printing.[221] However, it is worth noting that the latex/hydrogel resin materials reported by the Long research group are opaque white in colour due to the colloidal nature of the formulated resin material.[193,218–221] The non-transparent appearance of the

latex/hydrogel colloidal resin material imposes further challenges for its fabrication with VP printing as the latex colloidal particles can scatter light, which subsequently prolongs the curing time as the cure intensity reduces and lowers the printing resolution as the light focus deviates.[218] This necessitates further optimization of the printing parameters to cope with the VP printing of the series of latex/hydrogel colloidal resin material.

1.2.2.3 Styrenic Block Copolymers

Styrenic block copolymers (SBC) is a class of thermoplastic elastomers (TPE) with combined features of both elastomers and thermoplastics, allowing them to behave like a rubber, while at the same time, acquire the processibility of a thermoplastic polymer.[222–224] Besides, SBC was revealed to have superior oxidative stability and biocompatibility, leading to its wide use for the fabrication of implantable biomedical devices, such as medical implants, prosthetic valves, catheters, stents, and vent tubes.[222,223,225–227] Some of the common examples of biomedical grade SBC include styrene-butadiene-styrene (SBS), styrene-ethylene-butadiene-styrene (SEBS), and styrene-*block*-isobutylene-*block*-styrene (SIBS). Chemically, SBC is a multiphase polymer consisting of styrene units as the hard segment and elastomeric units (e.g., butadiene, ethylene, isobutylene) as the soft segment.[222–224] The hard segment is mainly responsible for the mechanical strength while the soft segment provides the SBC with elasticity. The differences in miscibility between the hard and soft segments further encourage the formation of phase-separated microdomains within the SBC polymer matrix, in which the physically crosslinked hard segment acts as the physical junction point that holds the soft elastomeric segment in place for shape recovery after deformation. This effectively eliminates the need for chemical crosslinking in SBC to achieve elastomeric properties. The physical crosslinking within the SBC polymer matrix also contributes to its thermal reprocessibility, allowing the SBC to soften and melt as the physical crosslinks destabilize above the melting

temperature of the hard segment, and harden as the crosslinks reform upon cooling. However, it is essential to note the absence of chemical crosslinking between the soft elastomeric segment would result in the loss of rubbery behaviour in SBC at elevated temperatures, degrading its elastic properties upon heating, rendering it unsuitable for high-temperature applications. Also, it is important to note that SBC, distinct from SBR mentioned in **Section 1.2.2.2**, is a block copolymer consisting of two or three different blocks of homopolymer repeating units linked together in a specific sequence in a single polymer chain.[222–224,228–231] Despite the similar monomer composition, SBR is a copolymer made up of styrene and butadiene monomer units randomly linked together without any specific sequence or arrangement, resulting in a slightly inferior melting point and mechanical properties as opposed to SBC owing to its lower crystallinity.

As emphasized earlier, SBC is a physically crosslinked polymer network and relies heavily on heating for processing. This makes it unsuitable for VP printing as SBC does not require light activation for the formation of a chemically crosslinked polymer network for structural fabrication. It is true that the elastomeric segment of certain SBC, such as those with butadiene, can be made photocrosslinkable in the presence of photoinitiator. However, further chemical crosslinking is redundant and will most likely result in a brittle elastomer as a consequence of overcrosslinking. Moreover, the additional chemical crosslinking reaction reduces the reprocessibility of SBC, losing one of its special features as a thermoplastic elastomer. Therefore, it is no surprise that there are no studies reporting on the VP printing of structural material with SBC until recently, in 2024, where the Long research group reported on their attempt to fabricate SIBS-based material using VP printing with their usual approach of latex/hydrogel colloidal resin material.[232]

1.2.2.4 Polyurethane

Similar to SBC, polyurethane (PU) is also a TPE with combined elastomeric and thermoplastic characteristics. Owing to its excellent biocompatibility and mechanical properties, PU is commonly used for the fabrication of a wide range of implantable (e.g., artificial valves, artificial vessels, and vascular stents) and non-implantable biomedical devices (e.g., wound dressings). [233] Chemically, PU consists of repeating urethane groups (-R_1-NH-O-C=O-R_2-) obtained by the polyaddition of polydiols and diisocyanates in the presence of chain extenders **(Figure 1.2)**. [233–235] This results in a linear copolymer with alternating hard (i.e., diisocyanate and chain extender) and soft segments (i.e., polydiol) that assemble into segregated microdomains. The hydrogen bonding between the urethane groups further functions as physical junction points, providing PU with elastomeric properties **(Figure 1.4)**.

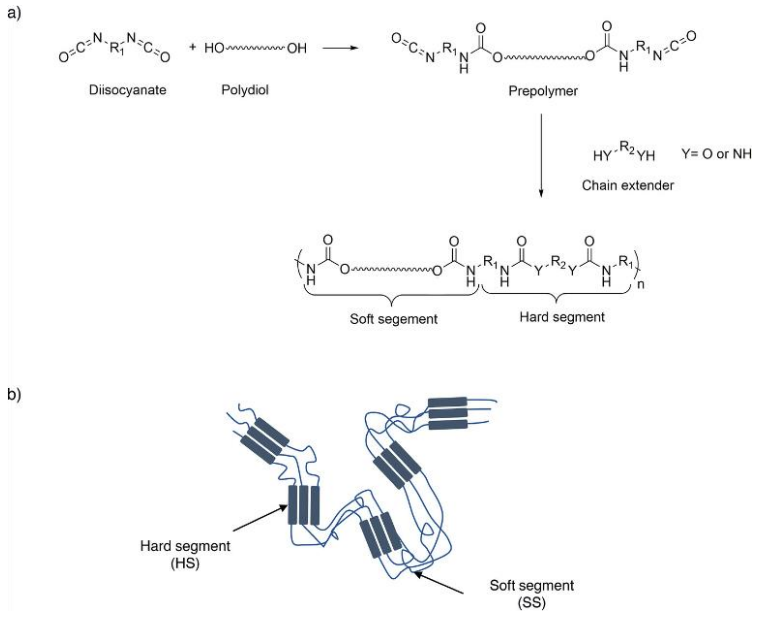


Figure 1.4: The chemical structure and molecular arrangement of PU. (a) The synthesis of PU in a two-step process involving the first reaction between the diisocyanate and polydiol to form a PU prepolymer followed by a second reaction to modify or extend the diisocyanate with chain extender, resulting in a PU chain with the diisocyanate and chain extender moiety

as the hard segement and polydiol as the soft segment. **(b)** The arrangement of the hard and soft segments of the PU chains in segregated microdomains due to the immiscibility between the different phases. The figure is reproduced from Mauriello et al.[235] with permission. Copyright © 2023, John Wiley & Sons.

Besides, PU is well-known to be able to achieve a wide range of material characteristics catering to different applications based on the different ratios, chemical structures, and chemical compositions of the three main components. As mentioned earlier, diisocyanate is a component in the hard segment and can be further classified as symmetric or asymmetric, and as aliphatic or aromatic. Specifically, symmetric diisocyanate often results in better phase separation between the microdomains, leading to higher crystallinity for enhanced mechanical strength, than its asymmetric counterpart. In another aspect, aromatic diisocyanate result in a higher glass temperature than their aliphatic counterpart due to the presence of the benzene ring, increasing the overall strength and rigidity at room temperature.[234–237] However, the aromatic diisocyanate can potentially degrade into carcinogenic diamines, posing potential risk for biomedical applications. Chain extender is another component in the hard segment, capable of extending and modifying the hard segment upon reaction with diisocyanate. This allows them to introduce changes to the polymer backbone, and thus, alter the mechanical properties of the PU polymer. The two common chain extenders are diamine and diol. Particularly, the diamine chain extender, which forms urea linkages, exhibits higher tensile strength and modulus than its diol counterpart, which forms urethane linkages with diisocyanate. This is highly attributed to the formation of bidentate hydrogen bonds between the urea linkages. Despite that, it is important to note that the enhanced tensile strength and modulus from the urea linkages results in a decrease in elongation. Hence, a diol chain extender is preferred for the synthesis of highly elastic PU for applications requiring better elongation. Finally, polydiol serves as the component for the soft segment in PU.[233–237] Typically, polydiol is an oligomer

with an average molecular weight of 1000 to 3000 g/mol and can be further categorized based on its polymer backbone. Some common polydiols used for the synthesis of PU include polyether, polyester, and polycarbonate. Unfortunately, these common polydiols are highly susceptible to degradation upon contact with water and oxygen for a prolonged period, making them unsuitable for long-term implants due to their poor biostability. To overcome this, the soft segment of PU can be replaced with more stable oligomers, for instance, polysiloxane and polyisobutylene.[233–242] Despite the better biostability, the lack of hydrogen bonding in polysiloxane and polyisobutylene further results in poor mechanical properties.[238–242] From another perspective, the ease of PU degradation with water and oxygen makes it an attractive feature for the construction of tissue-engineering scaffolds and short-term implants.[233] This mandates further investigation into the degradation mechanism and the biocompatibility of degradation by-product to ensure its safe use as degradable biomaterial. It is true that PU is a versatile material capable of achieving a wide range of mechanical properties, biocompatibility, biostability, and biodegradability based on the different hard and soft segment variations. However, it is essential to select a combination of hard and soft segments with features best suited for the targeted application after considering both their advantages and disadvantages.

Unlike SBC, there are many studies reporting on the development of PU-based resin material for VP printing.[57–61,243–250] This is most probably due to the ease of modifying PU chain with photosensitive functional groups, owing to the presence of isocyanate groups terminated at the end of the linear oligomeric or polymeric urethane. Besides, several studies have reported on the successful development of biocompatible PU-based resin material for fabricating tissue scaffolds by substituting the synthesizing components, particularly the soft segment, with hydrophilic alternatives,[61,243,251,252] rendering it a promising material for the fabrication of biomedical products with VP printing. However, it is vital to note that most of the studies focus mainly on biodegradability, with little information on the biostability of PU-

based resin material for the fabrication of long-term implantable devices. In general, there are three major steps involved in the production of a photocurable PU-based resin material. To begin, a urethane pre-polymer is synthesized by reacting diisocyanate with polydiol according to the conventional PU synthesis process.[57–61,243–245] In cases where the toxicity of isocyanate is a concern, the urethane pre-polymer can be synthesized with a carbonate and diamine instead.[248–250] Chain extenders can be included during this process. [57–61,243–245,248–250] Then, the urethane pre-polymer is functionalized with photosensitive functional groups upon reaction with the isocyanate groups capped at the end of the urethane oligomer or polymer chain. It is important to note that, at this stage, the modified urethane pre-polymer displays a high viscosity due to the increase in molecular weight and the presence of intermolecular hydrogen bonding between the urethane groups. [235,253] The high viscosity of the modified urethane pre-polymer is not ideal for its fabrication with VP printing. Therefore, in the final step, additional monomers with low molecular weight are often incorporated as reactive diluents to reduce the viscosity, and at the same time, elevate the photocrosslinking density of the modified urethane pre-polymer.[57–61,243–245,248–250] It is critical to note that most studies have adopted an acrylate/methacrylate-based system when formulating PU-based resin material for VP printing. As a result, the urethane pre-polymer is commonly functionalized with acryloyl and methacryloyl groups, and low-molecular-weight acrylate or methacrylate monomers are often included as the reactive diluents. Due to the high crosslinking density, the PU-based resin material exhibits material characteristics resembling thermosets more than thermoplastics upon photocuring, with higher brittleness and poorer elastic properties than the conventional PU material. [235,253] In conjunction with that, Carbon Inc. established a two-component PU-based resin material for VP printing.[254] The two-component PU-based material was revealed to be able to achieve a high tensile strength (35 MPa) and elongation at break (~100 %) with the formation of a IPN upon dual curing,[254–256] successfully resolving the issue of high brittleness

and low elongation as with the one-component PU-based resin material. As illustrated in **Figure 1.5**, a first acrylate/methacrylate polymer network is formed in the presence of photoinitiator. The acrylate or methacrylate oligomer contains blocked isocyanate (BI) groups, which is a major component for the formation of the secondary PU polymer network. Upon heating, the BI can be unblocked and activated to react with polydiols for the synthesis of PU polymer. A second PU polymer network is then formed via thermal curing. The physical entanglement between the acrylate/methacrylate and the PU polymer network further enhances the elastic properties of the PU-based resin material. Despite the enhanced elasticity, it is important to recognize that the need for thermal curing necessitates an additional thermal post-processing process after VP printing for the two-component PU-based resin material. Also, the PU-based resin material developed by Carbon Inc. is catered towards industrial use, and not for biomedical use.

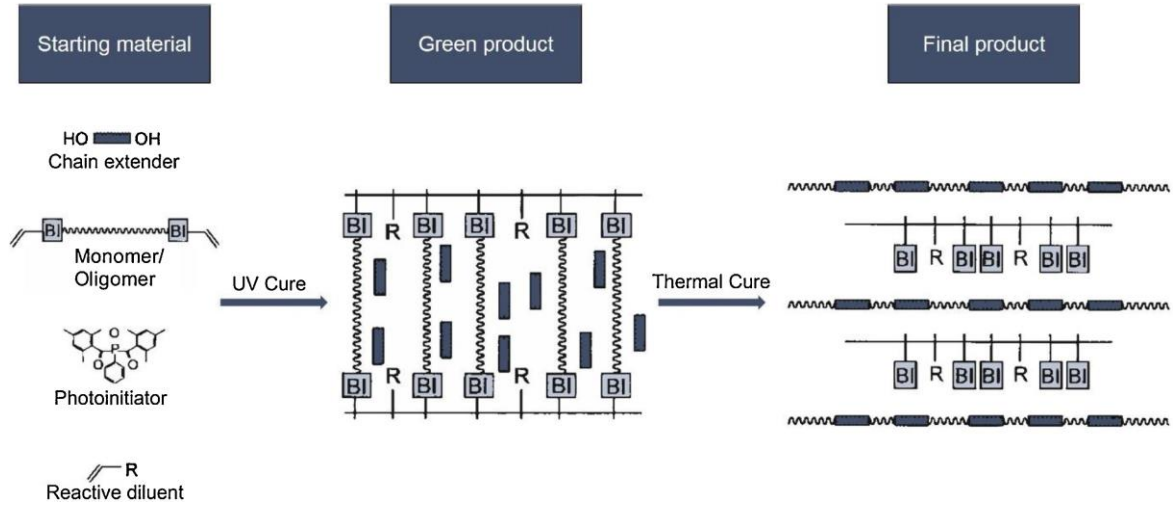


Figure 1.5: The dual cure reaction of the PU-based resin material developed by Carbon Inc. The starting material will undergo UV curing followed by thermal curing to achieve the final dual polymer network of acrylate/methacrylate and PU. Upon UV curing, the first acrylate/methacrylate polymer network with blocked isocyanate (BI) is formed in the presence of photoinitiator. Then, upon heating, the BI can be unblocked, allowing the formation of the

second PU polymer network as the unblocked isocyanate reacts with the diol chain extender via thermal curing. The figure is reproduced from Obst et al.[255] with permission. Copyright © 2020, Elsevier.

1.2.2.5 Silicone

Silicone, chemically known as polydimethylsiloxane (PDMS), is a semi-inorganic elastomer with a polymer backbone consisting of repeating units of silicon and oxygen atoms covalently bonded together by siloxane (Si-O) linkages along with methyl groups (-CH_3), attached to the silicon atoms **(Figure 1.2)**.[257–260] Due to the nature of siloxane linkages, silicone exhibits exceptional flexibility as indicated by its very low glass transition temperature at approximately -125 ºC.[70,257–261] Besides, the higher stability of Si-O bonds as compared to C-O bonds provides silicone with better thermal and oxidative resistance, resulting in better aging properties than PU. In addition to that, owing to the presence of silicon atoms and the absence of double bonds in the siloxane polymer backbone, silicone also displays a range of other unique properties, such as excellent chemical inertness, biocompatibility, and oxygen permeability. [70,257,260–267] These properties further contribute to its common use in a variety of biomedical devices, including implants, prosthetics, catheters, valves, and lenses.

To obtain a silicone rubber, the silicone pre-polymer will need to undergo a curing process, where the oligomeric siloxane chains crosslink to form a silicone polymer network, transforming the liquid pre-polymer into solid rubber. The cure system for conventional silicones can be commonly categorized into two main categories based on their respective curing conditions: room-temperature vulcanizing (RTV) and high-temperature vulcanizing (HTV), in which the RTV silicones can be cured at room temperature while the HTV silicones require heat for curing to occur.[257,260] RTV silicones can be further classified into one- (RTV-1) and two-component (RTV-2). Specifically, the RTV-1 silicone relies heavily on atmospheric

moisture to kickstart the curing process. [257,260,268] Upon contact with the moisture in the air, the acetoxy, alkoxy, amine, or oxime functional groups of the respective functionalized siloxane chain would undergo hydrolysis, forming silanol (Si-OH) groups that can further react with each other to result in curing via the condensation reaction in the presence of tin (Sn) catalyst **(Figure 1.6)**. However, it is important to note that the RTV-1 silicone can only be used for the fabrication of thin films (< 6 mm) as the slow moisture penetration rate imposes further limits on the curing of silicone in deeper areas, making it unsuitable for the fabrication of thick objects.

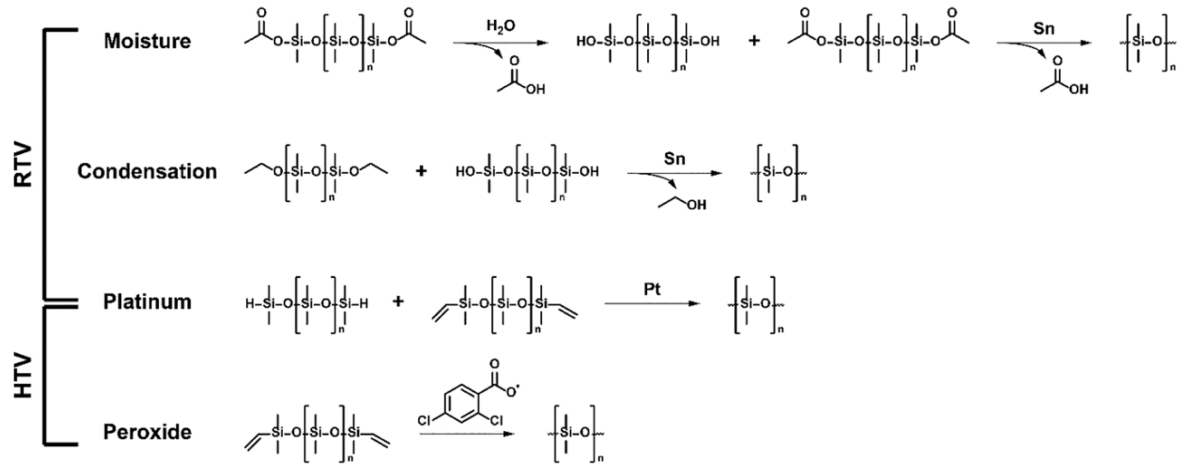


Figure 1.6: The silicone cure chemistries of RTV and HTV silicones. The RTV-1 silicone cure through moisture curing with the first step involving hydrolyzation of functional groups followed by curing via condensation reaction. RTV-2 silicone cure through either condensation reaction in the presence of Sn catalyst or addition reaction in the presence of Pt catalyst. HTV silicone cure through either the Pt-catalysed addition reaction of the peroxide initiated free radical polymerization. The figure is reproduced from Marmo et al.[260] with permission. Copyright © 2023, American Chemical Society.

Whereas in RTV-2 silicone, the use of two separate components: base compound and curing agent, that can be readily cured via either condensation or addition reaction upon mixing, eliminates the need for moisture to initiate the curing process. This further allows the

fabrication of thick silicone objects. Particularly, RTV-2 silicone with a condensation cure system consists of a base component made of silanol-terminated siloxane chain oligomers, which cures upon mixing with curing agents containing siloxane crosslinker and Sn catalyst **(Figure 1.6)**. However, it is essential to note that the condensation cure system generates cure by-products that need to be effectively evaporated to achieve full cure, and therefore, would not be suitable for the fabrication of completely sealed assemblies. Also, the use of Sn catalyst introduces a certain level of toxicity, rendering the Sn-cured silicone material unsuitable for the fabrication of implantable biomedical devices.[260,269] On the other hand, the addition cure system presents a better alternative for the fabrication of biomedical grade silicone due to the non-toxicity of platinum (Pt) catalyst at its zero-oxidation state.[260,270] The addition cure system generally consists of vinyl-terminated siloxane and Pt catalyst as the base component, and the hydride-terminated siloxane and additional vinyl-terminated siloxane as the curing agent, where the vinyl and hydride groups undergoes hydrosilylation reaction in the presence of Pt catalyst and cures upon mixing **(Figure 1.6)**. [257,260,268] Despite that, it is vital to note that the Pt catalyst highly favours the formation of a strong complex with certain components (e.g., sulfur, amine, chlorine), which deactivates its catalytic activity and leads to cure inhibition. This further complicates its fabrication involving direct contact with certain materials, unless a barrier coating is applied. Besides, the Pt-catalysed cure system can also be conducted at elevated temperatures for an accelerated curing process, allowing it to be used interchangeably as RTV or HTV silicone depending on the ideal curing conditions required by the application **(Figure 1.6)**. Another common HTV silicone cure system uses peroxide to initiate the curing of vinyl-terminated siloxane chains through free radical polymerization upon heating **(Figure 1.6)**. It is important to recognize that the peroxide-catalysed cure system can generate volatile by-products during the curing process, demonstrating increased toxicity as opposed to the Pt-catalysed cure system with no cure by-products. Furthermore, the less controlled cure rate and

crosslinking distribution in the peroxide-catalysed system can further compromise the transparency of the silicone material. Overall, the various silicone cure systems offer valuable insights into the factors to consider when designing a silicone cure system. Moreover, the fundamental of forming a thermosetting silicone polymer network with functionalized siloxane chains upon curing further establishes the groundwork for the development of photocurable silicone resin material.

Building upon the common photocrosslinking systems, several research groups have presented the formulation of silicone-based material for VP printing based on either acrylate [62–64,271] or thiol-ene system [65–71,272,273]**(Table 1.2)**. In the acrylate system, the siloxane chains are functionalized with acrylate and/or methacrylate groups consisting of C=C bonds that can polymerize via chain-growth polymerization upon photoinitiation **(Figure 1.7a)**. [62–64] In the thiol-ene system, the siloxane chains are functionalized with thiol (SH) and vinyl (C=C) groups that can polymerize via step-growth polymerization upon photoinitiation **(Figure 1.7b)**. [65–71,272,273] The polymerization of the siloxane chains results in the formation of a thermosetting siloxane polymer network, thereby facilitating the solidification of the silicone-based resin material for structural fabrication upon photoinitiation. Furthermore, there are also studies reporting on the formulation of silicone-based material with IPN upon dual curing.[66,67] The dual cure system involves the formation of a first polymer network upon photocuring during the VP printing process followed by the formation of a second polymer network post-printing. In one example, Wallin et al. [66] presented the formation of a second siloxane polymer network via Sn-catalysed condensation reaction at room temperature post-printing, interpenetrating the first thiol-ene siloxane polymer network for mechanical properties enhancement. In another example, Liu et al. [67] revealed the formation of a second ionic siloxane polymer network via thermal curing following the printing of the first thiol-ene siloxane polymer network, equipping the silicone material with self-healing properties for better reprocessibility. In spite of the

numerous VP-printable silicone-based materials reported by research groups, it is important to note that most of commercially available silicone-based materials are not true silicone but rather silicone-like materials that share certain material characteristics with commercial silicone. The silicone-like material may partially or may not at all contain silicone. Not until 2024, Drazba et al. from Carbon Inc.[274] introduced a dual cure silicone resin material containing acrylate-functionalized siloxane chains, forming the first silicone polymer network with acrylate crosslinking upon photocuring with VP printing, and vinyl- and hydride-functionalized siloxane chains, forming the second silicone polymer network in the presence of Pt catalyst with addition curing upon thermal curing after printing. To the best of my knowledge, this makes it the first commercially available true silicone-based material for VP printing.

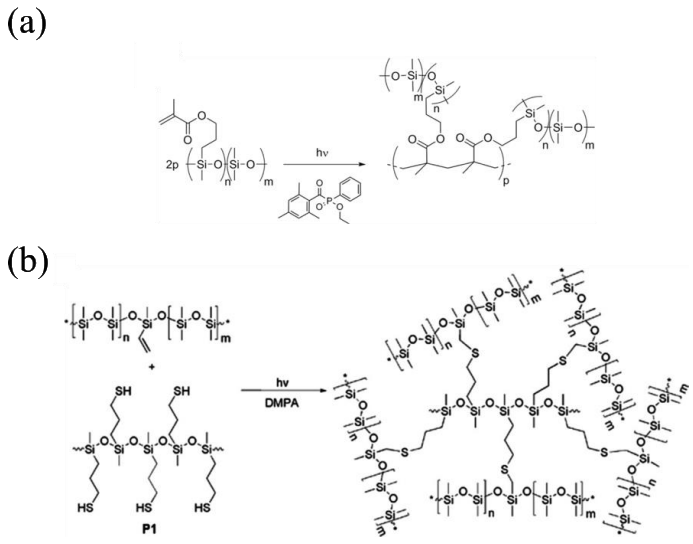


Figure 1.7: The different photocrosslinking mechanisms of functionalized siloxane chains. **(a)** The acrylate crosslinking of methacrylate-functionalized PDMS and **(b)** the thiol-ene crosslinking of vinyl- and thiol-functionalized PDMS in the presence of photoinitiator upon light exposure. Figure 1.7a is reproduced from Femmer et al.[64] with permission. Copyright © 2001, Royal Society of Chemistry. Figure 1.7b is reproduced from Xue et al.[275] with permission Copyright © 2013, Elsevier.

Despite the successful development, there are still a number of challenges remaining with the current silicone-based resin material reported for VP printing. Owing to the high molecular weight of siloxane polymer, the silicone-based resin material often has a high viscosity with a gel- or paste-like consistency, which is not favourable for VP printing. To solve the problem, Rodriguez et al.[70] and Wang et al.[65] proposed to modify the printer vat with a spreader and heater, respectively, to ease the flowability of the high-viscosity silicone-based resin material for VP printing. As discussed in **Section 1.1.2.2**, the approach to mechanically modifying the printer vat is rather complicated and is often irreversible. In conjunction with that, most of the studies reported on the use of oligomeric siloxane chains with a lower molecular weight for the formulation of a low-viscosity silicone-based resin material instead to cope with VP printing. [62–64,66–69,71,271–273,276,277] However, the use of low-molecular-weight siloxane oligomers generally results in a silicone material with compromised strength and elongation upon curing due to the lack of chain entanglements **(Table 1.2)**. Alternatively, a second polymer network can be introduced as a strategy to increase the chain entanglements within the silicone network for enhanced mechanical properties. Yet, the silicone-based material with dual IPN reported by Wallin et al., [66] Liu et al., [67] and Drazba et al.[274] still fails to match the strength and elongation of the conventional silicone material **(Table 1.2)**. In another approach, Du et al.[276] and Zhao et al.[68] revealed the possibility of achieving a high elongation at about 1000 %, matching the conventional silicone material, by manipulating the crosslinking density with siloxane oligomer ratio variation. Despite that, the strength of the respective silicone-based material remains relatively low **(Table 1.2)**. Indeed, the low crosslinking density can allow the siloxane chains to slide past each other more easily, providing the silicone with higher elongation. However, the low crosslinking density also indicates that there is a smaller number of crosslinking points holding the silicone network in place, failing to provide the silicone with sufficient strength. In another perspective, the compromised mechanical

properties of the silicone-based material can also be partly induced by the layered structure generated by VP printing. [278–280] Due to the nature of VP printing, the next layer is printed on top of the previously cured layer. This results in a layered structure with weak interlayer bonding. As a consequence, the VP-printed layered structure is more prone to stress failure as opposed to the compact moulded samples, which explains the comparatively lower mechanical properties of the silicone-based material even after the integration of IPN. Similar to the other 3D printing techniques, it is believed that the mechanical properties of the layered structure can be effectively enhanced by improving the layer integration between the printing layers. [13,14]

Furthermore, despite the common use of conventional silicone for biomedical applications, it is worth noting that most of the silicone-based materials developed for VP printing are not intended for biomedical applications. [62,64–70,271–273,277] Hence, there is limited information on the biocompatibility of the VP-printable silicone-based material **(Table 1.2)**. From the few studies that have investigated on the biocompatibility of the silicone-based material, it is clear that the initial silicone-based material is cytotoxic after VP printing. [63,71,276] This is most likely due to the use of toxic solvents as the resin medium as well as the presence of toxic cure by-products and initiating components remaining in the silicone-based material after printing. To improve biocompatibility, studies have shown that the silicone-based material needs to undergo a series of washing and extraction processes post-printing to ensure the complete removal of toxic substances prior to biomedical applications. [63,71,276] In addition to that, due to its hydrophobic nature, the silicone-based material will also need additional surface treatment for the acquisition of hydrophilic surface properties to increase its biocompatibility, especially for cell-based applications. Overall, the development of silicone-based material fabricated with VP printing for biomedical use is still in its infancy. Further studies are required to investigate the biocompatibility of the silicone-based material extensively before subjecting it to real-world biomedical applications.

Table 1.2: The compilation of literature reporting on the silicone-based resin material developed for VP printing.

Literature	Year	Silicone network	Resin medium	Stress (MPa)	Strain (%)	Surface properties	Biocompatibility	Cell type	Application
Conventional silicone			Solvent-based	5 – 6[281]	1000 - 1500 [281]	Hydrophobic[282]	Non-cytotoxic[283]	Murine mouse fibroblast cells (L929)	Adhesive, sealants, coatings, gaskets, medical parts, etc.
Femmer et al.[64]	2014	Methacrylate	Solvent-based	X	X	Hydrophobic	X	X	Membrane
Yang et al.[62]	2018	Methacrylate	Solvent-based	X	X	Hydrophobic	X	X	X
Bhattacharjee et al.[63]	2018	Methacrylate	Solvent-based	0.4 – 0.7	40 - 160	Hydrophobic	Non-cytotoxic	Chinese hamster ovary cells (CHO-K1)	Microfluidic devices
Du et al.[276]	2021	Methacrylate	Solvent-based	0.04 – 0.4	150 - 1000	Hydrophobic	Non-cytotoxic	Murine mouse fibroblast cells (L929)	Medical devices, wearable devices, soft robotics
Gonzalez et al.[271]	2020	Acrylate	Solvent-based	0.6 – 0.7	43 - 83	Hydrophobic	X	X	Microfluidic devices
Wallin et al.[69]	2017	Thiol-ene	Solvent-based	0.013 - 0.13	45 - 400	Hydrophobic	X	X	Soft robotics
Xiang et al.[71]	2019	Thiol-ene	Solvent-based**	0.2	158	Hydrophobic	Non-cytotoxic	Human prostate cancer cells (LNCap)	Wound dressing, soft tissue scaffolds
Sirrine et al.[273]	2019	Thiol-ene	Solvent-based	X	X	Hydrophobic	X	X	X
Zhao et al.[68]	2019	Thiol-ene	Solvent-based	0.3 - 2.59	311 - 1403	Hydrophobic	X	X	Soft robotics, wearable devices

***use less toxic solvent (ethanol) as resin medium.*

X no data available.

Table 1.2 continued: The compilation of literature reporting on the silicone-based resin material developed for VP printing.

Literature	Year	Silicone network	Resin medium	Stress (MPa)	Strain (%)	Surface properties	Biocompatibility	Cell Type	Application
Wang et al.*[65]	2020	Thiol-ene	Solvent-based	0.3	150	Hydrophobic	X	X	X
Rodriguez et al.*[70]	2021	Thiol-ene	Solvent-based	1 - 2.5	100 - 350	Hydrophobic	X	X	X
Yu et al.[272]	2023	Thiol-ene	Solvent-based	0.5	600	Hydrophobic	X	X	X
Sirrine et al.[277]	2018	Thiol-acrylamide	Solvent-based	0.25 - 3	58 - 138	Hydrophobic	X	X	X
Wallin et al.[66]	2020	Thiol-ene and Sn-catalysed condensation	Solvent-based	1	400	Hydrophobic	X	X	Medical simulator, wearable soft actuators and sensors
Liu et al.[67]	2020	Thiol-ene and thermal ionic crosslink	Solvent-based	0.25	350	Hydrophobic	X	X	Wearable electronic devices
Drazba et al.[274]	2024	Acrylate and Pt-catalysed addition	Solvent-based	0.43 – 2.14	72 - 171	Hydrophobic	X	X	Medical implants, electronic devices, microfluidic devices, soft robotics, moulds, kitchenware

**high viscosity silicone ink; require printer vat modification to cope with printing.*

X no data available.

1.2.3 Natural Hydrogel

1.2.3.1 Gelatin

Gelatin is a natural protein-based hydrogel material derived from collagen, the main structural protein of the extracellular matrix (ECM) in animal connective tissues, by controlled hydrolysis. [284–287] As such, gelatin retains molecular structure similar to the native ECM, enabling it to closely mimic the tissue environment, making it highly suitable for cell-culturing. Besides, gelatin has excellent biocompatibility and biodegradability due to the presence of arginine-glycine-aspartic acid (RGD) cell-binding sites, which promote cell adhesion, and matrix metalloproteinase (MMP)-sensitive sites, which allow enzymatic degradation, respectively. The excellent biocompatibility and biodegradability of gelatin further contribute to its popular use for the construction of tissue engineering scaffold. To make it photocurable, gelatin is commonly modified with methacryloyl groups. [286,287] Specifically, methacrylic anhydride is introduced to graft the lysine and hydroxyl residues of gelatin with methacryloyl groups, synthesizing gelatin methacryloyl (GelMA). It is important to note that the modification of gelatin with methacryloyl groups does not affect the RGD and MMP sites. Therefore, GelMA remains biocompatible and biodegradable while equipping the additional photocurable properties.

Despite its photocurable properties, the fabrication of GelMA with VP printing remains challenging. This is mainly due to the high viscosity of GelMA, forming a gel-like substance, at high concentrations.[288–290] As such, it is worth noting that most studies demonstrating the successful VP printing of GelMA employed a low concentration of GelMA, at about 15 wt% and below, for an optimally low viscosity to cope with VP printing. [291–296] However, the low concentration of GelMA often results in poor mechanical properties. In conjunction with that, without significantly elevating the viscosity of the GelMA ink material,

Gao et al.[292] and Wang et al.[296] demonstrated the incorporation of a second PMMA and hyaluronic acid methacrylate (HAMA) network, respectively, while Song et al.[295] presented the inclusion of micro- or nano-hydroxyapatite filler, as a strategy to enhance the mechanical properties of GelMA upon photocuring. However, there is a tendency for the additional polymer network or filler to alter the porosity of GelMA, impacting the overall cell growth and proliferation.[297,298] Alternatively, Han et al. [299] demonstrated the printing of a slightly viscous GelMA ink solution, formulated with 20 wt% of GelMA, with constant heat applied to the printer vat. Despite the successful printing, it is vital to note that heating can accelerate the reactivity of the ink precursor. With the same printer setting throughout the printing process, the gradual increase in reactivity of the ink precursor due to heat can lead to inhomogeneous curing between the different layers, compromising structural accuracy. Furthermore, prolonged heating increases the likelihood for premature gelation, reducing the overall shelf-life of the ink material. Finally, to improve biocompatibility, studies revealed the need for additional steps to wash and condition the GelMA-printed structure with ethanol, phosphate-buffered saline (PBS) solution, and cell-culture medium prior to biological testing and applications. [291–293,295,296]

1.2.3.2 Alginate

Alginate is a natural polysaccharide-based hydrogel material extracted from the cell wall of brown algae or bacteria.[300–303] Specifically, alginate is a linear copolymer comprised of 1,4-linked α-L-guluronic acid (G) and β-D-mannuronic acid (M) monosaccharide units arranged in blocks of consecutive G units (G-block) and consecutive M units (M-block) interspersed with randomly organized alternating M and G units (MG-block). Typically, alginate is crosslinked via ionic crosslinking between the carboxylate groups of the G units in the presence of divalent cations, such as Ca^{2+} and Mg^{2+}. Therefore, alginate with a higher G

composition tends to form a stiffer hydrogel as compared to the ones with a higher M composition. Alternatively, the hydroxyl and carboxyl groups of alginate can be chemically modified with reactive functional groups to enable the formation of a crosslinked alginate polymer network via covalent crosslinking. Despite its use in tissue engineering, it is vital to note that alginate lacks both cell-binding and enzyme degradation sites due to its non-mammalian source. Further modifications are often mandatory to equip alginate with cell attachment and enzymatic degradation properties for its function as a tissue engineering scaffold. Thus, alginate is more commonly used in other biomedical products, such as wound dressings and drug delivery systems.

Since alginate is not naturally photocurable, it typically requires grafting of photoreactive functional groups to gain photocurability for fabrication using VP printing.[304–306] The grafting of photoreactive functional groups is commonly done on the carboxyl groups of alginate, where it can be functionalized with either methacrylate groups[304,305] or thiol- and vinyl- groups[306] to enable crosslinking via methacrylate or thiol-ene crosslinking, respectively, in the presence of radical photoinitiator upon light exposure. In another approach, Valentin et al.[307] demonstrated the feasibility of fabricating an alginate scaffold using VP printing without requiring any grafting of photoreactive functional groups. Instead, Valentin et al. utilize the initial ability of alginate to form ionic crosslinks by incorporating a photoacid generator, which is a cationic photoinitiator, to kickstart the cationic crosslinking mechanism in the presence of divalent cation salts upon light exposure. However, it is important to note that the ionic crosslink is reversible with chelating agents and that the intention of ionic crosslinking is to enable scaffold degradability. Hence, ionic crosslinking may not be ideal for applications that require material stability over degradability. Similar to GelMA, to ensure a low pre-gel viscosity, a low concentration of alginate (i.e. 10 wt% and below) is typically used in most alginate ink developed for VP printing, [305–307] as the viscosity of alginate tends to increase with

its concentration.[308] Likewise, the low concentration of alginate leads to poor mechanical properties due to the lack of chain entanglements. In terms of biocompatibility, studies also highlight the necessity for sterilization processes, such as washing and conditioning, to be performed on the printed alginate structure prior to its biomedical use. [304–307]

1.2.4 Synthetic Hydrogel

Synthetic hydrogel materials are synthetic hydrophilic polymers constructed from synthetic monomer precursors upon polymerization, where the monomer consists of hydrophilic functional groups, such as hydroxyl, carboxyl, and amino groups. [309] These hydrophilic functional groups are capable of water absorption, thereby contributing to the water swelling properties of the synthetic hydrogel material. Some common examples of synthetic hydrogel materials used in the biomedical field include polyacrylamide (PAM), [310,311] polyacrylic acid (PAA),[312,313] poly(vinyl alcohol) (PVA),[314,315] poly(vinyl acetate) (PVAc),[316] poly(hydroxyethyl methacrylate) (pHEMA),[317,318] and poly(ethylene glycol) (PEG)[319] **(Figure 1.2)**. Due to their better controllability and mechanical properties, synthetic hydrogels are often preferred over natural hydrogels. [309] However, synthetic hydrogels typically lack cell binding motifs, compromising their functionality as tissue engineering scaffolds for effective cell growth and proliferation. [320] To resolve this, synthetic hydrogel can be combined with natural hydrogel to create hybrid materials that offer both good mechanical properties and cell-compatibility.[321] Alternatively, studies have also demonstrated the approach of functionalizing synthetic hydrogels with RGD cell-binding sites to enhance cell-compatibility.[322–324]

Unlike natural hydrogels, the original process of synthesizing synthetic hydrogels via radical polymerization enables synthetic hydrogel material to be readily fabricated with VP printing upon the incorporation of photoinitiator. [325–330] The ability of the monomer precursors to polymerize upon photoinitiation eliminates the need for additional functionalization with

photoreactive functional groups, which is otherwise required by natural hydrogels for photocurability. Moreover, the use of low-molecular-weight monomer precursors results in a pre-gel material with low viscosity, making the synthetic hydrogel pre-gel material an ideal resin material for VP printing. As a result, numerous studies have investigated the fabrication of synthetic hydrogel constructs using VP printing. [325–330] Yet, it is important to note that VP printing generates a highly crosslinked polymer network, which can affect the swelling properties of the synthetic hydrogel construct. [331,332] Hence, both the monomer precursor ratio and printing parameters need to be carefully optimized to achieve the targeted swelling capacity of the printed hydrogel construct.

1.2.5 Summary

Considering the overall aim of fabricating a wide range of biomedical devices, the selected elastic material must be highly versatile to cope with both implantable and non-implantable applications. As such, commercial rubbers, such as NR, IR, BR, CR, NBR, SBR, EPDM, and SBC, which have distinct material characteristics suited to specific applications, might not be suitable for this purpose. The same applies to hydrogels, which rely heavily on moisture for their mechanical and physical properties. In another aspect, PU and silicone with a long history in both implantable and non-implantable biomedical devices appear to be the ideal material for this purpose. Specifically, the material characteristics of PU depend highly on the composition of its hard and soft segments. It is true that the different combinations of hard and soft segments provide PU with distinct material characteristics. However, with a specific combination, PU can only display certain material characteristics, limiting its application to a completely different application contradicting its current properties. For instance, both degradable and non-degradable PU material can be synthesized by substituting the soft segment with polydiol and polysiloxane, respectively. Yet, the degradable PU material

will not be suitable for applications demanding for non-degradable properties, and vice versa. Besides, it is vital to note that the by-product of the degradable PU material can be toxic, with the hazardous effect being amplified for implantable biomedical devices. On the other hand, silicone, consisting of mainly siloxane chains with low toxicity, good aging properties, and superior biostability, emerges as a better choice to be used interchangeably for the fabrication of a variety of biomedical devices with a single composition. Hence, I proceed with silicone as the elastic resin material for this project.

As discussed previously, both high viscosity and the inability to photocure remain the biggest challenges to adapting elastic material for VP printing. In terms of viscosity, many studies employed the method to either incorporate reactive diluent or use lower-molecular-weight oligomeric precursor for a lower viscosity. In terms of photocurability, most of the studies approached modifying the elastomeric chain with photoreactive functional groups for optimum photocurability, with both acrylate and thiol-ene being the most popular photocrosslinking system used. As outlined in **Table 1.2**, it is worth noting that the development of silicone-based resin material for VP printing is still in its early stages. Thus, there is not much variety in the type of silicone network employed by the existing silicone-based resin material, rendering it with many possibilities to explore. This includes the development of a hydrophilic silicone-based resin material catering directly to biomedical applications, removing the need for additional surface treatment for hydrophilicity. One interesting aspect would be to combine silicone with hydrogel components for hydrophilicity. However, the immiscibility of silicone with hydrogel components remains a huge hurdle due to the non-polar and polar characteristics of silicone and hydrogel, respectively. This might be one of the major reasons for the lack of development on hydrophilic silicone-based resin material for VP printing.

1.3 Biomedical Devices

Biomedical devices have been an integral part of the healthcare industry, encompassing all products, devices, and apparatuses used for the prevention, treatment, and diagnosis of diseases and illnesses, or for the detection, measurement, restoration, correction, and modification of the function or anatomy of the human body for health purposes.[333] This includes both implantable and non-implantable devices, ranging from medical implants, artificial valves, catheters, and vascular stents to prosthetic devices, skin patches, wound dressing, and microfluidic devices. The global market for biomedical devices is expected to grow from $739.6 billion in 2023 to $1.3 trillion by the end of 2029, at a compound annual growth rate of 9.8 % during the forecast period.[334] Some of the key market drivers include the increase in the aging population, the rise in the prevalence of chronic diseases, and technological advancement.[334,335] Despite the attractive market revenue, it is important to recognize that the design and development of biomedical devices demand an average global spending of $350 billion annually. [335] The huge investment required for the design and development of biomedical devices further reduces the affordability and accessibility of biomedical devices for patients, which can delay diagnosis and treatment, and eventually cause death in critically ill patients. Hence, there is a pressing need for an alternative fabrication method to produce high-quality biomedical devices at low cost for improved patient outcomes. In conjunction with that, 3D printing emerges as a viable solution for the fabrication of high-quality biomedical devices at low cost. Besides, the use of 3D printing enables the generation of patient-specific devices owing to its ability to create customized structures. In fact, there are already commercialized 3D-printed biomedical devices existing in the current market, including dental aligners,[336,337] hearing aid casings,[338] and surgical planning models.[338,339] This further establishes the potential of 3D printing in fabricating biomedical devices for practical applications beyond the prototyping stage. However, it is worth noting that the commercialized

3D-printed biomedical devices are mainly for non-implantable applications, and there are still some limitations with the 3D-printed biomedical devices. One of the common limitations of 3D-printed biomedical devices includes the compromised device features due to the layer-by-layer printing process, producing staggered edges with staircase effect, as well as the inability of 3D printing to produce ultra-fine features due to the nature of 3D printing techniques. Another common limitation would be attributed to the limited range of printing material for selection, resulting in a mismatch in material properties for the respective devices. In this section, I will be exploring the use and application of some specific biomedical devices, and their current status and challenges with VP printing.

1.3.1 Biomimetic Implants

Biomimetic implants are generally regarded as structural devices that can imitate or replicate the structure and function of a damaged body part.[340,341] These structural devices are implanted into the human body to replace or support the damaged body parts for the restoration of impaired body function. Traditionally, biomimetic implants are made of alloys, polymers, and composites, and are considered non-living. [342] Some common examples of non-living biomimetic implants include titanium knee implant [343,344] and silicone vascular graft.[345,346] However, non-living biomimetic implants are considered a foreign material by the human body and may cause unwanted side effects to the patient in the long term.[347,348] Additionally, the synthetic material used for the fabrication of these non-living biomimetic implants has a certain lifespan, and revision surgery will most likely be required to replace the implant once it fails to function. Therefore, regular follow-ups with the patient are essential to monitor the performance of the non-living biomimetic implants after implantation and to provide immediate remediation when a problem arises.

In contrast, the emergence of tissue engineering further revolutionized the medical field with its ability to generate living biomimetic implants comprised of functional tissues and organs. [342] The ability to construct functional tissues and organs as replacements expands the range of biomimetic implants that can be used for body function restoration, including heart, liver, kidney, and pancreas, which were not previously possible with non-living implants due to the lack of suitable material for construction. This offers great potential to resolve one of the most critical issues in healthcare concerning the significant shortage in organ supply for transplantation. [349,350] In conjunction with that, the ability to quickly construct functional structures as replacements with tissue engineering lowers the probability of patient death as a result of organ failure due to the inability to obtain a transplant in time. Moreover, the ability to construct genetically compatible structures with tissue engineering for implantation reduces the probability of patient death as a consequence of tissue or organ rejection due to the incompatibility of the donor organ with the blood and tissue of the recipient. This further contributes to the rapid growth and development of tissue-engineered structures as biomimetic implants.

Tissue engineering builds upon the concept of using cells from the patient for the fabrication of biomimetic implants. [349] The cells are first harvested from the patient followed by isolation and expansion before seeding onto a scaffold. A scaffold is a construct made up of biomaterials that encourages the growth of cells by providing the initial biomechanical profile for the development of the targeted organ or tissues. Some common biomaterials that can be used for scaffold construction include decellularized matrices and hydrogels. To ensure adequate cell growth and proliferation, the scaffold will need to have a 3D interconnected porous structure for ECM formation and vascularization.[351] Once the seeded cells generate the ECM, the scaffold is either metabolized or degraded by the cells, leaving a functional tissue or organ structure for implantation. [349] The scaffold seeded with cells *in vitro* prior to implantation

is regarded as a cellular scaffold. In another approach, an acellular scaffold can be used for implantation. Instead of seeding cells prior to implantation, the acellular scaffold utilizes the concept of guided tissue regeneration to encourage the repopulation of the host cells onto the scaffold after implantation. However, the capability to reseed a large surface area with an acellular scaffold in the human body remains a huge challenge. Regardless, the scaffold structure plays a vital role in the development of living biomimetic implants for implantation.

With the emergence of 3D printing, scaffolds can be constructed in a more precise and efficient manner as compared to the conventional fabrication techniques involving freeze-drying,[352] foaming,[353] electro-spinning,[354] and salt leaching.[355] Specifically, the 3D printing of biomaterials is termed 3D bioprinting, and the ink material can be further categorized into bioink and biomaterial ink. [74,356] Bioinks are ink materials containing living cells as part of the formulation for bioprinting and require a set of well-controlled processing parameters to retain a cell-friendly environment for cell growth. This includes the surrounding temperature, pressure applied, and the exposure time and intensity of heat or light source used for printing as cells are highly sensitive to external stimuli. On the contrary, biomaterial inks do not contain living cells as part of the formulation. Instead, the living cells are seeded onto the structure after printing. Hence, biomaterial inks enable a more lenient control of the processing parameters due to their less stringent physiological demands as opposed to bioinks, which further expands the range of 3D printing techniques that can be used to fabricate tissue-engineered implants.

Hydrogel is widely adopted as the fabrication material for tissue-engineered implants due to their excellent biocompatibility and water-rich properties, making them highly compatible with the conditions of the soft tissues in the human body, such as skin, cartilage, and tendons.[4,357] Although not as popular as compared to extrusion-based printing, numerous

studies [358–360] have reported on the successful fabrication of tissue scaffolds with VP printing using hydrogel as the printing material **(Figure 1.8)**. For instance, Kim et al.[358] demonstrated the potential to fabricate highly complex organ structures, such as the brain, ear, trachea, heart, lung, and vessel, with VP printing using silk fibroin-glycidyl methacrylate (Silk-GMA) hydrogel **(Figure 1.8a)**. Similarly, Hong et al. [360] fabricated a trachea implant with VP printing using chondrocyte-laden Silk-GMA hydrogel **(Figure 1.8b)**. The excellent chondrogenic expression *in vitro* and *in vivo* transplantation in rabbits of the printed trachea implant further reveals its potential for application in cartilage tissue engineering. In another example, Zhu et al. [359] constructed nerve guidance conduits (NGCs) with VP printing using hydrogel formulated with GelMA and poly(ethylene glycol) diacrylate (PEGDA) **(Figure 1.8c)**. The printed NGCs demonstrate effective directional regeneration of sciatic nerves *in vivo* in rodents, resulting in the recovery of motor and sensory function for peripheral nerve repair. In general, there are not many difficulties reported for the VP printing of biomimetic scaffolds with hydrogels. However, most conventional hydrogels are mechanically weak and brittle due to the inhomogeneous polymer network, low polymer density, and small friction between polymer chains, causing failure to match the strength and flexibility found in most human tissues and organs.[4,357,361] The mismatch in mechanical properties between the scaffold and the native tissues can negatively affect the regeneration of functional tissues and organs.[362] Therefore, it is of great importance to develop a strong elastic biomimetic material that can cope with the strength and flexibility found in most human organs as a strategy to widen the scope of application in tissue engineering. In parallel with that, biomedical elastomers appear to be a promising candidate material for the development of a strong elastic biomimetic material owing to its high strength, elasticity, and biocompatibility properties. Yet, conventional elastomers are hydrophobic in nature, rendering them unsuitable for the fabrication of tissue-engineered implants. It would be interesting to develop a new class of materials combining the

benefits of hydrophilicity from hydrogels and mechanical properties from biomedical elastomers for the fabrication of tissue-engineered scaffold with excellent cell compatibility and optimum strength to cope with its function as a living biomimetic implant.

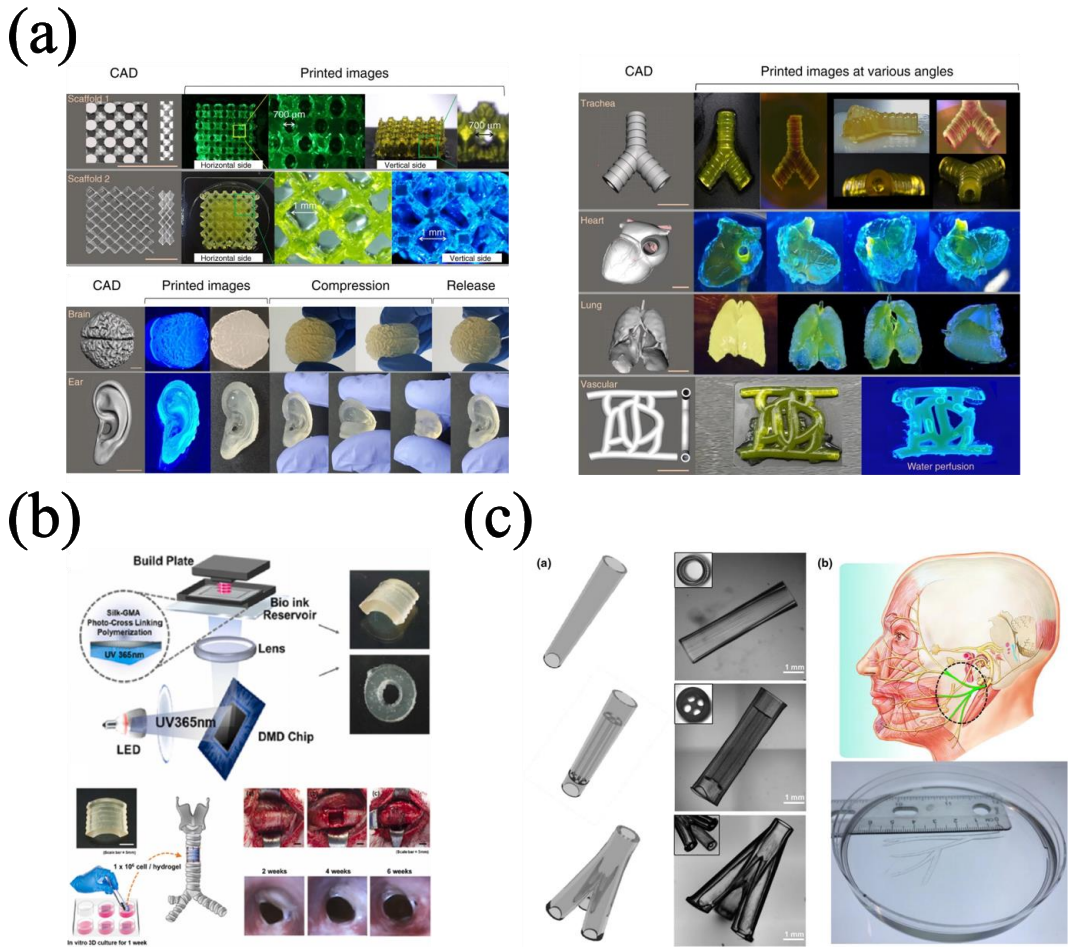


Figure 1.8: Fabrication of tissue-engineered biomimetic scaffold with VP printing. (a) Fabrication of a wide range of biomimetic structures, including brain, ear, trachea, heart, lung, and vessels, with VP printing using Silk-GMA hydrogel. Figure is reproduced from Kim et al.[358] with permission. Copyright © 2018, Springer Nature. **(b)** Development of a trachea implant with VP printing using Silk-GMA hydrogel. Figure is reproduced from Hong et al.[360] with permission. Copyright © 2020, Elsevier. **(c)** Creation of NGCs with VP printing using GelMA/PEGDA hydrogel. Figure is reproduced from Zhu et al.[359] with permission. Copyright © 2018, Elsevier.

1.3.2 Microfluidic Devices

Microfluidic devices are micromachines capable of manipulating small volumes of fluid (10^{-9} to 10^{-18} L) through microchannels with a scale dimension ranging from 1 to 1000 μm in width and height. [5,363–367] The ability of microfluidic devices to run experiments and tests using a small volume of fluids brings upon several advantages that subsequently contributed to their rapid growth and development in the biological and chemical fields. One of the significant advantages of scaling down experiments and tests with microfluidic devices is the tremendous reduction in processing cost due to the smaller amount of reagent consumed and waste generated for the scaled-down reactions. Besides, the miniaturization of experiments and tests presents the benefit of quicker turnaround times for research and testing outcomes owing to the shorter processing times with smaller-scale reactions. These advantages have contributed to the wide use of microfluidic devices for various biomedical applications, including disease diagnosis,[368] disease modeling,[369] drug screening,[370,371] cell culture,[372,373] scaffold fabrication,[374] nanoparticle synthesis,[375,376] and biosensing.[377,378]

In general, microfluidic devices can be categorized into two main categories: passive and active microfluidic devices. In the passive approach, microfluidic devices rely primarily on capillary action, surface tension, hydrostatic pressure, gravity, osmosis, and vacuums to achieve fluid flow, and thus, depend heavily on the channel geometry for fluid processing.[147,379,380] In parallel with that, the channels are incorporated with curvature, grooves, poles, or valves to help with fluid flow and manipulation. However, due to the geometry-dependent nature, passive microfluidic devices are only limited to certain applications, such as fluid mixing and particle manipulations. [147] On the other hand, in the active approach, microfluidic devices utilize external forces, such as electrical fields, magnetic fields, thermal fields, acoustic fields, and pressure fields, to drive fluid flow.[147,380] As such, there are more

factors, such as the type of external energy source and the properties of the target particles, to be considered in addition to the flow rate, fluid viscosity, and channel geometry for the successful manipulation of fluids and particles with active microfluidic devices. Regardless, the use of external forces further expands the use of microfluidic devices for advanced biological and chemical applications involving particle trapping and sensing. [147]

Conventionally, microfluidic devices are commonly fabricated with soft-lithography, which is an extremely time-consuming and expensive process, owing to the multiple steps of material deposition and removal involved and the need for cleanroom facilities.[364,365] This severely restricts the possibility of mass-producing microfluidic devices inexpensively. Furthermore, it was found to be exceptionally challenging to produce channels and pole structures with curvature using soft-lithography, which subsequently limits the channel geometry that can be generated with soft-lithography. In conjunction with that, the emergence of 3D printing has successfully revolutionized the field of microfluidic devices by providing an alternative method for the fabrication of microfluidic devices at a higher production output and lower cost. [147,148,380] Besides, 3D printing enables the accurate replication of any pattern of channels and pole structures, including structures with curvature, which were previously challenging to produce with soft-lithography, owing to their nature in slicing the designed 3D structure into layers of 2D images for printing in a layer-by-layer manner.[1,3–6]

Several groups have reported on the fabrication of microfluidic devices with VP printing.[381–384] Nonetheless, most of the successfully printed microfluidic devices are fabricated using acrylate- and methacrylate-based resin material with only a few studies[63,271] demonstrating the printing of microfluidic devices with silicone-based resin material **(Figure 1.9)**. The use of rigid acrylate- and methacrylate-based material for microfluidic device fabrication further reduces the resistance of the channel walls towards high fluid pressure and

restricts the integration of elastic components, such as valves and pumps, for advanced fluid processing. Moreover, there are not many studies reporting on the direct printing of a complete microfluidic device with embedded channels. For example, Razavi Bazaz et al.[382] showcased the fabrication of microfluidic devices with VP printing by assembling the VP-printed top layer consisting of open channel patterns with the polymethyl methacrylate (PMMA) sheet as the bottom layer as a strategy to produce a final microfluidic device with embedded channels **(Figure 1.9a)**. On the other hand, Linden et al.[384] demonstrated the creation of microfluidic device by assembling different VP-printed parts with screws **(Figure 1.9b)**. This is because the approach to direct printing of embedded channels with VP printing is extremely challenging as it often results in a compromised minimum channel resolution due to the overcuring of the trapped resin material within the channel as the printing progresses to print the subsequent top layers enclosing the embedded channels.[63,271,381,383] In fact, several studies recognized the limitation of VP printing in generating embedded channels and have reported on the tuning of photocuring depth with photoabsorber as a strategy to minimize the overcuring effect for a higher embedded channel resolution. Despite that, the overcuring effect cannot be completely eliminated upon the inclusion of photoabsorber. Further effort in positioning the embedded channels close to the top of the designed structure is necessary to minimize the frequency at which the trapped resin material is exposed to UV light as the printer progresses to print the subsequent top layers.[63,381] Regardless, the direct printing of embedded channels with VP printing is still in its early stage of development as most of the studies only managed to showcase simple channel geometries when printing embedded channels. In addition to that, most of the studies focused on displaying the feasibility of fabricating silicone-based microfluidic devices using VP printing with a lack of exploration of the fluid processability of the printed device. As such, further investigation is required for the fabrication of embedded

channels with complicated designs in a one-step printing process and the functionality of the printed device in fluid processing when subjected to actual experimental conditions.

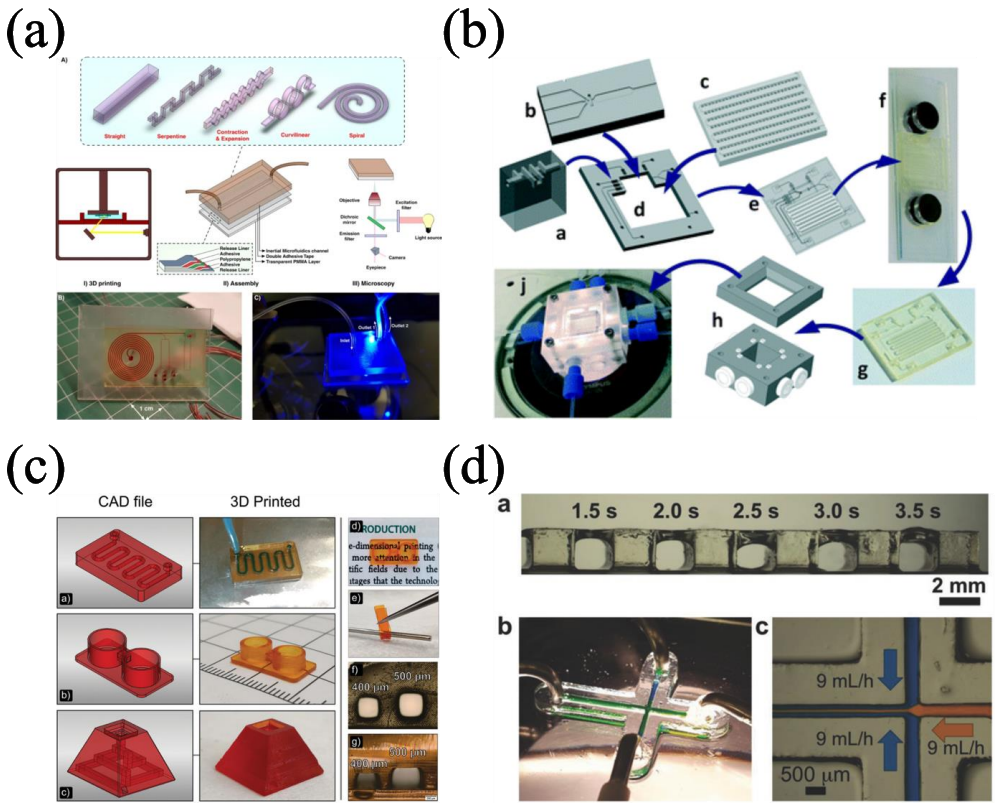


Figure 1.9: Fabrication of microfluidic devices with VP printing. (a) Fabrication of microfluidic devices by attaching the VP-printed acrylate-based open-channel microfluidic devices to PMMA sheet using double adhesive tape. Figure is reproduced from Razavi Bazaz et al.[382] with permission. Copyright © 2020, Springer Nature. **(b)** Creation of microfluidic devices by assembling the different VP-printed acrylate-based parts with screws. Figure is reproduced from Linden et al.[384] with permission. Copyright © 2020, Royal Society of Chemistry. **(c, d)** Direct fabrication of silicone-based microfluidic devices with embedded-channel using VP printing. **(c)** Red dye (DR1-MA) was included as photoabsorber. Figure is reproduced from Gonzalez et al.[271]with permission. Copyright © 2020, John Wiley & Sons. **(d)** Isopropyl-thioxanthone (ITX) was included as photoabsorber. Figure is reproduced from Bhattacharjee et al.[63] Copyright © 2018, Wiley-VCH GmbH.

1.4 Motivation and Scope of the Thesis

As discussed above, 3D printing presents several prominent advantages over conventional manufacturing techniques for product fabrication, such as low setup cost, fast on-demand fabrication speed, easy fabrication process, and easy customization of structural geometries. These advantages of 3D printing are particularly important for the rapid fabrication of high-quality biomedical devices at a relatively low cost, further lowering the product turnaround time and heightening the affordability of biomedical products. Besides, the ability of 3D printing to easily generate any structural geometries based solely on CAD design is especially beneficial for the fabrication of biomedical devices that require customized features. With the overall goal to generate highly detailed structures, VP printing was further selected as the printing technique of focus for the development of resin material throughout this thesis, owing to its high printing accuracy and resolution. However, the photosensitive resin material used for VP printing is often toxic and not suitable for biomedical applications. Hence, it is of great importance to develop a new class of resin materials for biomedical applications. Moving on, elastic material is crucial in the biomedical sector for the fabrication of elastic biomedical products, including biomimetic implants and microfluidic devices. Particularly, biomimetic implants require elasticity to closely mimic the mechanical profile of the human tissue or organ in order to effectively function as a replacement upon implantation into the human body. As for microfluidic devices, elasticity is necessary to enhance the susceptibility of the fluidic channel towards deformation, thereby improving its resistance to high fluid pressure and preventing fluid leakage during fluid processing. In conjunction with that, silicone is a well-established elastomeric material with a long history in the biomedical field due to its excellent flexibility, biocompatibility, and biostability, rendering it a promising candidate material for the development of a VP-printable elastomer-based resin material catering to biomedical applications. Despite that, the conventional silicone material presents several material

characteristics that further hinder its fabrication with VP printing. Specifically, the conventional silicone material commonly solidifies through moisture or thermal curing, which further restricts its fabrication with VP printing as VP printing constructs solids via the photocuring mechanism. Furthermore, the conventional silicone material often has a high pre-gel viscosity, which further impacts the surface quality of the printed structure as a sufficiently low pre-gel viscosity is necessary to ensure the effective replenishment of each printing layer during the printing process for a better-quality print. Moreover, the conventional silicone material is typically hydrophobic in nature, which often requires additional surface treatment post-fabrication for the acquisition of hydrophilic surface properties to suit its application for biomedical use.

With the aforementioned motivation, the overall objective of this project is to develop a new class of hydrophilic silicone-based resin materials with low pre-gel viscosity, high transparency, and rapid photocuring properties for the 3D VP printing of highly detailed constructs for biomedical use. Besides, the material developed will need to possess all the relevant material characteristics required for its functionality according to its respective biomedical applications. In the aspect of fabrication technique, I aim to investigate the feasibility of VP printing in customizing and generating biomedical products with fine features in a one-step printing process, establishing VP printing as an alternative method to conventional manufacturing technologies for the fabrication of silicone-based biomedical products. In the aspect of fabrication material, I aim to resolve the difficulties associated with the VP printing of silicone-based resin material from the perspective of material formulation instead of printer modification as reported by Rodriguez et al.[70] and Wang et al.[65] Specifically, I proceed with the investigation of two different approaches for the formulation of a silicone-based resin material with low pre-gel viscosity and good photocuring properties for excellent VP printability. The first approach involves the use of monomers as reactive diluents to

effectively lower the pre-gel viscosity when incorporated into the silicone polymer material. The second approach employs silicone oligomer with a low molecular weight as the base ingredient for the formulation of the silicone-based resin material. Both the approaches utilize photoreactive monomers and oligomers to encourage material solidification via photocuring for an effective VP printing process. Additionally, I also aim to develop a hydrophilic silicone-based material, catering the printed structure to biomedical applications without the need for additional surface treatment post-fabrication. Indeed, there have been multiple studies investigating the formulation of VP-printable silicone-based resin material. [62–71] However, it is important to note that most of the silicone-based resin materials reported for VP printing are not intended for biomedical applications and are not hydrophilic in nature. In parallel with the main objectives, I aim to optimize both the material formulation and printing parameters of the developed resin material to suit the respective product application of the printed structure, specifically as biomimetic implants and microfluidic devices. Subsequently, I aim to understand and characterize the printability and material behaviour of the developed material upon formulation and printing variation. This includes an extensive investigation of all the relevant material characteristics, including physical, mechanical, chemical, and biological properties. Finally, I aim to evaluate the functionality of the printed structure according to their respective application, providing evidence on the feasibility of the 3D VP-printed devices for biomedical applications.

This thesis consists of five chapters. In **Chapter 1**, I have provided a comprehensive discussion on the different 3D printing technologies along with their respective advantages, disadvantages, and ink material requirement for printing. I have also provided an overview on the types of elastic materials with suitable properties for biomedical applications and their respective potential to be fabricated with VP printing, along with a review on the recent advancement regarding the VP printing of biomimetic implants and fluidic devices.

In **Chapter 2**, I present a strategy to improve the VP printability of silicone polymer material upon the addition of monomers as reactive diluents. This particular formulation is intended for the fabrication of biomimetic implants and is developed according to their respective material requirements. The results demonstrate the effectiveness in mitigating the high pre-gel viscosity and slow photocuring rate of aminosilicone methacryloyl (SilMA) upon the inclusion of acrylamide (AA) and poly(ethylene glycol) dimethacrylate (PEGDMA) as a second interpenetrating polymer network for the VP printing of biomimetic implants with excellent surface quality. This chapter is adapted from the following publication:

Wong, L. Y., *Ganguly, S., & Tang, X. (Shirley), 2024, Design and fabrication of a 3D stereolithography-printable hydrophilic silicone-based elastic composite biomimetic hydrogel. Polymers, 307, 127305. https://doi.org/10.1016/j.polymer.2024.127305; Copyright © 2024 is licensed under CC BY-NC 4.0, Elsevier B.V.*

Despite achieving excellent VP printability, the hydrophilic silicone-based ink material exhibits signs of overcuring, which further hinders its application for the printing of ultra-fine features. In **Chapter 3**, I demonstrate the improvement of printing accuracy and resolution upon the integration of cellulose nanocrystals (CNC) into the hydrophilic silicone-based resin material as developed in the previous chapter. I further adapt the formulation for the VP printing of microfluidic devices. The results reveal the potential of CNC as an additive for its novel use in photocuring depth tuning and the VP printing of highly precise open-channel fluidic devices with the silicone-based ink upon the integration of CNC. This chapter is adapted from the following publication:

Wong, L. Y., *Ganguly, S., & Tang, X. (Shirley), 2024, 3D vat photopolymerization printing of hydrophilic silicone-based microfluidic devices and the effect of cellulose nanocrystals as additives for improved printing accuracy. Additive Manufacturing, 86, 104177.*

https://doi.org/10.1016/j.addma.2024.104177; Copyright © 2024 is licensed under CC BY 4.0, Elsevier B.V.

Yet, the printing of fluidic devices with embedded channels remains challenging due to the relatively high pre-gel viscosity of the hydrophilic silicone-based ink developed with aminosilicone owing to its polymeric nature, and the insufficient photocuring depth adjustment in the Z printing direction with small amount of CNC. In **Chapter 4**, I outline the tuning of amphiphilic siloxane oligomer (silmer) complemented with AA and glycidyl methacrylate (GMA) for the formulation of a new version of hydrophilic silicone-based ink material for the VP printing of embedded-channel fluidic devices. This version of hydrophilic silicone-based ink reveals an even better flowability and photocuring depth control, enabling the printing of embedded-channel fluidic devices upon the optimization of formulation and printing parameters. Moreover, I believe that the unprecedented approach to formulating silicone-based ink material with silmer as the major component has opened up a new avenue for photocurable elastomeric ink materials. This chapter is adapted from the following publication:

Wong, L. Y., *Ganguly, S., & Tang, X. (Shirley), 2025, Hydrophilic silicone-based ink derived from amphiphilic siloxane oligomers for the 3D vat photopolymerization printing of fluidic devices. Additive Manufacturing, 100, 104691. https://doi.org/10.1016/j.addma.2025.104691; Copyright © 2025 is licensed under CC BY-NC 4.0, Elsevier B.V.*

Finally, **Chapter 5** summarizes the research outcome as I progress to develop and optimize the hydrophilic silicone-based ink material for the VP printing of silicone-based biomedical devices, ranging from biomimetic implants to fluidic devices. I will also be discussing on the recommendations for future work regarding the VP printing of silicone-based biomedical devices.

Chapter 2 Development of Hydrophilic Silicone-based ink with Aminosilicone for the 3D Printing of Biomimetic Structures via Vat Photopolymerization

2.1 Introduction

To cope with the strength and flexibility found in most human organs, I envision developing a new class of hydrophilic silicone-based materials for the fabrication of strong and elastic biomimetic implants with VP printing. The development of hydrophilic silicone-based material is an interesting avenue to be explored as most of the silicone-based materials developed for VP printing are not intended for biomedical use and none of the research groups have reported on the development of hydrophilic silicone-based material for VP printing thus far. For this purpose, I will be using aminosilicone for the formulation of the hydrophilic silicone-based material. Aminosilicone is a type of modified silicone polymer with linear chains of aminoethylaminopropyl groups branching out from the main PDMS backbone. The presence of amino groups in aminosilicone further contributes to its distinct hydrophilicity upon curing. As discussed previously, the high viscosity and lack of photocurability remain the two major hurdles for the VP printing of silicone-based ink material. Herein, I adopted the approach to include additional monomers as reactive diluents into the hydrophilic silicone-based ink material as a strategy to lower the overall pre-gel viscosity and to increase the overall availability of photocrosslinking sites for its effective fabrication of biomimetic implants with VP printing.

In parallel to that, I implemented a double-network polymer system upon the incorporation of acrylamide (AA) and poly(ethylene glycol) dimethacrylate (PEGDMA) as reactive diluents, with both the AA and PEGDMA forming a secondary polymer network

interpenetrating the pre-existing aminosilicone methacryloyl (SilMA) polymer network. Both AA[310,311] and PEGDMA[385] are selected due to their well-established characteristics as a hydrogel material with good elastic properties and excellent swelling capacity for the fabrication of biomimetic scaffolds. As illustrated in **Figure 2.1**, the first polymer network was synthesized by grafting the amino groups of the aminosilicone with methacryloyl groups via methacrylation. Subsequently, the AA monomer, PEGDMA crosslinking monomer, and LAP photoinitiator were introduced into the SilMA polymer network and polymerized to form a second polymer network upon UV exposure. This resulted in the formation of the SilMA/AA/PEGDMA IPN network. To the best of my knowledge, the approach to formulating a silicone-based ink material with a dual IPN network of silicone and AA/PEGDMA in a single photocuring step is not widely reported for VP printing. Instead, most of the silicone-based material reported either consists of a single polymer network or a dual IPN network with the formation of the second polymer network requiring a secondary curing process after printing **(Table 1.2)**. It is also important to note that the SilMA/AA/PEGDMA ink material reported here is formulated with water as the medium, which differs significantly from all the silicone-based ink material reported previously in the literature **(Table 1.2)**. The elimination of solvent serves as an effort to improve the biocompatibility of the developed hydrophilic silicone-based ink material for biomedical applications.

In this chapter, I aim to resolve the issues of high viscosity and lack of photocurability with the hydrophilic silicone-based ink material upon the incorporation of AA and PEGDMA for the printing of high-strength elastic biomimetic structures. In conjunction with that, I investigated the impact of incorporating AA and PEGDMA on the pre-gel properties of the silicone-based ink material. Thereafter, the optimal printing parameters and the printing resolution of the silicone-based ink material with VP printing are discussed to showcase the potential to instantaneously fabricate biomimetic structures with high resolution via VP

printing using the hydrophilic silicone-based ink material. Furthermore, the surface properties and biocompatibility of the developed material are examined to assess its potential as a biomimetic material. Finally, in order to showcase the potential of the developed material as a high-strength elastic biomimetic structure, the swelling behaviour and mechanical properties of the hydrophilic silicone-based material are benchmarked against articular cartilage as an example.

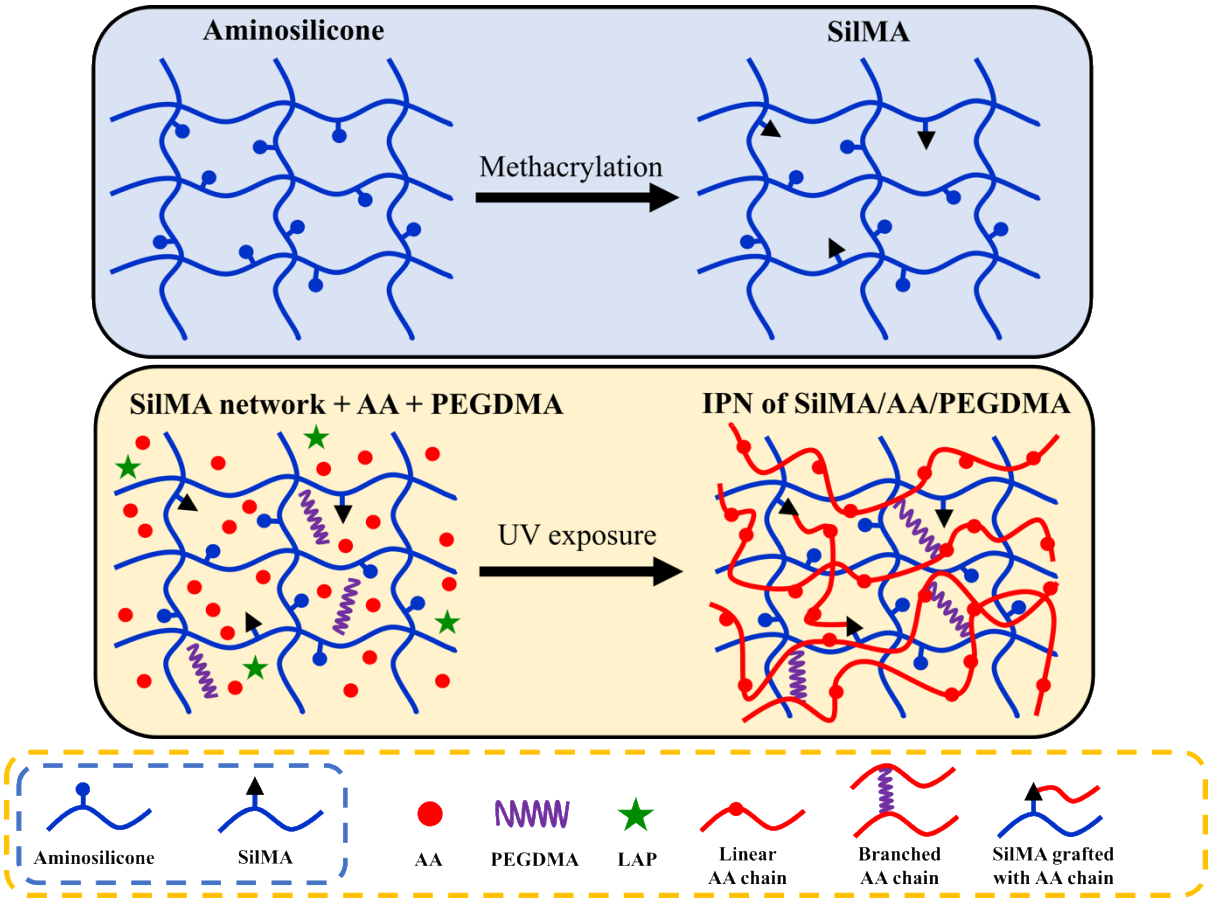


Figure 2.1: The illustration on the formation of SilMA/AA/PEGDMA interpenetrating (IPN) network. The first polymer network consists of SilMA generated via the methacrylation of aminosilicone and the second polymer network consists of linear and branched AA chain formed upon UV exposure.

2.2 Materials and Methods

2.2.1 Materials

Aminosilicone (Silamine D2-EDA) was purchased from Siltech Corporation, Canada. Poly(ethylene glycol) dimethacrylate (PEGDMA, M_w = 400 g/mol) was purchased from Polysciences, Inc., USA. Methacrylic anhydride (MA), acrylamide (AA), lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP), deuterated chloroform ($CDCl_3$), bovine serum albumin (BSA) and 10X phosphate buffered saline (PBS) were purchased from Sigma-Aldrich Canada Ltd., Canada. Sodium chloride (NaCl) was purchased from ACP Chemicals, Canada. Sodium hyaluronate (NaHa, M_w = 66 to 99 kDa) was purchased from Lifecore Biomedical, USA. Trypsin-EDTA (1X) was purchased from Thermo Scientific Chemicals, Canada. Penicillin/streptomycin was purchased from Wisent Inc., Canada. Dulbecco's Modified Eagle's Medium with 4.5 g/L glucose and L-glutamine (DMEM) was purchased from Lonza Inc., USA. Fetal Bovine Serum (FBS) was purchased from Avantor Inc., USA. MTT cell proliferation assay kit was purchased from ATCC Bioproducts, USA. All the chemicals were laboratory-grade and used as received. All the aqueous solutions were prepared using Milli-Q water (18.2 MΩ·cm).

2.2.2 Synthesis of Aminosilicone Methacryloyl (SilMA)

SilMA was prepared by reacting aminosilicone with MA. Initially, the aminosilicone with an active polymer content of 70 % was dispersed in water with a 1.5:1 parts ratio of aminosilicone:water to obtain a pre-gel solution with a concentration of 0.5 g/mL^{-1}. After the dispersion of aminosilicone in water at 65 °C, 5 wt% of MA calculated based on the active polymer content was added while stirring. The reaction mixture was stirred at 65 °C for another 3 hours in the dark with a closed cap for direct substitution to occur between the amino groups presenting on the side chains of aminosilicone and the methacryloyl groups in MA.[386,387]

Particularly, the temperature was carefully controlled as specified and the pH of the reaction mixture was controlled to be within pH 8-9 to ensure effective methacrylation of aminosilicone. The reaction mixture was then left to cool before proceeding with either the characterization of SilMA or the preparation of SilMA/AA/PEGDMA polymer.

2.2.3 Quantifying the Degree of Substitution (DOS) of SilMA

50 mg of SilMA was dissolved in 1 mL of $CDCl_3$ for the characterization and quantification of the DOS of SilMA using proton nuclear magnetic resonance, ^{1}H-NMR (Avance 300 MHz, Bruker, Germany). Aminosilicone was prepared with the same method to serve as a control before polymer modification. The DOS for SilMA was quantified by analysing the peak reduction of aminoethylaminopropyl group before and after polymer modification with the equations as shown below:

$$\sum RA = \frac{RA_{2.77ppm} + RA_{2.76ppm} + RA_{2.66ppm}}{RA_{0.043ppm}} \qquad \text{Equation 2.1}$$

$$\text{DOS } \% = \frac{(\sum RA_0 - \sum RA_a)}{\sum RA_0} \times 100\% \qquad \text{Equation 2.2}$$

where $\sum$RA indicates the sum of relative absorbance of aminoethylaminopropyl group at 2.77, 2.76, and 2.66 ppm (NH_2-C**H$_2$**-C**H$_2$**-NH-C**H$_2$**-CH_2-CH_2-) after being normalized with the relative absorbance of the methyl group of the siloxane backbone at 0.043 ppm (**H$_3$**C-Si-) **(Equation 2.1)** followed by $\sum RA_0$ and $\sum RA_a$ representing the normalized sum of relative absorbance for aminoethylaminopropyl group of aminosilicone (before polymer modification) and SilMA (after polymer modification), respectively, for the calculation of DOS **(Equation 2.2)**.

2.2.4 Preparation of SilMA/AA/PEGDMA Pre-gel Solution

The composite pre-gel solution was prepared by adding AA as additional monomer units into SilMA followed by PEGDMA as crosslinking monomers to form a second crosslinking network in addition to SilMA upon photoinitiation. SilMA was stirred with 0.2- to 0.8-part of AA for about 1 hour or until fully dissolved before dosing in 0.0001 to 0.005-part of PEGDMA. After the dissolution of the pre-gel solution, 0.5 wt% of LAP was added and stirred at room temperature (22 ± 2 °C) for 1 hour in the dark. The dosage of LAP in wt% was calculated based on the total pre-gel solution mass. All the dosage in part mentioned in this section was calculated based on part ratio with respect to 1-part of SilMA. The material characterization of SilMA/AA pre-gel solution was performed by ^{1}H-NMR with the sample preparation method as mentioned in **Section 2.2.3**.

2.2.5 Pre-gel Solution Properties

The optical transmittance of the pre-gel solution between 300 to 750 nm was measured using the UV-vis spectrophotometer (Molecular Devices SpectraMax M2, Marshall Scientific, USA). To begin with, 200 µL of the pre-gel solution was loaded into one of the wells of a 96-well plate before loading the 96-well plate into the UV-vis spectrophotometer for measurement. The shear viscosity of the pre-gel solution was measured for three continuous cycles between the shear rate of 1.000 to 100.0 s^{-1} with 5 sample readings per decade at 25 °C with the rheometer (Kinexus Ultra+, Malvern, United Kingdom) using spindle DG25 L0381 SS. The gel point of the pre-gel solution was determined by measuring the rheological properties of the pre-gel solution cured at different UV exposure times. Several samples with 1 mL of pre-gel solution aliquot were prepared in 20 mL glass vials and exposed to UV light in a UVP crosslinker (Analytik jena, Germany) at 4000 µJ cm^{-2} for 60 seconds. The samples have a thickness of 4 mm. The samples were removed intermittently and the UV exposure time for

the respective samples was recorded. The storage modulus (G′), loss modulus (G″), and tan δ of the samples with different UV exposure time intervals across the 60 seconds of UV curing were measured with a rheometer and graphed to identify the crossover point of storage and loss modulus (G′=G″) as the gel point.[410,411]

2.2.6 Three-dimensional Printing

3D structures were printed with the VP printer (Photon Mono 4K, Anycubic, China). Prior to printing, the 3D structure was designed using FreeCAD and sliced with Photon workshop (Anycubic, China). The pre-gel solution was poured into the vat and the structure was printed on the build plate with a 100 % UV power of 4000 μJ cm^{-2} at 405 nm. The structure was printed with a layer thickness of 0.05 mm at a lift speed of 4 to 6 mm s^{-1} and a retract speed of 6 to 8 mm s^{-1} with 6 bottom layers. The exposure time per layer for the bottom layers varied from 2 to 40 seconds and for the normal layers was varied from 1 to 10 seconds. Once the printing process was finished, the printed structure was removed from the build plate and washed in water at 800 to 900 rpm for 30 seconds to remove any remaining uncured pre-gel solution on the printed structure. Then, the printed structure was post-cured in a UVP crosslinker (Analytik jena, Germany) at 4000 μJ cm^{-2} for 0 to 5 minutes. Finally, the cured composite polymer was characterized with Fourier transform infrared spectroscopy, FTIR (Tensor 27 FTIR, Bruker, Germany).

2.2.7 Printing Resolution

The X, Y, and Z resolutions of the composite polymer were evaluated with the test models developed by Gensler et al., 2020, [388] with a resolution of down to 50 μm for X and Y resolution and down to 20 μm for Z resolution. The printed test models were photographed with a digital microscope (Trinocular Stereo Microscope, Amscope, USA) and measured using

ImageJ. About 40 to 80 intra- and inter-sample measurements were made and reported as an average. The deviation of the printed width for X and Y resolution and the printed height for Z resolution were calculated with the equations below:

$$\text{Deviation}_{\text{X or Y}}\ (\%) = \frac{W_1 - W_0}{W_0} \text{ x } 100\% \qquad \text{Equation 2.3}$$

$$\text{Deviation}_{\text{Z}}\ (\%) = \frac{H_1 - H_0}{H_0} \text{ x } 100\% \qquad \text{Equation 2.4}$$

where W_0 and W_1 denote the width designed in the test model and the actual width printed for X and Y resolution, respectively, while H_0 and H_1 denote the actual height designed in the test models and the actual height printed for Z resolution, respectively.

2.2.8 Swelling Test

The swelling behaviour of the polymer was investigated in water at room temperature (22 ± 2 °C). During swelling, the weight changes of the polymer were recorded at regular time intervals to calculate the swelling degree (SD) with the following equation:

$$\text{SD } \% = \frac{W_t - W_0}{W_0} \text{ x } 100\% \qquad \text{Equation 2.5}$$

where W_0 and W_t represent the weight of the polymer before swelling and after swelling at a predetermined time, respectively. The swelling test was conducted until the polymer reached a state of equilibrium. In order to investigate the swelling behaviour of the polymer in human physiological conditions, the swelling test was further conducted with the same method in water (as control), 0.84 % NaCl solution (mimicry of general body fluid), and a mixture of 30 mg/mL BSA and 3 mg/mL of NaHa in PBS at pH 7.1 to 7.4 (mimicry of synovial fluid), [389,390] respectively, at 37 °C in a water bath (Fisher Scientific Isotemp 105, Fisher Scientific, USA).

2.2.9 Contact Angle

The surface of the swollen polymer was pat dry with paper towels and a 10 μL of water drop was dispensed onto the surface of the swollen polymer followed by photographed with a digital camera. The contact angle was further analysed with ImageJ. A total of 20 readings were recorded from the same sample to rule out any possible errors in measurement using ImageJ. The measurements were repeated with a different sample and the values were reported as an average.

2.2.10 Compression Test

The ultimate compressive strength of the polymer was evaluated using the universal tensile machine (CETR-UMT-2MT Tribological Tester, Bruker, Germany). The polymer sample was compressed at a speed of 0.05 mm s^{-1} with a 1000 N load until the polymer sample fractures and the ultimate compressive strength of the respective polymer sample was recorded. The cyclic compression of the polymer was performed with a different tensile machine (UniVert, CellScale, Canada) at a speed of 0.05 mm s^{-1} with a 10 N load. The polymer sample was compressed up to 15 % of displacement for 10 cycles and the compressive stress for each cycle was recorded.

2.2.11 Rheological Properties

The storage modulus (G′), loss modulus (G″), and phase angle (δ) of the polymer were measured across a frequency sweep from 0.1 to 10 Hz with a constant shear strain at 1.0 % using the rheometer (Kinexus Ultra+, Malvern, United Kingdom). The test was conducted at 25 ºC with 10 sample readings per decade using spindle CP2/20 L0219 SS.

2.2.12 Biocompatibility Test

The biocompatibility test was investigated based on the cell viability of human corneal epithelial (HCEC) cells with the cured polymer samples for up to 6 days and quantified using the MTT test. HCEC cells were selected due to its high sensitivity towards cytotoxic agents . Firstly, the HCEC cells were cultured in DMEM supplemented with 10 % (v/v) of FBS and 1 % (v/v) of penicillin/streptomycin at 37 ºC with 5 % CO_2. Prior to the test, the cured polymer samples were sterilized by soaking in 70 % ethanol for 24 hours followed by soak washing with PBS solution several times to remove any ethanol residue. The cured polymer samples were then cultured with cells in 6 well-plate and the cell viability of the respective samples at predetermined days were quantified using MTT test. The MTT test was conducted based on the manufacturer's protocol with 10 µL of MTT reagent added to 100 µL of cell media and incubated at 37 ºC for 4 hours followed by the addition of 100 µL of detergent solution to 100 µL of cell media and incubate at room temperature for another 2 hours before checking the absorbance of the respective wells at 570 nm using the UV-vis spectrophotometer (Molecular Devices SpectraMax M2, Marshall Scientific, USA).

2.3 Results and Discussion

2.3.1 SilMA/AA/PEGDMA Pre-gel Solution

SilMA was prepared by modifying the aminosilicone polymer with methacrylic anhydride for the grafting of amino groups with the methacryloyl group as shown by **Figure 2.2a**. Additional modification is required for the existing aminosilicone due to the lack of readily available functional groups to form covalent crosslinking upon photoinitiation. As such, the inclusion of methacryloyl group consisting of C=C bond would enable SilMA to form a crosslinked polymer network via covalent crosslinking upon photoinitiation. Upon successful

polymer modification, SilMA was observed to have a reduction in peak signals for the aminoethylaminopropyl group at 2.66, 2.76, and 2.78 ppm (b, c, and d) accompanied by the emergence of new peak signals for methyl protons of the methacrylamide group at 1.93 ppm (a) and acrylic protons of the methacrylamide group at 5.20, 5.29, and 5.71 ppm (e) [387,391–394] in the ^{1}H-NMR spectra as shown in **Figure 2.2b**. Subsequently, the degree of substitution (DOS) for SilMA was calculated based on the reduction in ^{1}H-NMR peak signals for the aminoethylaminopropyl group upon polymer modification.

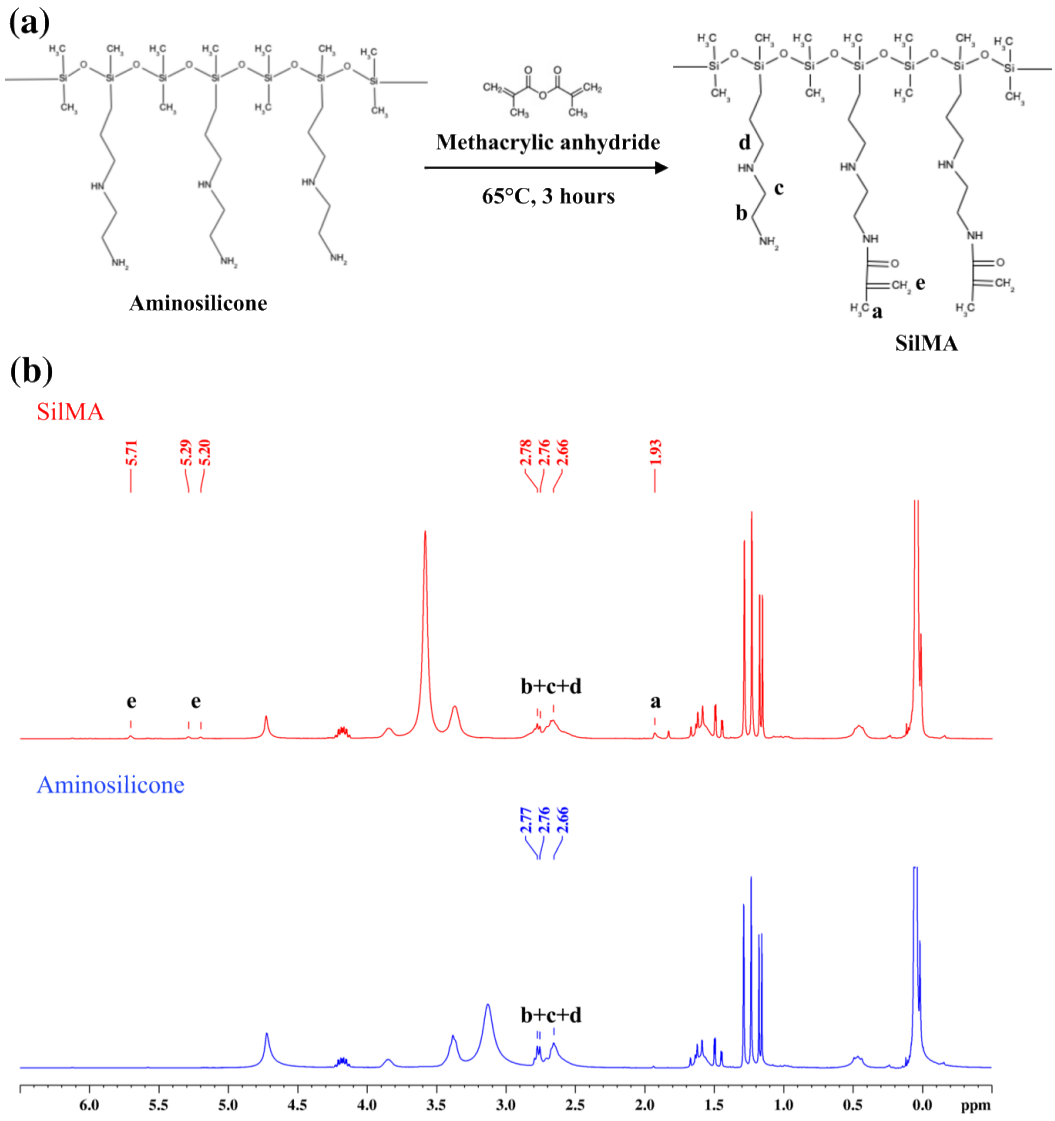


Figure 2.2: The synthesis of SilMA. (a) Schematic diagram on the polymer modification of aminosilicone with methacrylic anhydride. **(b)** ^{1}H-NMR spectra of aminosilicone and SilMA

with [a] at 1.93 ppm representing methyl protons of the methacrylamide group, [b, c, and d] at 2.66, 2.76, and 2.78 ppm representing aminoethylaminopropyl group, and [e] at 5.20, 5.29, and 5.71 ppm representing acrylic protons of the methacrylamide group.

Unfortunately, the DOS for three batches of SilMA was calculated to be an average of 34.8 ± 2.2 %, which is relatively low compared to the complete DOS of 100 % **(**

Table 2.1**)**. Several common parameters that are known to have increased the DOS in gelatin-methacryloyl (GelMA), such as a longer stirring time, an optimum stirring temperature, and the usage of carbonate-bicarbonate (CB) buffer for a buffering capacity at a higher pH,[387,394] were attempted with SilMA but no significant increase in DOS was observed. There is a possibility that the aminoethylaminopropyl group branching out from the siloxane backbone of the aminosilicone remained buried within the polysiloxane chains and is not readily available on the polymer surface for polymer modification. The use of different solvent has been well-known to be able to alter polymer conformation. As such, the use of solvent other than water might be able to resolve the issue of low DOS with SilMA. However, to align with our goal to create a water-based ink for the fabrication of biomimetic structure, I further proceed with water as the reaction medium for this ink formulation.

Table 2.1: The Degree of Substitution (DOS) of SilMA.

Batch	Sample	Aminoethylaminopropyl group				Siloxane backbone	∑RA	DOS (%)
		$RA_{2.77ppm}$	$RA_{2.76ppm}$	$RA_{2.66ppm}$	RA_{sum}	$RA_{0.043ppm}$		
1	RA_0	0.527	0.510	0.609	1.646	12.500	0.132	35.6
	RA_a	0.343	0.286	0.430	1.059	12.500	0.085	
2	RA_0	0.527	0.510	0.609	1.646	12.500	0.132	36.4
	RA_a	0.334	0.287	0.429	1.050	12.500	0.084	
3	RA_0	0.500	0.477	0.575	1.552	12.500	0.124	32.3
	RA_a	0.336	0.285	0.435	1.056	12.500	0.084	
							Average	34.8 ± 2.2

Despite the successful polymer modification, the low availability of grafted methacryloyl groups in SilMA to serve as crosslinking sites and the relatively high viscosity of the SilMA pre-gel solution pose further challenges for SilMA to be printed with VP printing. For the former, an adequate number of crosslinking sites is required for rapid crosslinking to occur upon photoinitiation during the VP printing process. For the latter, VP printing prefers printing material with low viscosity to replenish each printing layer better and to minimize turbulence caused by the movement of the build-plate during the printing process.[85] In conjunction with that, monomers have a comparatively lower viscosity than polymers [395,396] and often serve as a single unit for chemical crosslinking.[310,311] Hence, AA monomers are added as a strategy to lower the overall viscosity of the SilMA pre-gel solution and, at the same time, increase the availability of crosslinking sites for rapid crosslinking to occur within the SilMA pre-gel solution upon photoinitiation. The addition of AA into SilMA was characterized by ^{1}H-NMR as shown in **Figure 2.3c**. The peak signals representing the vinyl protons of AA at 6.23, 6.17, and 5.71 ppm (b, c, and d) [397,398] were observed to increase proportionally with the reduction in peak signal for the methyl group in the siloxane backbone of SilMA at 0.043 ppm (a) as the dosage of AA increases.[391] This verifies that the AA content increases relative to SilMA in the overall polymer system upon the addition of AA. Consequently, the additional vinyl groups contributed by AA would elevate the overall number of available crosslinking sites in the SilMA/AA pre-gel solution. Thereafter, the abundance of crosslinking sites in SilMA/AA pre-gel solution would help facilitates the crosslinking process, and thus, results in a pre-gel solution with rapid crosslinking properties.

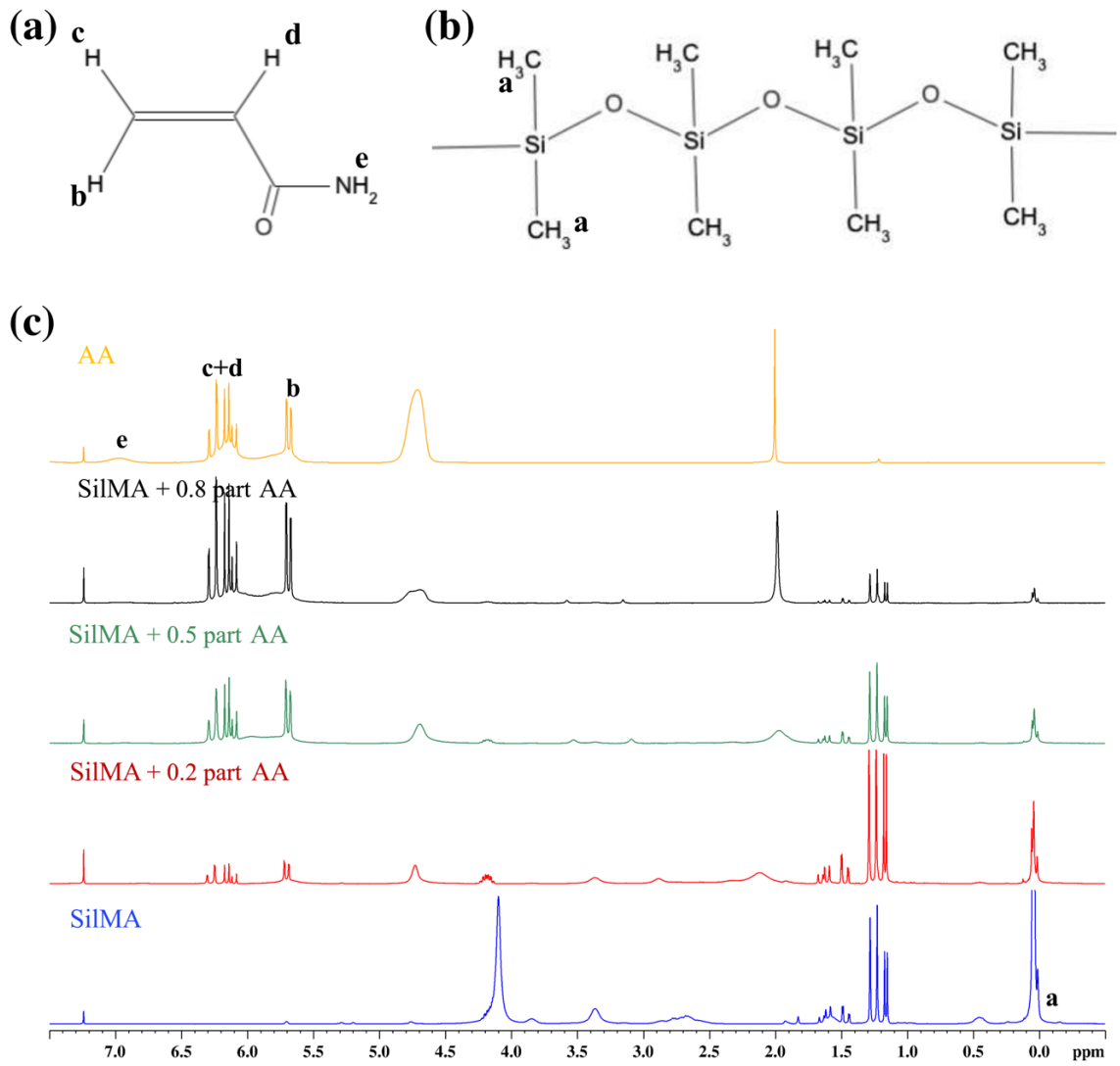


Figure 2.3: The addition of acrylamide monomers into SilMA. The chemical structures of **(a)** acrylamide monomers (AA) and **(b)** siloxane backbone of SilMA. **(c)** ^{1}H-NMR spectra of SilMA with different dosages of AA.

Besides, the addition of AA into SilMA was found to increase the light penetration depth of the pre-gel solution as reflected by the higher percentage of light transmitted through the pre-gel solution. Prior to the addition of AA, SilMA demonstrated a translucent appearance when dispersed in water. This is most probably attributed to the high content of the hydrophobic polysiloxane chain in SilMA. Despite its excellent dispersibility in water due to the presence of amino groups, the hydrophobic polysiloxane chain in SilMA remains insoluble

in water, which results in the translucent appearance of the SilMA pre-gel solution. This is further justified by the slight mismatch in the refractive index (RI) of the polysiloxane chain (RI=1.42)[399] with water (RI=1.33).[400] The non-transparent nature of the SilMA pre-gel solution further hampers its photocurability by limiting the penetration of sufficient light to reach the crosslinking sites within the pre-gel solution for crosslinking to occur upon UV exposure. Based on **Figure 2.4a**, the light transmittance of the pre-gel solution across the UV-visible region ranging from 300 to 700 nm was observed to increase simultaneously with the dosage of AA. Specifically, the transmittance was compared at 405 nm to align with the wavelength of UV light emitted by the VP printer. In parallel with the translucent appearance of SilMA, a low light transmittance of 8.84 ± 0.27 % at 405 nm was recorded for the SilMA pre-gel solution. Upon the addition of 0.2-part of AA to 1-part of SilMA, the light transmitted across the pre-gel solution at 405 nm increases up to 25.95 ± 3.28 %. The light transmittance further rises up to 45.48 ± 3.23 and 59.02 ± 10.10 % upon the addition of 0.5- and 0.8-part of AA, respectively. The gradual increase in light transmittance of the pre-gel solution with increasing AA dosage is likely attributed to the dilution of the SilMA content within the overall pre-gel solution as the dosage of AA increases. This is because AA was revealed to have a refractive index of 1.33,[401] which highly matches that of the water medium. As such, the overall increase in AA with respect to SilMA in the pre-gel solution further narrows the gap of refractive index mismatch in the overall pre-gel solution, and thus, resulting in the improvement in pre-gel transparency. Alternatively, the incorporation of AA might have altered the interaction of the SilMA polymer network with water and resulted in the rearrangement of the SilMA polymer network to expand instead of forming micelles that give off the white translucent appearance when interacting with visible light. There is evidence showing that amphiphilic polymer consisting of both hydrophobic and hydrophilic groups changes in polymer conformation as the solvent changes.[402,403] However, further study is required to verify the alteration of the

polymer conformation of SilMA in the presence of AA. Regardless, the increase in light transmittance of the pre-gel solution upon the incorporation of AA heightens the amount of light penetrating through the pre-gel solution. As a result, this provides more light energy to photoinitiate the crosslinking reaction within the pre-gel solution upon UV exposure, which subsequently results in an ink material with rapid curing properties.

Apart from facilitating rapid crosslinking, the inclusion of AA into SilMA addressed the crucial problem of high viscosity with the SilMA pre-gel solution. Based on **Figure 2.4b**, the shear viscosity of SilMA with the shear rate ranging from 0 to 82 s^{-1} reduces as the dosage of AA increases. The addition of AA was thought to be able to help disrupt the polymer entanglement within SilMA, and thus, contributing to a lower viscosity as the dosage of AA increase. However, the addition of 0.2-part of AA to 1-part of SilMA did not significantly lower the shear viscosity of SilMA. Conversely, the addition of 0.5- and 0.8-part of AA to 1-part of SilMA lowered the shear viscosity of SilMA from 0.88 to 0.41 and 0.19 Pa·s at the shear rate of 82 s^{-1}, respectively. Theoretically, the viscosity of the resin material material is recommended to be less than 5 Pa·s for a stable VP printing process.[85,86] However, based on our findings, both the pre-gel solution of SilMA and SilMA with 0.2-part of AA remain viscous for a stable VP printing process with the need for a slower printing speed to accommodate the poor flowability of the respective ink material. Conversely, both SilMA with 0.5- and 0.8-part of AA demonstrates excellent VP printability, which concludes that an ink material with a viscosity lower than 0.5 Pa·s is preferred for VP printing at regular printing speed, without the need to slow down the printing process to accommodate the poor flowability of viscous ink material. Moreover, both SilMA and SilMA/AA composite pre-gel solution was observed to exhibit the behaviour of non-Newtonian fluid with shear-thinning properties, as reflected by the reduction in shear viscosity with an increase in applied shear rate.[404,405] The shear-thinning properties of the pre-gel solution are attributed to the disentanglement of intermolecular chains

as the polymer chains lose their intra- and interchain interactions, which further align to the flow direction when applied with high shear force at a high shear rate.[405] In contrast, at very low shear rates, the Brownian forces predominate the shear forces and the shear viscosity remains relatively stable as no reformation of macromolecular entanglements occurs. The shear-thinning properties of both the SilMA and SilMA/AA composite pre-gel solutions appear to be beneficial as this indicates that the force exerted by the build-plate on the pre-gel solution during the printing process will not elevate the viscosity of the pre-gel solution. However, there is no obvious trend of shear-thinning observed for SilMA with 0.8-part of AA, which might be due to the differences being too subtle to be distinguished by the rheometer. Regardless, the shear viscosity of both SilMA and SilMA/AA composite pre-gel solutions is reversible as the shear viscosity at an apparent shear rate recovers throughout the three cycles of increasing and decreasing shear rates between 0 and 82 s^{-1}.

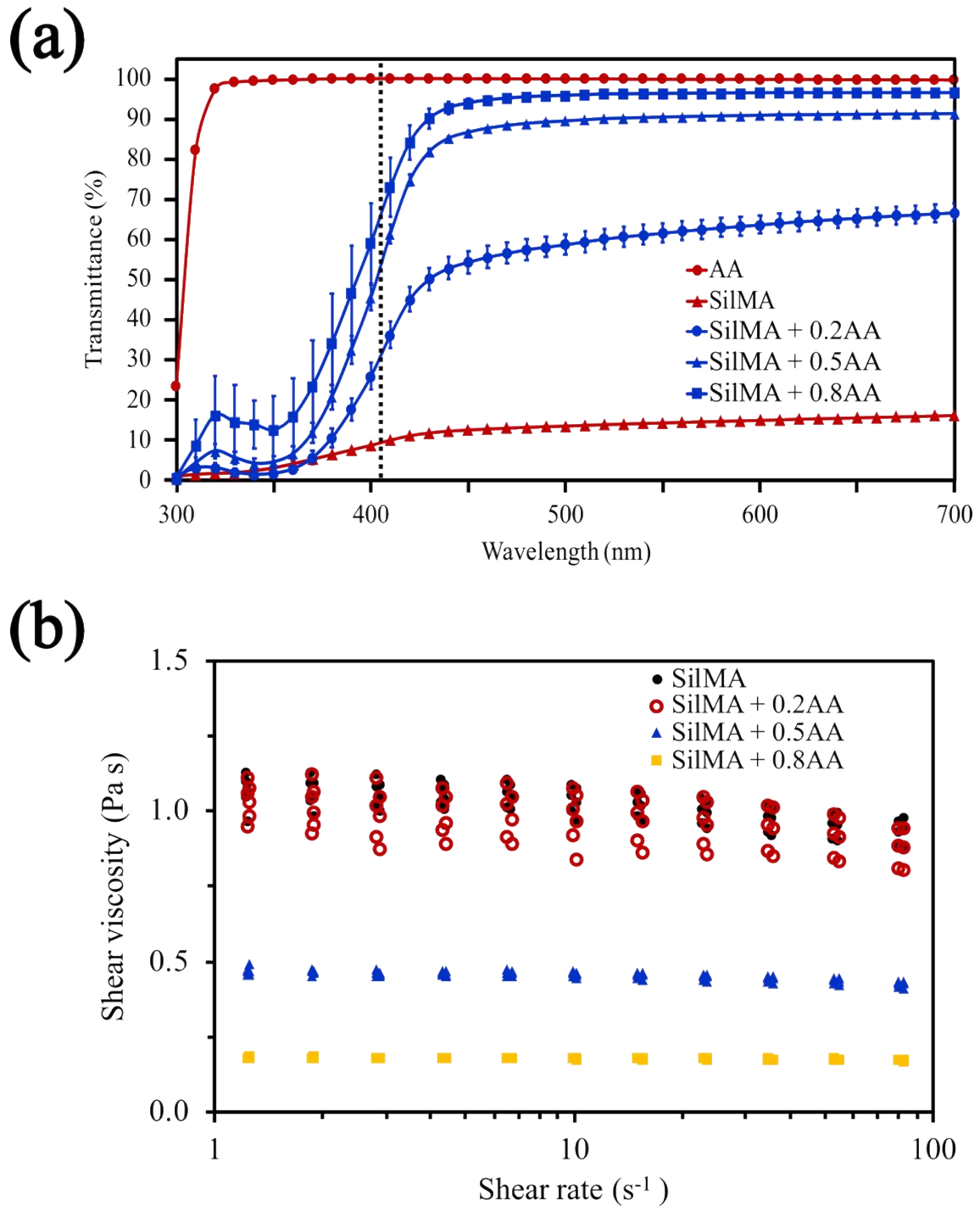


Figure 2.4: The pre-gel solution properties of SilMA with different dosages of AA in part ratio with respect to 1-part of SilMA. (a) The transmittance of the pre-gel solutions in the UV-visible region ranges from 300 to 700 nm with the region at 405 nm marked in dashed line. Error bar represents ± SD, n ≥ 3. **(b)** The shear viscosity of the pre-gel solutions against shear rate for three continuous shear cycles.

In general, the addition of AA to SilMA improves the VP printability of the SilMA pre-gel solution by increasing the number of available crosslinking points for the formation of an IPN network, elevating the light transmittance at 405 nm, and reducing the viscosity of the pre-gel solution. However, the addition of AA itself is insufficient to form an IPN network upon photoinitiation. In the absence of crosslinking monomers, acrylamide monomers tend to form only linear polyacrylamide chains upon polymerization.[406–408] Therefore, crosslinking monomers are required to form branched polyacrylamide in order to achieve the IPN network of SilMA/AA composite polymer upon photoinitiation. In conjunction with the aim to formulate an elastic material, PEGDMA was selected over the other variation of crosslinking monomers due to the presence of the long hydrophilic chain in between the methacrylate groups that can potentially contribute to the elasticity of the SilMA/AA composite polymer. Although the addition of 0.005-part of PEGDMA with respect to 1-part of SilMA slightly deviates the light transmittance at 405 nm **(Figure 2.5a)** and the shear viscosity **(Figure 2.5b)** of the SilMA/AA composite pre-gel solution, the SilMA/AA/PEGDMA pre-gel solution still has a significantly lower shear viscosity and higher light transmittance at 405 nm than the SilMA pre-gel solution.

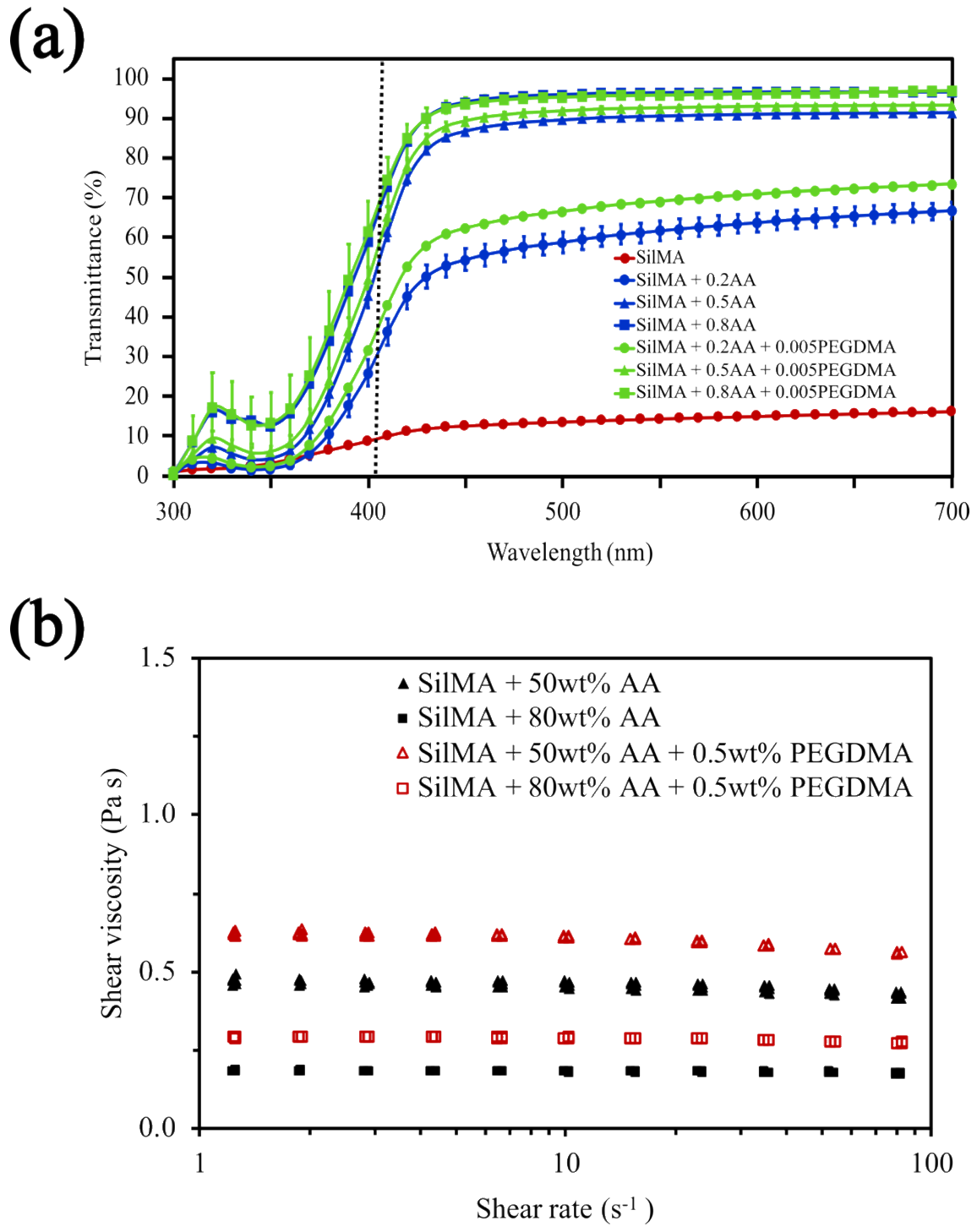


Figure 2.5: The pre-gel solution properties of SilMA with different dosages of AA in part ratio and 0.005-part of PEGDMA with respect to 1-part of SilMA. (a) The transmittance of the pre-gel solutions in the UV-visible region ranges from 300 to 700 nm with the region at 405 nm marked in dashed line. Error bar represents ± SD, n ≥ 3. **(b)** The shear viscosity of the pre-gel solutions against shear rate for three continuous shear cycles.

2.3.2 Three-dimensional Printing of SilMA/AA/PEGDMA

The VP printability of the SilMA/AA/PEGDMA was further evaluated through a preliminary printing of cylindrical structures. To begin with, the UV light exposure time per printing layer for both the bottom and normal layers was optimized to better suit the printability of the SilMA/AA/PEGDMA composite polymer. The bottom layers are the initial printing layers while the normal layers are the remaining printing layers of the 3D structure. In an ideal situation, layers of printing material are cured with a light penetration depth higher than the layer height to allow the attachment of two consecutive layers via gelation and integration.[70,74,409] Thus, the exposure time for the bottom layers is usually longer than the normal layers to ensure that the base of the printed structure is well attached to the build-plate. However, due to the rapid curing properties of the SilMA/AA/PEGDMA pre-gel solution, an exposure time longer than 2 seconds causes excessive light to penetrate beyond the designated layer thickness and forms an overcured ring as shown in **Figure 2.6b** and **2.6c**. Based on **Figure 2.6a**, the 2 seconds of exposure time for the bottom layers did not eliminate the overcured ring with slightly overcured fragments observed at the bottom of the printed structure. However, further attempts in reducing the exposure time to 0.5 and 1 second failed to attach the base of the printed structure to the build-plate. This is in line with the 2 seconds gel point of the SilMA/AA/PEGDMA pre-gel solution as shown by **Figure 2.7**, which indicates that at least 2 seconds of UV exposure is required to form a solid gel. The gel point of the SilMA/AA/PEGDMA pre-gel solution was evaluated with respect to the changes in the rheological behaviour of the pre-gel solution upon UV exposure. Particularly, the gel point of the pre-gel solution was identified as the point where the storage modulus (G′) crossover with the loss modulus (G″) (G′=G″), when the liquid pre-gel solution (G′<G″) solidifies to form a solid cured gel (G′>G″) upon UV exposure.[410,411] As for the normal layers, 2 seconds of exposure time per layer was revealed to create printed structures with smooth surfaces **(Figure**

2.6d). In contrast, layer delamination was observed on the printed structures as the exposure time increased **(Figure 2.6e and 2.6f)**. Hence, 2 seconds of exposure time for both the bottom and normal layers were deemed to be the optimized UV exposure time per printing layer and were applied for all the printed structures in this study for the best results.

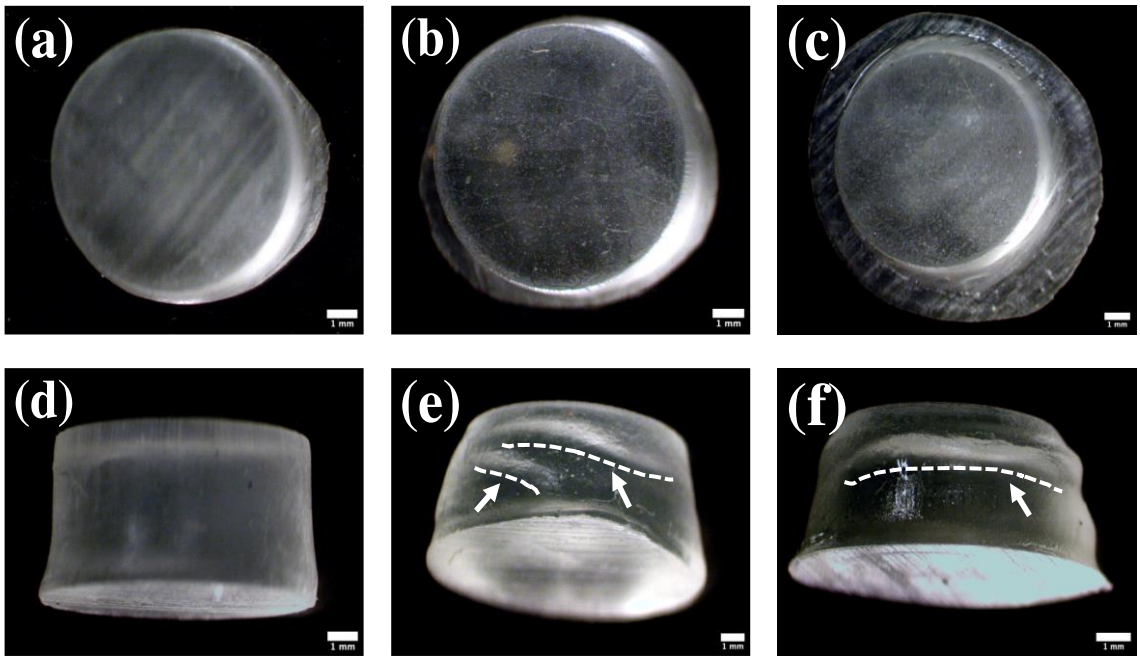


Figure 2.6: The optimization on the printing time per layer for the SilMA/AA/PEGDMA polymer. The microscopic images of the SilMA/AA/PEGDMA polymer with bottom layers printed with **(a)** 2 seconds, **(b)** 5 seconds, and **(c)** 40 seconds followed by the standardization of **(d)** 2 seconds, **(e)** 5 seconds and **(f)** 10 seconds for every printed layer (both bottom and normal layers). The dashed lines directed with arrows indicate the delamination layer observed in (e) and (f). The SilMA/AA/PEGDMA composite polymer consists of 0.8-part of AA and 0.001-part of PEGDMA with respect to 1-part of SilMA. Scale bar: 1mm.

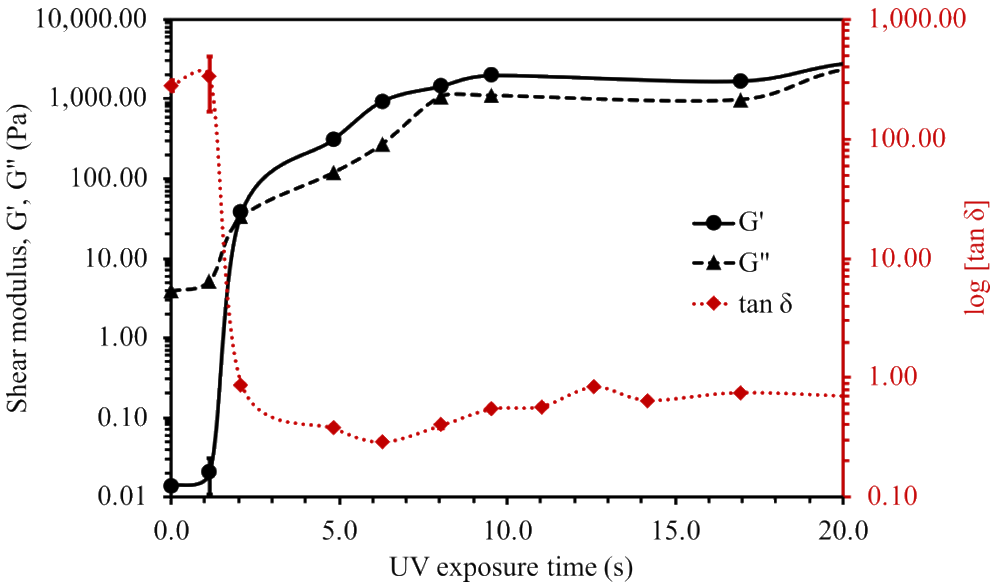


Figure 2.7: The gel point of SilMA/AA/PEGDMA pre-gel solution based on rheological properties. The storage modulus, G′, loss modulus, G″, and tan δ of the SilMA/AA/PEGDMA upon UV exposure for 20 seconds. The SilMA/AA/PEGDMA composite pre-gel solution consists of 0.8-part of AA and 0.001-part of PEGDMA with respect to 1-part of SilMA. Error bar represents ± SD, n ≥ 3.

Following the optimization of printing parameters, the printing resolution of SilMA/AA/PEGDMA composite polymer with VP printing was evaluated with the test models developed by Gensler et al., 2020.[388] The evaluation was carried out on SilMA with 0.8-part of AA and 0.001-part of PEGDMA due to its better printability and flowability as opposed to SilMA with either 0.2- or 0.5-part of AA. Generally, a positive deviation from the true value indicates that the printed structure appears to be thicker than expected while a negative deviation from the true value indicates that the printed structure appears to be thinner than expected.[388] In terms of X and Y resolution, all the dimensions of the test models were printed. However, the printing accuracy reduces with an increasing deviation as the printing dimension decreases **(Figure 2.8a and 2.8b)**. On average, the deviation from true value fluctuates near zero deviation up to 300 µm. Thereafter, the printing dimension deviates up to 7.1 ± 10.8 %

for 200 µm, 8.9 ± 15.0 % for 100 µm, and 13.2 ± 18.4 % for 50 µm for X resolution, and 4.5 ± 6.7 % for 200 µm, 4.2 ± 11.0 % for 100 µm, and 14.6 ± 16.4 % for 50 µm for Y resolution. As for Z resolution, dimensions below 100 µm are hardly distinguishable with deviations up to 6 ± 23 % for 80 µm, -27 ± 17 % for 60 µm, -13 ± 24 % for 40 µm, and the height at 20 µm is not identifiable. The general trend of positive deviation for X and Y resolution aligns with the observation of the slightly overcured printing as shown in **Figure 2.6**. Overall, the SilMA/AA/PEGDMA composite polymer has an X, Y, and Z printing resolution of up to 100 µm with an average positive and negative deviation lesser than 10 % with VP printing.

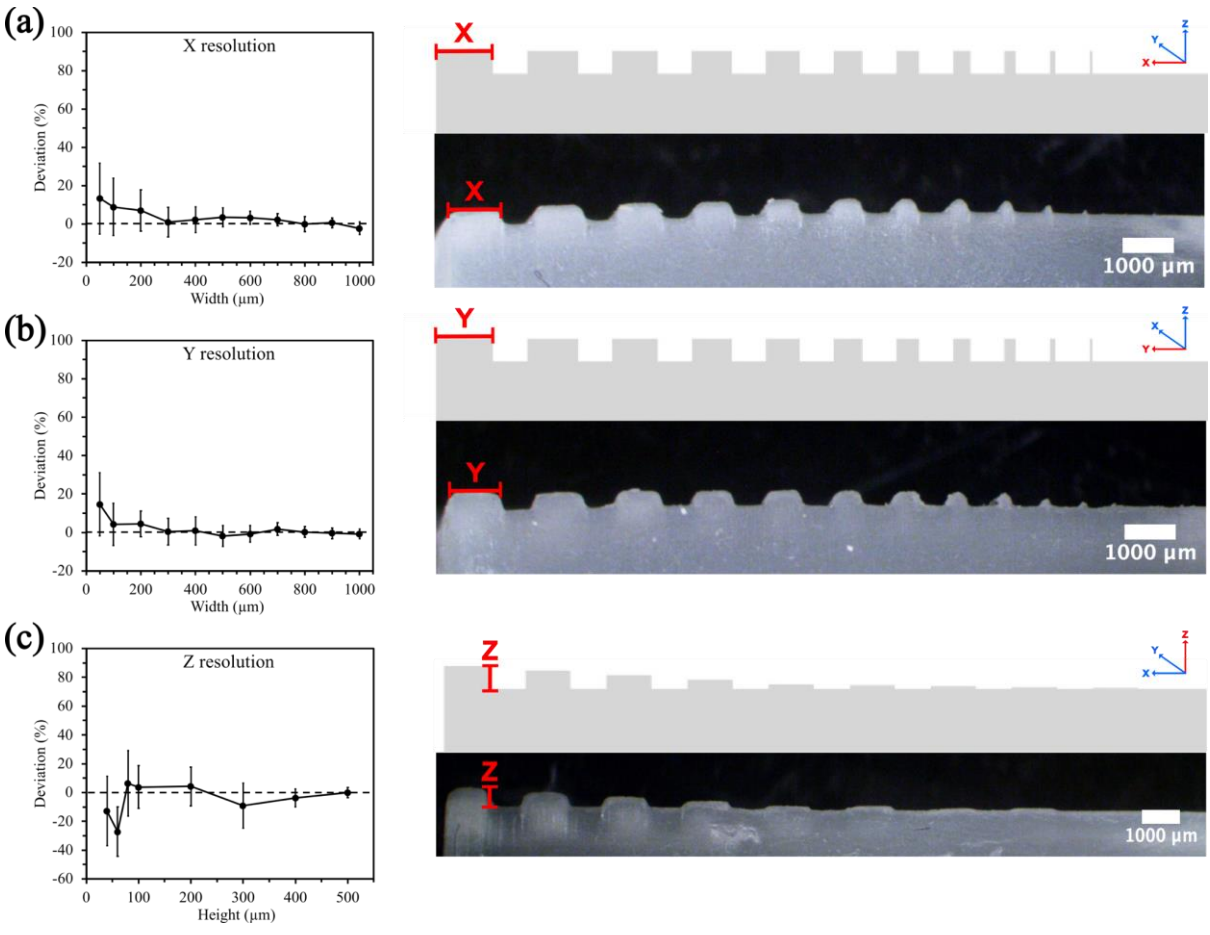


Figure 2.8: The printing resolution of SilMA/AA/PEGDMA polymer. The **(a)** X, **(b)** Y, and **(c)** Z printing resolution of the SilMA/AA/PEGDMA polymer with 0.8-part of AA and 0.001-part of PEGDMA with respect to 1-part of SilMA. Error bar represents ± SD, n ≥ 60.

Each graph is accompanied by the CAD model and the microscope image of the printed structure with the printing orientation indicated on the top right along with a red bar indicating the measurement for X, Y, and Z, respectively. Scale bar: 1000 μm.

Subsequently, examples of high-strength elastic biomimetic structures were printed as a proof-of-concept for the VP printing of biomimetic structures using the developed silicone-based polymer material. The accurate replication of a scaled-down articular cartilage **(Figure 2.9a)** and a human-sized artery **(Figure 2.9b)** from the CAD model further demonstrates the potential to fabricate high-quality biomimetic structures with VP printing. Besides, the elastic nature of the printed material as shown by **Figure 2.9b** further expands the scope of the silicone-based polymer material for the fabrication of elastic biomimetic structures.

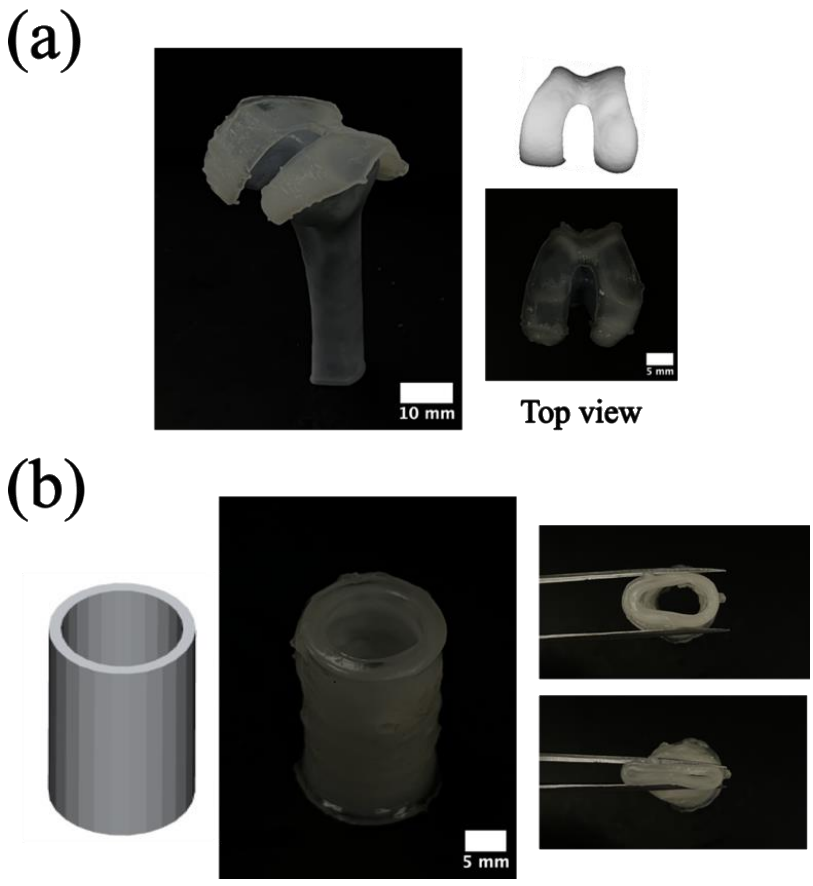


Figure 2.9: The printing of biomimetic structure with the SilMA/AA/PEGDMA polymer. The printed biomimetic structure of **(a)** a scaled-down articular cartilage on a bone model with

the top view shown with the CAD model, and **(b)** a human-sized artery shown with the CAD model complemented with a demonstration of the elasticity of the printed artery. The SilMA/AA/PEGDMA composite polymer consists of 0.8-part of AA and 0.001-part of PEGDMA with respect to 1-part of SilMA.

The SilMA/AA/PEGDMA composite polymer was further characterized with FTIR after printing. Upon the addition of AA into SilMA, peaks at 794, 1014, and 1259 cm^{-1} representing Si-CH_3, Si-O-Si, and Si-CH_3, respectively,[412] were observed to reduce as the peaks at 1405, 1656, and 3336 cm^{-1} representing C-H, C=O, and N-H, respectively,[413] emerged as demonstrated by **Figure 2.10**. The reduction in peaks representing the functional groups of polysiloxane in SilMA confirms that the overall composition of SilMA reduces upon the addition of AA. Furthermore, the emergence of peaks representing the functional groups of AA reaffirms the formation of a double-network polymer upon the addition of AA into SilMA. As for PEGDMA, the dosage added to the overall polymer system is relatively low for the peak representing the COC functional group in PEGDMA to be distinguished from the FTIR spectrum.

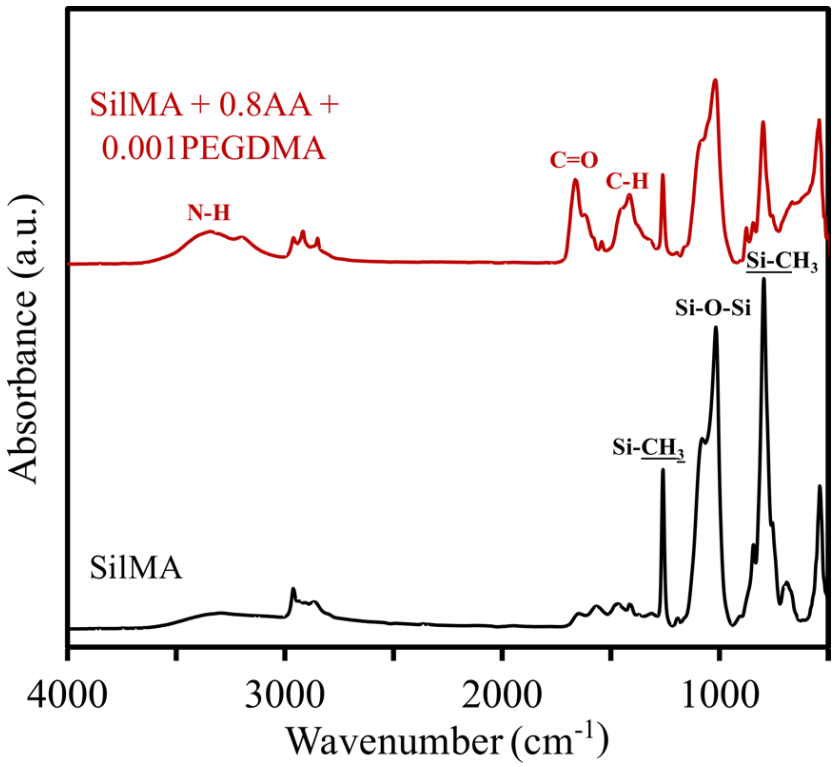


Figure 2.10: The FTIR spectra of SilMA and SilMA/AA/PEGDMA polymer. The SilMA/AA/PEGDMA composite polymer consists of 0.8-part of AA and 0.001-part of PEGDMA with respect to 1-part of SilMA.

2.3.3 Properties of SilMA/AA/PEGDMA Cured Gel

Ideally, biomimetic materials are expected to possess material characteristics resembling that of hydrogels, with a high-water content to better facilitate the transport of nutrients for cell growth and to provide optimum elasticity matching the structure of native tissues for cellular support.[414] Thus, swelling test was conducted to evaluate the swelling capacity of the SilMA/AA/PEGDMA composite polymer. Prior to the swelling test, SilMA was moulded and cured with UV conditions in reference to the VP-printed counterparts due to its inability to be VP-printed as a control because of its low flowability and slow curing speed. Based on **Figure 2.11a**, both SilMA and SilMA/AA/PEGDMA composite polymers were observed to achieve swelling at equilibrium at 16h. Specifically, the composite polymer was

observed to have a faster initial rate of swelling and a higher swelling degree at equilibrium as opposed to SilMA. Despite that, the addition of 0.2-part of AA appears to be insufficient to elevate the swelling capacity with a similar swelling degree at equilibrium obtained at 37.9 ± 1.9 % as compared to that of SilMA at 42.5 ± 1.2 %. Conversely, the addition of 0.8-part of AA increases the swelling degree at equilibrium of the composite polymer up to 104.4 ± 3.2 %. Therefore, a sufficiently high dosage of AA is required to increase the swelling capacity of the composite polymer in order to maintain a high-water content intended for tissue-mimetic structures.

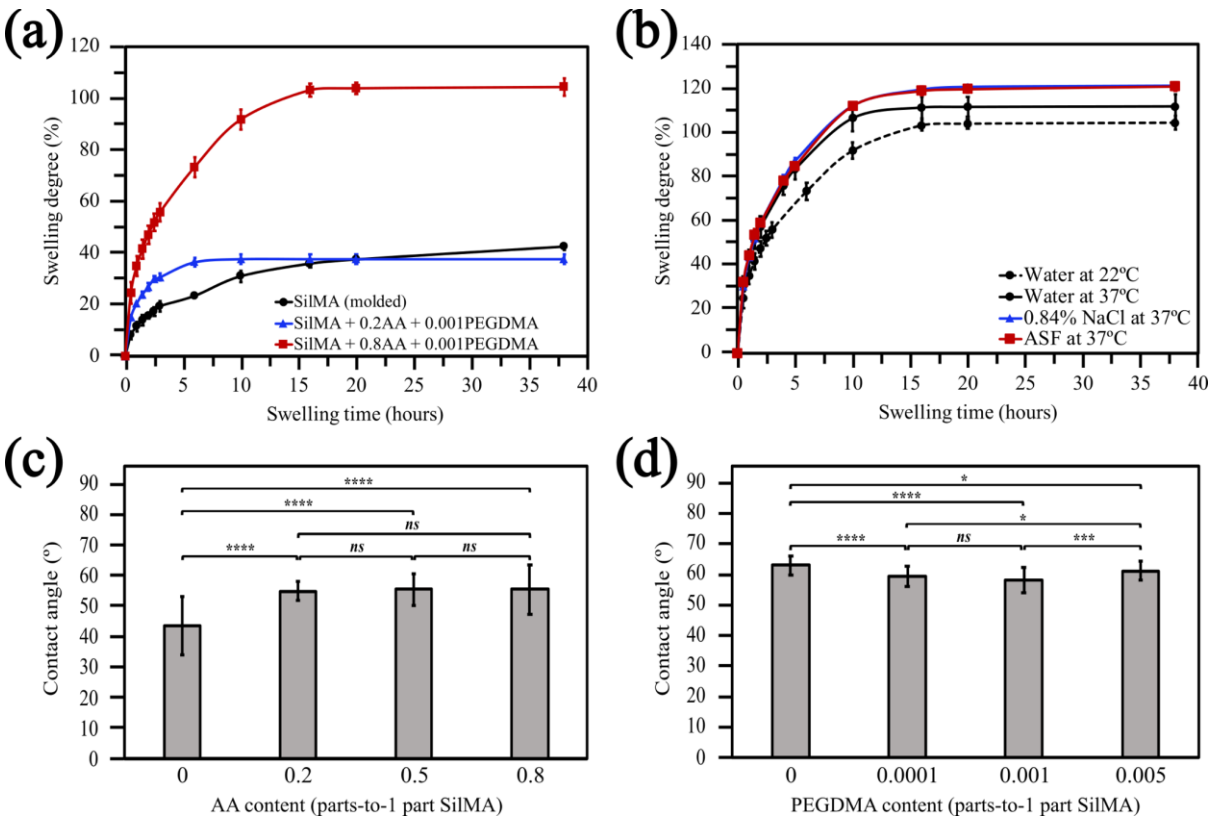


Figure 2.11: The swelling degree and contact angle of the SilMA/AA/PEGDMA. The swelling degree of **(a)** SilMA with different dosages of AA in part ratio and 0.001-part of PEGDMA, and **(b)** SilMA with 0.8-part of AA and 0.001-part of PEGDMA at various tissue-mimetic conditions. Error bar representing ± SD, n ≥ 9. The contact angle of **(c)** SilMA with different dosages of AA in part ratio and 0.001-part of PEGDMA, and **(d)** SilMA with 0.8-part

of AA and different dosages of PEGDMA in part ratio after 96 hours of incubation in water at room temperature. All the AA and PEGDMA components are in part ratio with respect to 1-part of SilMA. The statistical significance of the data was analysed with a two-sided t-test with unequal variances with *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$; ****$p < 0.0001$; *ns*, not significant. Error bar representing ± SD, $n \geq 60$.

The SilMA/AA/PEGDMA composite polymer with 0.8-part of AA was further evaluated in tissue-mimetic conditions to ensure that the swelling behaviour of the composite polymer is replicable in the human body upon insertion or implantation. Based on **Figure 2.11b**, the increase in incubation temperature from room temperature (22 ± 2 ºC) to body temperature (37 ± 2 ºC) elevates the swelling degree at equilibrium of the composite polymer from 104.4 ± 3.2 to 111.7 ± 5.6 %. Upon the substitution of the swelling medium, the swelling degree of the composite polymer at equilibrium for 0.84 % NaCl (mimicry of general body fluid) and artificial synovial fluid, ASF, (mimicry of synovial fluid) further rises up to 121.2 ± 0.4 and 120.9 ± 2.1 %, respectively. In brief, the incubation temperature of 37 ºC and the body-mimicry swelling medium increase the swelling degree by approximately 10 % as each condition applies. However, the slight increment in swelling degree should not be of major concern as the composite polymer retains its capability to hold a high amount of water with a similar swelling behaviour as its counterparts incubated in water at room temperature.

Besides having high water content, hydrophilicity is an equally important feature of tissue-mimetic structure for the promotion of cell attachment and proliferation.[415–417] In fact, the swelling capacity of hydrogels is closely related to the hydrophilicity of hydrogels as the hydrophilic functional groups in the hydrogel are responsible for water absorption.[309] This is in good agreement with the higher swelling degree observed for SilMA upon the addition of AA as the presence of amine groups (-NH_2) in AA is proven to have superior hydrophilicity.[415–

[418] However, **Figure 2.11c** shows that the hydrophilicity of the composite polymer reduces instead with an increase in contact angle from 43.2 ± 9.6º to 54.5 ± 3.1º upon the addition of 0.2-part of AA. This phenomenon might be due to the increase in other functional groups with less hydrophilicity, for instance, the ethyl group (-CH_2), alongside the hydrophilic amine groups upon the addition of AA. Interestingly, further addition of AA has no significant impact on the surface properties of the composite polymer as reflected by the similar contact angle of 54.5 ± 3.1º, 55.0 ± 5.2º, and 55.0 ± 8.2º upon the addition of 0.2-, 0.5- and 0.8-part of AA, accordingly. This is most likely attributed to the similar polymer arrangement of SilMA, AA, and PEGDMA in water, regardless of the dosage of AA. Several studies have demonstrated that polymer tends to expand when being subjected to good solvents with similar polarity to the polymer, owing to their ability to interact with the solvent molecules.[49,50] Conversely, the polymer collapses when being subjected to poor solvent with different polarity to the polymer as the polymer favours the polymer-polymer interaction over the polymer-solvent interaction. Therefore, with water as the medium for the SilMA/AA/PEGDMA composite polymer, the AA/PEGDMA polymer with polar properties would favour the interaction with water, while the SilMA polymer with mainly non-polar properties would repel from water. As a result, the SilMA/AA/PEGDMA composite polymer would probably end up with a final polymer arrangement where the non-polar components are sandwiched by the polar groups as demonstrated by several studies reporting on the effect of solvent on the arrangement of amphiphilic polymers.[402,403] Hence, it is safe to conclude that the further addition of AA would probably not result in a change of surface properties as the further addition of AA does not alter the preferred polymer arrangement of SilMA/AA/PEGDMA with water. On the other hand, the addition of 0.0001-, 0.001-, and 0.005-part of PEGDMA increases the hydrophilicity of the composite polymer with a slight reduction in contact angle from 62.6 ± 3.0º to 59.1 ± 3.4º, 57.8 ± 4.1º, and 60.9 ± 3.1º, respectively, as shown in **Figure 2.11d**. The increase in

hydrophilicity upon the addition of PEGDMA aligns with the expectation as PEGDMA consists of hydrophilic carbonyl groups (-C=O) that can potentially form carboxyl groups ($-COO^-$) upon reaction with water. Despite the variations in hydrophilicity, all the SilMA/AA/PEGDMA composite polymers have a contact angle below 90º, which reaffirms the hydrophilicity of the SilMA/AA/PEGDMA composite polymers to be potentially used as tissue-mimetic structures.

In addition to the swelling capacity and hydrophilicity, biomimetic materials would need to achieve optimum strength and elasticity in order to fully mimic the functionality of a biomimetic structure as most human organs are made up of flexible soft tissues with a variety of elasticity among the different human organs. [361] Based on **Figure 2.12a**, both SilMA and SilMA/AA/PEGDMA composite polymers resemble the properties of viscoelastic solids with a higher storage modulus (G′) than loss modulus (G″) due to the presence of covalent bonds and any other strong physical-chemical interactions that hold the molecules together within the polymer network.[419,420] Furthermore, the storage modulus (G′), also known as the elastic component, of the composite polymer was observed to increase proportionally with the dosage of AA. Besides, based on **Figure 2.12b**, the composite polymers were revealed to become stiffer and more elastic upon the addition of AA as a lower tan δ value was obtained for the SilMA/AA/PEGDMA composite polymers as opposed to SilMA. As the damping factor, tan δ, represents the ratio of G″:G′, the tan δ value approaching zero would indicate that the respective polymer has a lower viscous component as compared to the elastic component.[419,420] As such, it is concluded that the addition of AA would help heighten the elasticity of the SilMA polymer as reflected by the increase in elastic component upon the addition of AA.

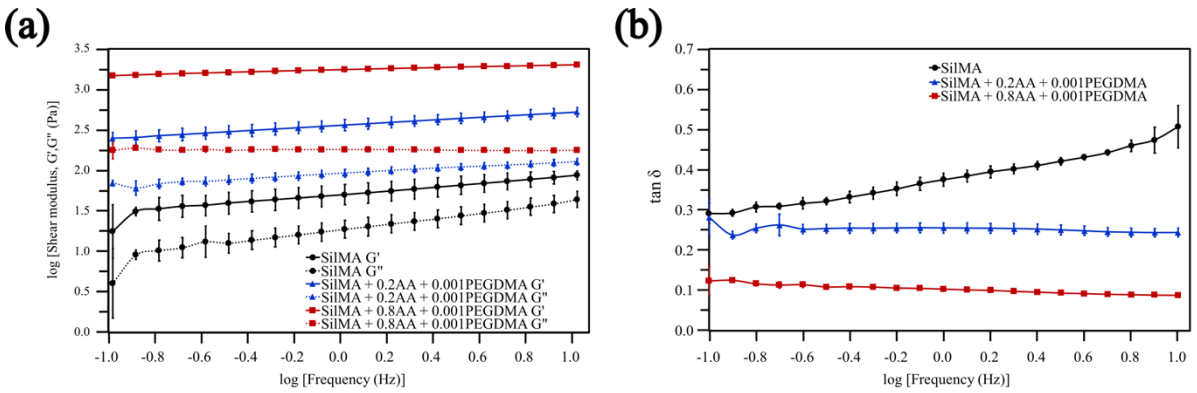


Figure 2.12: The rheological properties of SilMA/AA/PEGDMA composite polymer. The **(a)** storage modulus (G′), loss modulus (G″), and **(b)** tan δ with an increasing frequency sweep from 0.1 to 10Hz. Error bar representing ± SD, n ≥ 3.

With the aim to generate a strong and elastic material for biomimetic structures, the mechanical properties of the developed material were benchmarked against the human knee articular cartilage. In general, the human knee articular cartilage has a compressive modulus of 0.58 ± 0.17 MPa upon full-thickness compression.[421,422] Specifically, the superficial and the deep zone of articular cartilage have a compressive modulus of 0.28 ± 0.16 and 0.73 ± 0.26 MPa, respectively, at a compressive displacement between 10 to 15 %. [421,422] In reference to articular cartilage, both the ultimate compressive and cyclic compressive properties of the composite polymer were evaluated in order to assess its suitability to be used as an alternative material for shock absorption and wear resistance to withstand the compressive forces exerted during the joint movement. Based on **Figure 2.13a**, the modulus of the SilMA/AA/PEGDMA composite polymer was found to increase proportionally with the dosage of AA, which implies that the compressive strength increases with the AA content. Moreover, the different compressive properties of SilMA obtained with different AA content sheds light on the potential for the tuning of mechanical properties by varying the AA content. With the tuneable compressive properties, the composite polymer was found to have a modulus of 0.28 ± 0.04 and 0.72 ± 0.05 MPa at 10% when added with 0.5- and 0.8-part of AA, which closely mimics

the compressive modulus of the superficial and deep zone of articular cartilage, accordingly. Besides, it is important to note that the combination of SilMA and AA polymer has resulted in an exceptional improvement in terms of strength while retaining the elastic properties, as reflected by the significant increase in modulus as demonstrated by the compressive stress-strain curves **(Figure 2.13b)**. The SilMA/AA/PEGDMA was observed to achieve an 80-fold higher in modulus upon the incorporation of 0.8-part of AA as compared to both the SilMA and AA polymer when formulated solely. The high compressive modulus recorded for the composite silicone-based biomimetic material in this study is highly impressive, considering that many conventional hydrogel materials struggle to achieve a combination of high strength and elastic properties without requiring post-processing.[4,357,361]

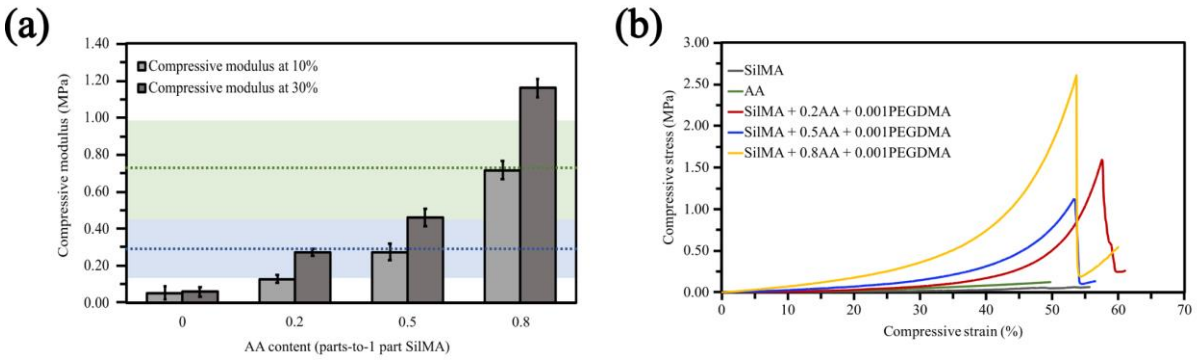


Figure 2.13: The compression properties of SilMA/AA/PEGDMA composite polymer. (a) The compressive modulus at 10 % and 30 % with the modulus at 10 to 15 % for the superficial and deep cartilage highlighted in blue and green, respectively. Error bar representing ± SD, n ≥ 4. **(b)** The compressive stress-strain curve.

On the other hand, the PEGDMA content was found to have minimal effect on the compressive properties of the composite polymer as reflected by the similar compressive modulus with different dosages of PEGDMA, which might be due to the relatively small amount in the overall polymer system **(Figure 2.14a)**. In terms of the effect of curing, the

increase in exposure time per printing layer was found to elevate the compressive modulus of the composite polymer as demonstrated by the increase in compressive modulus with exposure time per printing layer **(Figure 2.14b)**, with the same applies to the increase in post-curing time **(Figure 2.14c)**. However, the compressive modulus of the composite polymer was revealed to remain constant with post-curing time beyond 0.5 minute. This suggests that a maximum of 0.5 minute of post-curing is sufficient to fully strengthen the composite polymer after printing. In general, the overall composition of SilMA and AA was revealed to play a major role in dictating the tuneable compressive properties of the SilMA/AA/PEGDMA composite polymer when being applied with the optimum exposure time of 2 seconds per printing layer.

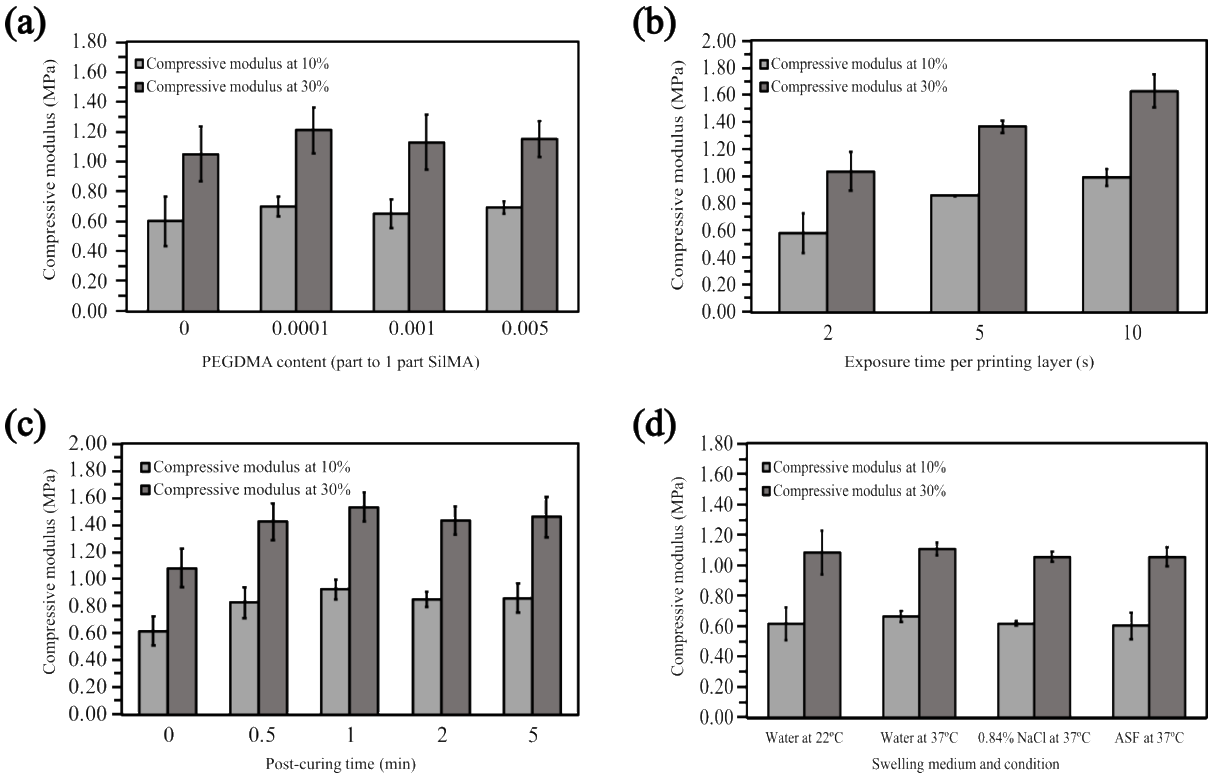


Figure 2.14: The compressive modulus at 10 % and 30 % of the SilMA/AA/PEGDMA polymer when being subjected to various conditions. (a) SilMA with 0.8-part of AA and different dosages of PEGDMA in part ratio. SilMA with 0.08-part of AA and 0.001-part of

PEGDMA when subjected to **(b)** different exposure time per printing layer, **(c)** different post-curing time after being printed with an exposure time of 2 seconds per printing layer, and **(d)** different swelling medium and condition after 96 hours of incubation. Error bars representing ± SD, $n \geq 4$.

In the aspect of durability, the SilMA/AA/PEGDMA composite polymer was revealed to have an excellent durability as reflected by the comparable compressive modulus throughout the 10 continuous compression cycles **(Figure 2.15a)**. The excellent recovery of the composite polymer after withstanding compression at a constant displacement for 10 cycles further exhibits the potential of the composite polymer to be used as articular cartilage substitutes or any elastic biomimetic implants. Additionally, the SilMA/AA/PEGDMA composite polymer demonstrates highly replicable compression properties **(Figure 2.14d)** and durability **(Figure 2.15b)** when being applied with body-mimicry conditions. This provides further evidence on the suitability of the SilMA/AA/PEGDMA composite polymer to be used as body implants.

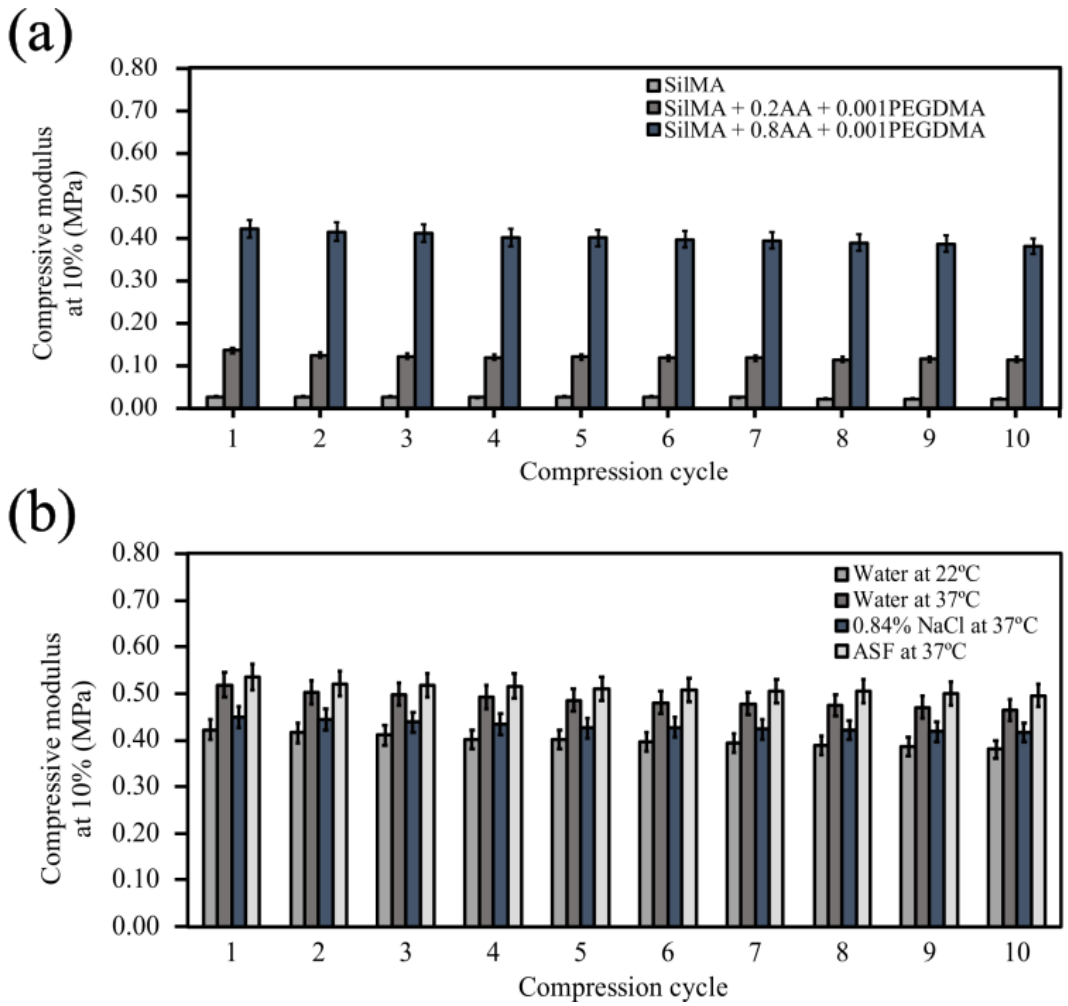


Figure 2.15: The compressive modulus at 10 % of SilMA/AA/PEGDMA composite polymer after 96 hours of swelling for 10 continuous compression cycles. (a) The compression cycle of SilMA with varying dosage of AA in part ratio and 0.001-part of PEGDMA. **(b)** The compression cycle of SilMA with 0.8-part of AA and 0.001-part of PEGDMA when being subjected to body-mimicry conditions.

Aside from the mechanical properties, the composite polymer material needs to demonstrate non-cytotoxic properties to be qualified as medical implants. Generally, the testing specimen would be classified as non-cytotoxic when presented with a cell viability greater than 70 % after at least 24 hours of cell culturing.[423] In this study, the cytotoxic properties of the SilMA/AA/PEGDMA composite polymer were assessed by quantifying the relative cell

viability as opposed to the control group after co-culturing with living cells for up to 6 days. Based on **Figure 2.16**, the composite polymer demonstrates no signs of cell cytotoxicity with good biocompatibility properties as reflected by the comparable cell viability as the control up to Day 6. Henceforth, the SilMA/AA/PEGDMA composite polymer shows great potential for the construction of biomimetic structures with viscoelastic properties, tuneable mechanical properties, and excellent durability that can be highly replicable in biomimetic conditions.

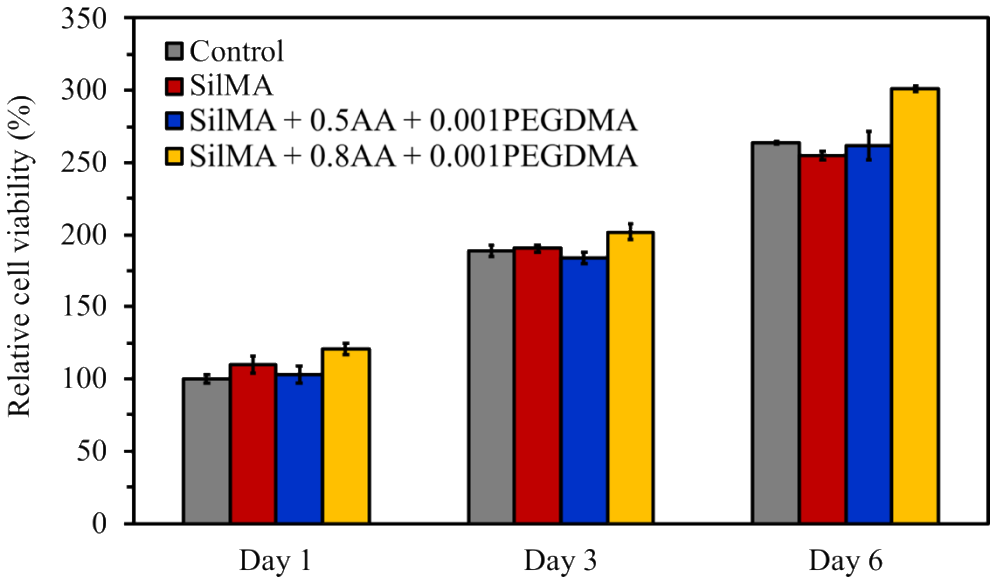


Figure 2.16: The biocompatibility properties of the SilMA/AA/PEGDMA composite polymer. The relative cell viability of the composite polymers for Day 1, 3, and 6. All the AA and PEGDMA components are in part ratio with respect to 1-part of SilMA. Error bar representing ± SD, n ≥ 5.

2.4 Conclusion

In summary, I have successfully demonstrated a novel approach to formulate an VP-printable silicone-based composite polymer material by incorporating AA and PEGDMA into SilMA to form an IPN network, departing from the conventional reliance on the typical composition of functionalized PDMS oligomers. The incorporation of AA and PEGDMA into

SilMA has successfully resolved the issue of high pre-gel viscosity and slow curing rate of SilMA for VP printing. Upon formulation optimization, the SilMA/AA/PEGDMA pre-gel solution was revealed to have excellent VP printability with fast printing speed, as indicated by the 2 seconds gel point of the formulated material. Besides, I revealed the capability to generate high-quality 3D structures with a printing resolution of X, Y, and Z down to 100 μm using the formulated material. In addition to the excellent VP printability, the SilMA/AA/PEGDMA polymer represents a new class of silicone-based biomimetic materials for the construction of biomimetic implants. Differing from the conventional silicone material, the SilMA/AA/PEGMDA composite polymer exhibits a hydrophilic nature with good swelling capacity in water. Furthermore, the SilMA/AA/PEGDMA composite polymer was revealed to have a comparatively high strength and elasticity as opposed to regular hydrogel material, which further aids in the expansion of scope on application for elastic biomimetic structures requiring high strength. Additionally, the tuneable mechanical properties of the SilMA/AA/PEGDMA composite polymer with the AA content allow for better catering toward the functionality of the biomimetic structure. For instance, I demonstrated the possibility of closely mimicking the compressive modulus of the superficial and deep zones of articular cartilage at 0.28 ± 0.04 and 0.72 ± 0.05 MPa with the silicone-based composite polymer consisting of 0.5- and 0.8-part of AA with respect to 1-part of SilMA, respectively. In conjunction with that, the developed composite polymer exhibits excellent shape recovery properties and good biocompatibility. Overall, the SilMA/AA/PEGDMA composite polymer shows great potential as a new class of biomimetic materials integrating strength and elasticity imparted by the silicone component in the composite polymer material for the fabrication of high-strength elastic biomimetic structures. Moreover, the ability to generate 3D structures with VP printing opens up a new avenue for the fabrication of elastic biomimetic structures using the developed material.

Chapter 3 Improving the Printing Accuracy and Resolution of the Hydrophilic Silicone-based Ink with Cellulose Nanocrystal for the 3D Printing of Open-channel Fluidic Devices via Vat Photopolymerization

3.1 Introduction

To adapt the hydrophilic silicone-based material for the fabrication of microfluidic devices, further photocuring depth tuning is required to improve the material's printing accuracy and resolution for the generation of highly accurate microfluidic components. Despite the successful VP printing with the hydrophilic silicone-based material developed in the previous chapter, the developed material was observed to experience a slightly compromised printing accuracy and resolution due to overcuring. Overcuring, or excessive curing, is a phenomenon mostly caused by the high transparency of the pre-gel solution, which allows an excessive amount of light to penetrate through the defined layer thickness and results in the curing of additional areas that were intended to remain uncured. The overcuring of a highly transparent pre-gel solution is not uncommon and several studies have attempted to circumvent the problem by incorporating colouring dye into the pre-gel solution as a photoabsorber to limit the amount of light penetrating through the designated layer.[74,271,409,424–428] While the use of colouring dyes has been effective in addressing the problem of overcuring in light-based printing, it is important to note that the inclusion of these dyes can permanently alter the colour of the printed structure. This is not desirable for the fabrication of microfluidic devices as microfluidic devices often prefer a clear and colourless interface to accurately quantify the biological, chemical, and mechanical interaction via the visualization of the fluid phenomenon.[429] Thus, an alternative photoabsorber with minimal impact on the final colour of the pre-gel solution is required to maximize the effectiveness of the fluid flow visualization in the final printed microfluidic device.

In parallel with that, cellulose nanocrystal (CNC) appears to be a promising alternative additive to function as a photoscatterer for the silicone-based composite pre-gel solution. Typically, CNC is incorporated as a nano-sized bio-filler to reinforce the mechanical properties of composite polymer materials due to its high specific strength and high aspect ratio.[430–435] Despite being uncommon, there is evidence showing that CNC confers light-scattering properties and can potentially be incorporated into composite polymer material for photocuring depth tuning.[436] For instance, Yadav et al.[436] reported on the incorporation of CNC into chitosan for the development of biodegradable food packaging film with UV barrier properties. Besides light scattering properties, the hydrophilicity of CNC further elevates its choice as the incorporating nanofiller due to its enhanced filler-matrix miscibility with the hydrophilic silicone-based composite pre-gel solution.[430,431,433,436] Additionally, the integration of CNC results in a more uniform appearance compared to colouring dyes, which is in line with the objective of creating microfluidic devices using the pre-gel solution. As such, CNC exhibits great potential to be incorporated into the formulated pre-gel solution as a photoscatterer for the fabrication of microfluidic devices with its light scattering properties, hydrophilicity, and final neutral colour.

Several studies have attempted to demonstrate the potential of fabricating silicone-based microfluidic devices with VP printing. However, most of the studies reported on the use of colouring dyes as photoabsorber for improved printing accuracy without considering the staining of the final printed device as a significant drawback. For instance, Gonzalez et al.[271] demonstrated the printing of silicone-based microfluidic devices with a dark red interface upon the incorporation of red dye (DR1-MA) as photoabsorber. In addition to that, Gonzalez et al. revealed that the silicone ink material failed to generate microchannels with dimensions below 400μm despite the incorporation of red dye. This provides further evidence that the incorporation of colouring dyes does not fully eliminate the overcuring issue and further

measurements, particularly the printing parameters, need to be taken into account to precisely elevate the printing accuracy of the ink material. Conversely, Bhattacharjee et al.[437] recognize the staining of ink material with colouring dye as a drawback for microfluidics application and incorporated isopropyl-thioxanthone (ITX) as photosensitizer instead to regulate the photocuring depth of the silicone ink material without staining the ink material. Despite the successful printing of silicone-based microfluidics devices with clear interfaces, it is important to note that the silicone-based ink materials outlined in most of the studies are solvent-based and hydrophobic in nature **(Table 1.2)**. This differs significantly from the silicone-based material documented in this chapter, which is formulated as a water-based ink and exhibits hydrophilic properties upon curing. Moreover, many studies conducted thus far have primarily focused on demonstrating the feasibility of fabricating silicone-based microfluidic devices with VP printing, with a limited exploration of the functionality of these printed devices in fluid processing when being subjected to different conditions.

In this chapter, I further adapt the hydrophilic silicone-ink material for the fabrication of highly customized microfluidic devices via VP printing. Besides, I explore the novel use of CNC for photocuring depth tuning as a strategy to improve the printing accuracy and resolution of the hydrophilic-silicone ink without colour-staining the ink. Subsequently, the printing accuracy of the smallest possible channel dimension is used to evaluate the printing resolution of the pre-gel solution after CNC integration. Furthermore, I investigated the potential for on-demand manufacturing of microfluidic devices by showcasing the feasibility of fabricating typical designs of microfluidic device models with VP printing. Thereafter, the printed microfluidic devices are tested for fluid leakage under various solvent, temperature, and flow pressure conditions using static and dynamic flow measurements. Additionally, the chemical and biological properties of the developed material are explored to understand the compatibility

of the microfluidic device with different solvents and with living cells to potentially widen the scope of application of the VP-printed microfluidic device in the chemical and biological field.

3.2 Materials and Methods

3.2.1 Materials

Aminosilicone (Silamine D2-EDA) was purchased from Siltech Corporation, Canada. Poly(ethylene glycol) dimethacrylate (PEGDMA, M_w = 400 g/mol) was purchased from Polysciences, Inc., USA. Methacrylic anhydride (MA), acrylamide (AA), lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP), sodium hydroxide, 10X phosphate-buffered saline (PBS), chloroform, acetone, acetonitrile, N-N-dimethylformamide (DMF), hydrochloric acid, sulfuric acid, methanol, hexane, toluene, methylene chloride, and diethyl ether were purchased from Sigma-Aldrich Canada Ltd., Canada. Cellulose nanocrystal (CNC) was purchased from CelluForce Inc., Canada. Sodium chloride was purchased from ACP Chemicals, Canada. Cyclohexane, tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) were purchased from Caledon Laboratories Ltd., Canada. Sylgard 184 silicone elastomer kit was purchased from Dow Silicones Corporation, United States. Ethanol was purchased from Greenfield Global Inc., Canada. Ammonium hydroxide, 0.05 % Trypsin-EDTA (1X) was purchased from Thermo Scientific Chemicals, Canada. Isopropyl alcohol (IPA) and penicillin/streptomycin were purchased from Wisent Inc., Canada. Dulbecco's Modified Eagle's Medium with 4.5 g/L glucose and L-glutamine (DMEM) was purchased from Lonza Inc., USA. Fetal Bovine Serum (FBS) was purchased from Avantor Inc., USA. The 3-[4,5-dimethylthiazol-2-yl]-2,5 diphenyl tetrazolium bromide (MTT) cell proliferation assay kit was purchased from ATCC Bioproducts, USA. All the chemicals were laboratory-grade and used as received. All the aqueous solutions were prepared using Milli-Q water (18.2 MΩ·cm).

3.2.2 Preparation of SilMA/AA/PEGDMA/CNC Pre-gel Solution

Firstly, SilMA was prepared by reacting aminosilicone with MA followed by blending with AA monomer and PEGDMA crosslinking monomer. In brief, the aminosilicone was dispersed in water with a 1.5 to 1 ratio at 65 ºC followed by the addition of 5 wt% of MA. The polymer dispersion was stirred at 65 ºC for another 3 hours in the dark with a closed cap and left to cool once the reaction was complete. After that, 0.5-part ratio of AA and 0.002-part ratio of PEGDMA with respect to 1-part of SilMA were added into the pre-gel solution and stirred at room temperature (22 ± 2 °C) until complete dissolution. At this stage, CNC with different dosages ranging from 0 to 10 wt% can be added followed by stirring until the CNC has been homogeneously dispersed in the pre-gel solution. After that, 0.5 wt% of LAP was added and stirred at room temperature for 1 hour in the dark before proceeding with printing. All the dosage in wt% mentioned in this section was calculated based on the total pre-gel solution mass.

3.2.3 Pre-gel Solution Properties

The optical transmittance of the pre-gel solution between 300 to 500 nm was measured with a sample loading of 200 µL in the wells of 96 well-plate using the UV-vis spectrophotometer (Molecular Devices SpectraMax M2, Marshall Scientific, USA). The shear viscosity of the pre-gel solution was measured with an increasing shear rate from 0.10 to 100 s^{-1} consisting of 10 samples per decade at 25 °C with the rheometer (Kinexus Ultra+, Malvern, United Kingdom) using spindle DG25 L0381 SS. The gel point of the pre-gel solution was determined by measuring the rheological properties of the pre-gel solution cured at different UV exposure times. Several samples with 1 mL of pre-gel solution aliquot were prepared in 20 mL glass vials and exposed to UV light in a UVP crosslinker (Analytik jena, Germany) at 4000 µJ cm^{-2} for 60 seconds. The samples have a thickness of 4 mm. The samples were removed

intermittently and the UV exposure time for the respective samples was recorded. The storage modulus (G′), loss modulus (G″), and tan δ of the samples with different UV exposure time intervals across the 60 seconds of UV curing were measured with a rheometer and graphed to identify the crossover point of storage and loss modulus (G′=G″) as the gel point.[410,411]

3.2.4 Three-dimensional Printing

3D structures were printed using the VP printer (Photon Mono 4K, Anycubic, China). Before printing, the 3D models were designed using FreeCAD and sliced with Photon workshop (Anycubic, China). Then, the pre-gel solution was poured into the vat and the respective structure was printed on the build plate with a 100 % UV power of 4000 μJ cm^{-2} at 405 nm with the printing parameters as detailed in **Table 3.1**. After printing, the printed structure was removed and washed in water at 800 to 900 rpm for 30 seconds. Finally, the wet printed structure was air-dried in the open air.

Table 3.1: The 3D VP printing parameters and settings for all the printed structures.

Parameters	Settings
Layer thickness (mm)	0.05
Exposure time (s)	3.0
Off time (s)	5.0
Z Lift height [0] (mm)	2.5
Z Lift speed [0] (mm/s)	8.0
Z Retract speed [0] (mm/s)	10.0
Z Lift height [1] (mm)	4.5
Z Lift speed [1] (mm/s)	12.0
Z Retract speed [1] (mm/s)	15.0

**[0] = initial lift distance; [1] = subsequent lift distance after the initial lift distance*

3.2.5 Printing Resolution

The printing resolution of the channel width and height of the microchannel were evaluated in reference to the test models developed by Gensler et al., 2020 [388] with appropriate modifications to fit the purpose of printing microchannels. For channel width, the test model

was designed to have a gradual reduction in channel width from 1000 to 50 μm with a constant channel height of 1000 μm. For channel height, the test model was designed to have a gradual reduction in channel height from 1000 to 50 μm with a constant channel width of 1000 μm. The printed test models were photographed with a digital microscope (Trinocular Stereo Microscope, Amscope, USA) and measured using ImageJ. The deviation of the printed channel width and channel height were calculated with the equations below:

$$\text{Deviation (\%)} = \frac{X_1 - X_0}{X_0} \text{ x } 100\% \qquad \text{Equation 3.1}$$

where X_0 and X_1 denote the designed dimension and the actual printed dimension, respectively.

3.2.6 Fabrication of Microfluidic Devices

The 3D microfluidic device parts with open microchannel patterns on the structural surface were printed and processed with the 3D printing procedure as mentioned in **Section 3.2.4**. The printed microfluidic device part was then bonded to a glass slide with a biomedical grade pressure-sensitive double adhesive tape and left at room temperature (22 ± 2 °C) for at least 1 hour for secure bonding. After that, Tygon tubing is attached to the inlet and outlet of the microfluidic device using cyanoacrylate glue (Krazy Glue).

3.2.7 Preparation of PDMS

PDMS was prepared using Sylgard 184 silicone elastomer as a control material for the fabrication of microfluidic devices. Sylgard 184 was prepared following the instructions with a 10 to 1 mix ratio of base to curing agent by weight. The mixture was then poured into moulds and left to cure at room temperature (22 ± 2 °C) for 72 hours.

3.2.8 Contact Angle

A 10 μL water drop was dispensed onto the surface of the cured gel sample and photographed with a digital camera. Then, the contact angle was analyzed using ImageJ. A total of 20 readings were recorded from the same sample to eliminate any inaccuracy due to measurements using ImageJ. The measurements were repeated on different samples as replicates and the measurements were reported as an average.

3.2.9 Chemical Compatibility Test

The chemical compatibility of the cured gel samples with different solvents was evaluated in terms of their swelling degree when fully immersed in the respective solvent at room temperature (22 ± 2 °C) for 24 hours. The swelling degree (SD) was calculated with the following equation:

$$\text{SD } \% = \frac{W_t - W_0}{W_0} \text{ x } 100\% \qquad \text{Equation 3.2}$$

where W_0 and W_t represent the weight of the cured polymer before and after swelling, respectively.

3.2.10 Biocompatibility Test

The biological compatibility test was investigated based on the cell viability of the HCEC cells with the cured gel samples for up to 6 days and quantified using the MTT test. Firstly, the HCEC cells were cultured in DMEM supplemented with 10 % (v/v) of FBS and 1 % (v/v) of penicillin/streptomycin at 37 ºC with 5 % CO_2. Prior to the test, the cured gel samples were soaked in 70 % ethanol for 24 hours followed by soaking and washing with PBS solution for several days. The cured gel samples were cultured with cells using 6 well-plates. Subsequently, the cell viability of the respective samples at predetermined days was quantified

using the MTT test based on the manufacturer's protocol. Briefly, 100 µL of cell media was added with 10 µL of MTT reagent and incubated at 37 ºC for 4 hours followed by the addition of 100 µL of detergent solution and incubated at room temperature for 2 hours. Finally, the incubated cell media was transferred to a 96 well-plate for absorbance measurement at 570 nm using the UV-vis spectrophotometer (Molecular Devices SpectraMax M2, Marshall Scientific, USA).

3.3 Results and Discussion

3.3.1 Incorporation of CNC into the Pre-gel Solution

CNC was incorporated into the silicone-based composite pre-gel solution in an attempt to resolve the overcuring issue with the highly transparent pre-gel solution by reducing the light penetration depth for better printing accuracy and resolution. Specifically, the UV light emitted by the VP printer used in this work has a wavelength of 405 nm. Hence, the choice of additives used for photocuring depth tuning needs to confer suitable absorption properties at 405 nm to effectively reduce the light penetration depth of the pre-gel solution at a wavelength best complemented to that of the VP printer. Based on the initial evaluation, CNC was found to exhibit a wide range of absorbance from 300 to 700 nm **(Figure 3.1a).** Evidently, the light transmittance of the pre-gel solution at 405 nm was observed to reduce proportionally with the increasing CNC content from 1 to 10 wt% **(Figure 3.1b)**. The percentage of light scattered by CNC was further quantified by translating the difference between the light transmittance at 405 nm of the respective pre-gel solutions measured in **Figure 3.1b** to ratio in percentage for comparison.

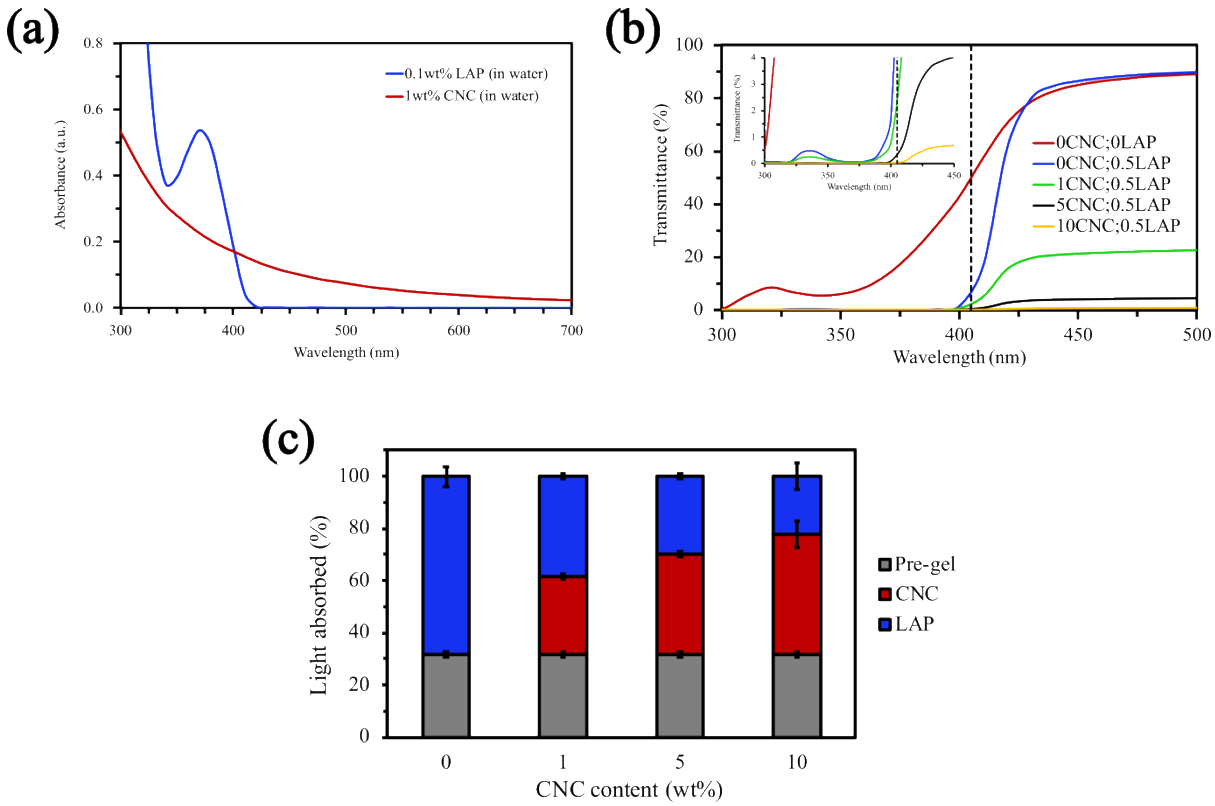


Figure 3.1: The optical properties of LAP, CNC, and the silicone-based pre-gel solution. **(a)** The absorbance of 0.1 wt% LAP and 1 wt% CNC in water from 300 to 700 nm. **(b)** The transmittance of pre-gel solution without and with 0.5 wt% of LAP followed by the inclusion of 0 to 10 wt% of CNC from 300 to 500 nm. The UV exposure wavelength of the VP printer at 405 nm is represented by the dashed line. **(c)** The amount of light absorbed by pre-gel solution and LAP, and scattered by CNC, respectively, when added with 0 to 10 wt% of CNC. The silicone-based composite pre-gel solution comprises SilMA/AA in a 1: 0.5 ratio followed by 0.2 wt% PEGDMA and 0.5 wt% LAP unless mentioned otherwise. Error bar represents ± SD, $n \geq 4$.

Prior to the incorporation of CNC, the addition of lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) results in a reduction of transmittance from 300 to 420 nm **(Figure 3.1b),** which aligns with the absorption range of LAP as a photoinitiator **(Figure 3.1a)**. The resulting difference in transmittance at 405 nm of the initial pre-gel solution with and

without 0.5 wt% of LAP was used to derive the amount of light absorbed by 0.5 wt% of LAP and the initial pre-gel solution, accordingly **(Figure 3.1c).** Subsequently, by assuming the amount of light absorbed by the initial pre-gel solution to remain constant, the further reduction in transmittance with CNC is regarded as the amount of light scattered by CNC itself. Based on **Figure 3.1c**, the amount of light made available to LAP was found to decrease from 68.0 ± 3.8 to 38.3 ± 1.1, 29.9 ± 1.0, and 22.3 ± 5.1 % as the amount of light scattered by CNC increases with the increasing CNC content from 0 to 1, 5, and 10 wt%, respectively. This reveals the ability of CNC to limit the amount of light for photoinitiation with its light-scattering properties. Despite that, an optimum CNC content is vital as an overdose of photoscatterer often causes the undercuring of printing layers, which results in either a structurally weak construct with layer misalignments or a complete failure in printing due to insufficient photocuring.

Besides considering the photocuring depth, it is crucial to investigate the effect of CNC on the viscosity of the pre-gel solution. This is because VP printing prefers resin material with a low viscosity for better flowability to effectively replenish the printing layer and to minimize the turbulence caused by the movement of the build plate during the VP printing process.[85] Based on **Figure 3.2**, the shear viscosity of the pre-gel solution was found to increase with the CNC content, which is most probably attributed to the formation of hydrogen bonding between the hydroxyl groups on the surface of CNC with its surrounding matrix of pre-gel solution.[438,439] On the contrary, the addition of 1 wt% of CNC was found to generate a pre-gel solution with minimal impact on the shear viscosity as shown by the comparable shear viscosity of pre-gel solution with 0 wt% of CNC. It is worth noting that the pre-gel solution with 1 wt% of CNC has a more prominent shear-thinning effect than the one with 0 wt% CNC. This is most probably due to the alignment of the CNC as shear applies. Overall, the pre-gel solution with 1 wt% of CNC was selected to proceed with the gel point evaluation.

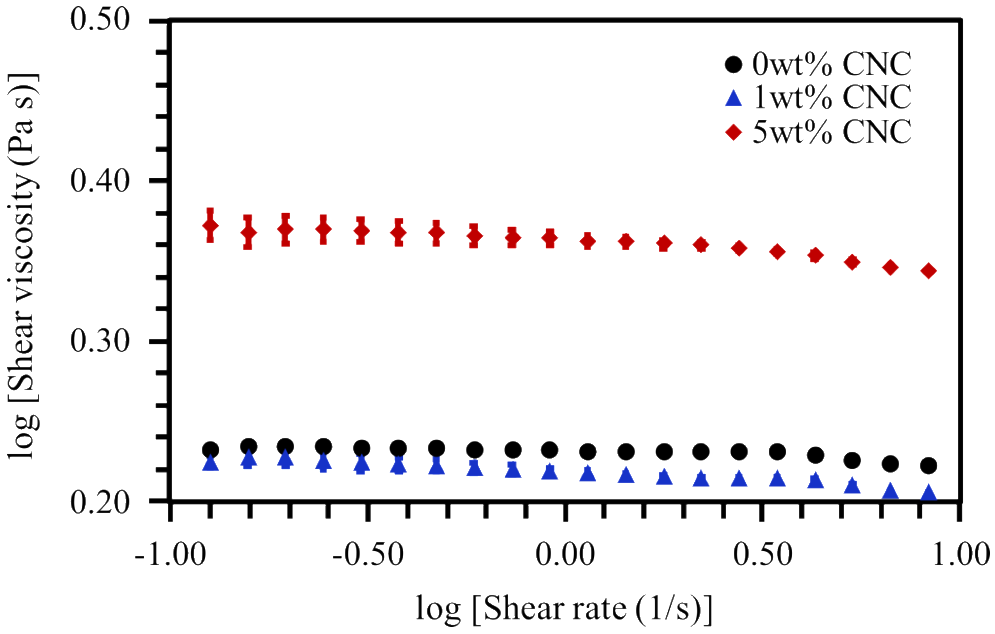


Figure 3.2: The pre-gel viscosity of the silicone-based pre-gel solution. The shear viscosity of the pre-gel solution with 0 to 5 wt% of CNC with increasing shear rate from 0 to 10 s^{-1} graphed in a log-log plot. The silicone-based composite pre-gel solution comprises SilMA/AA in a 1: 0.5 ratio followed by 0.2 wt% PEGDMA and 0.5 wt% LAP unless mentioned otherwise. Error bar represents ± SD, n ≥ 4.

The evaluation of the gel point of the pre-gel solution is critical to underpin the minimum UV exposure time required per printing layer to form a solid gel via gelation upon photocuring. Due to the nature of VP printing, the UV exposure time of the pre-gel solution for each printing layer is often limited to only a few seconds. Thus, it would be highly favourable for the pre-gel solution to have a gel point within a few seconds for rapid curing properties.[42] In parallel to that, the gel point of the pre-gel solution was determined based on the changes in the rheological behaviour of the pre-gel solution with the UV exposure time. Particularly, the gel point was identified as the point where the storage modulus (G′) crossover with the loss modulus (G″), for which G′=G″, as the pre-gel solution solidifies from the liquid pre-gel state (G′< G″) to the solid gel state (G′ > G″) upon UV exposure.[410,411] Based on **Figure**

3.3, the addition of 1 wt% of CNC demonstrates a similar gel point of approximately 2 seconds as opposed to the pre-gel solution with 0 wt% of CNC, which indicates that the addition of 1 wt% of CNC has no negative impact on the rapid curing properties of the pre-gel solution.

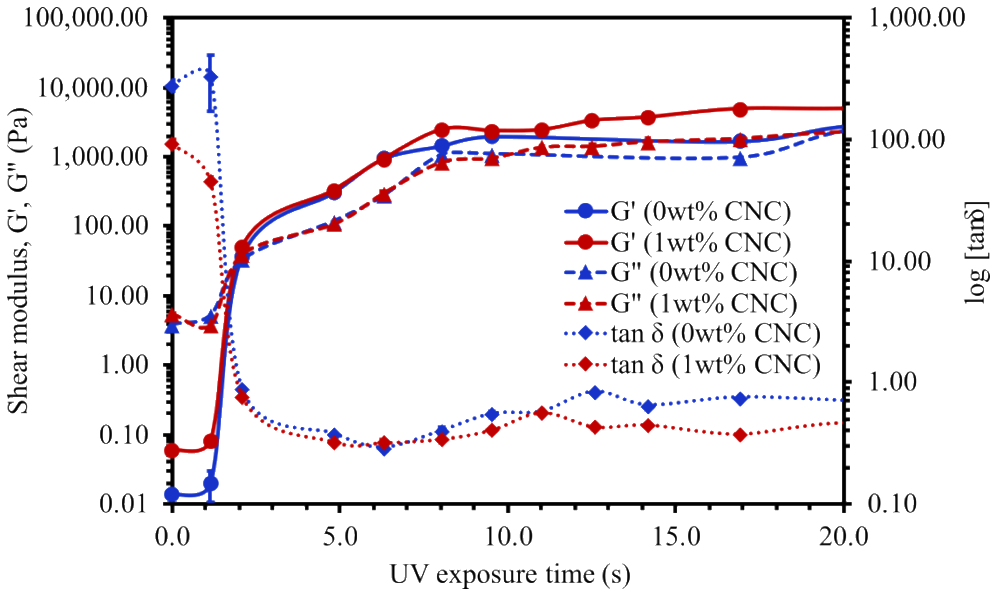


Figure 3.3: The gel-point of the silicone-based composite ink material based on rheological properties. The storage modulus, G′, loss modulus, G′′, and tan δ of pre-gel solution with 0 and 1 wt% of CNC upon UV exposure for 20 seconds plotted in log scale. The silicone-based composite pre-gel solution comprises SilMA/AA in a 1: 0.5 ratio followed by 0.2 wt% PEGDMA and 0.5 wt% LAP unless mentioned otherwise. Error bar represents ± SD, $n \geq 4$.

By considering the minimal impact on the viscosity and gel point of the pre-gel solution, 1 wt% of CNC was employed as the optimum dosage of photoscatterer for the following evaluation of the printing accuracy and resolution of the formulated pre-gel solution. Overall, the 1 wt% of CNC was observed to be homogeneously distributed and dispersed within the polymer matrix of the pre-gel solution as shown in **Figure 3.4**.

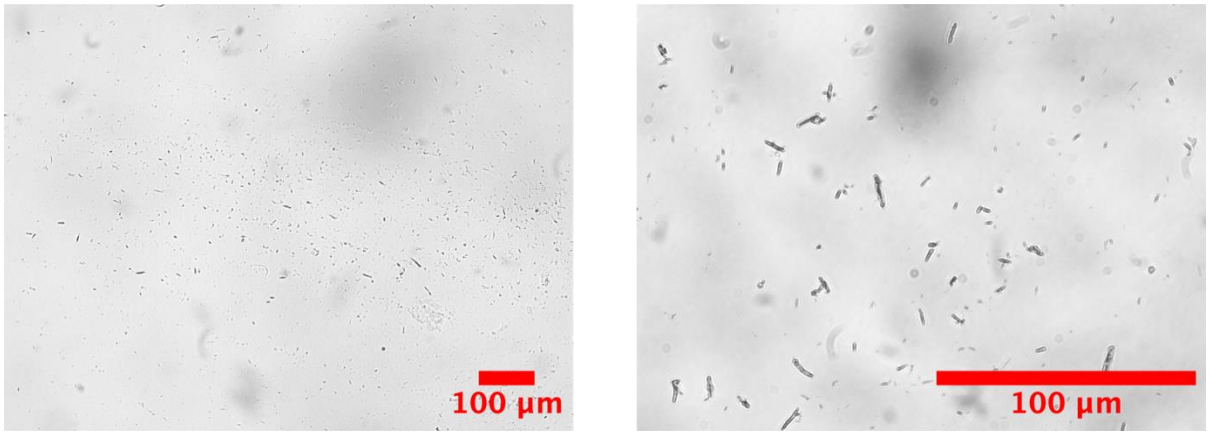


Figure 3.4: The observation on the homogeneous distribution of 1 wt% CNC in the silicone-based pre-gel solution. The microscope images of the silicone-based pre-gel solution added with 1 wt% of CNC under 10x and 20x magnification. Scale: 100µm.

3.3.2 Printing Accuracy and Resolution

The printing resolution of the microchannels was evaluated in reference to the test models developed by Gensler et al.[388] with appropriate modification, by measuring the printing accuracy of the smallest possible dimension of the microchannel. Specifically, a positive deviation indicates a larger than designed microchannel and a negative deviation indicates a smaller than designed microchannel. In terms of the printing resolution of channel width, a test model with a gradual decrease in channel width from 1000 to 50 µm with a constant channel height of 1000 µm was used for evaluation **(Figure 3.5a, top)**. The respective channel height and width of the microchannels were viewed and measured from the side as shown by the h and w labels in **Figure 3.5a (bottom)**, respectively. Based on **Figure 3.5b**, the printing accuracy of the channel width was found to increase significantly upon the addition of 1 wt% of CNC with the printed channel width better matching that of the designed channel width from 1000 to 100 µm. In conjunction with that, the respective microchannels were found to have a near zero deviation for the printed channel width down to 400 µm and a deviation of 6.4 ± 17.9, -17.8 ± 26.2, and -9.5 ± 22.2 % for 300 µm, 200 µm, and 100 µm, accordingly **(Figure 3.5d)**.

The printed channel width for 50 µm remains indistinguishable regardless of the addition of 1 wt% of CNC. The relatively large standard deviation recorded for the printed channel width below 300 µm reveals the increase in measurement inaccuracy as the dimension of the channel width reduces. As such, the printed channel width recorded below 300 µm does not fully represent the incapability of the VP printer to accurately generate fine features below 300 µm in dimension. Therefore, the respective test models can only serve as a preliminary reference to gauge the printing accuracy and resolution of microchannels with the newly developed printing material using the optimized printing parameters. Overall, the VP printer can resolve channel width down to 100 µm with minimal deviation using the formulated pre-gel material **(Figure 3.5b)**.

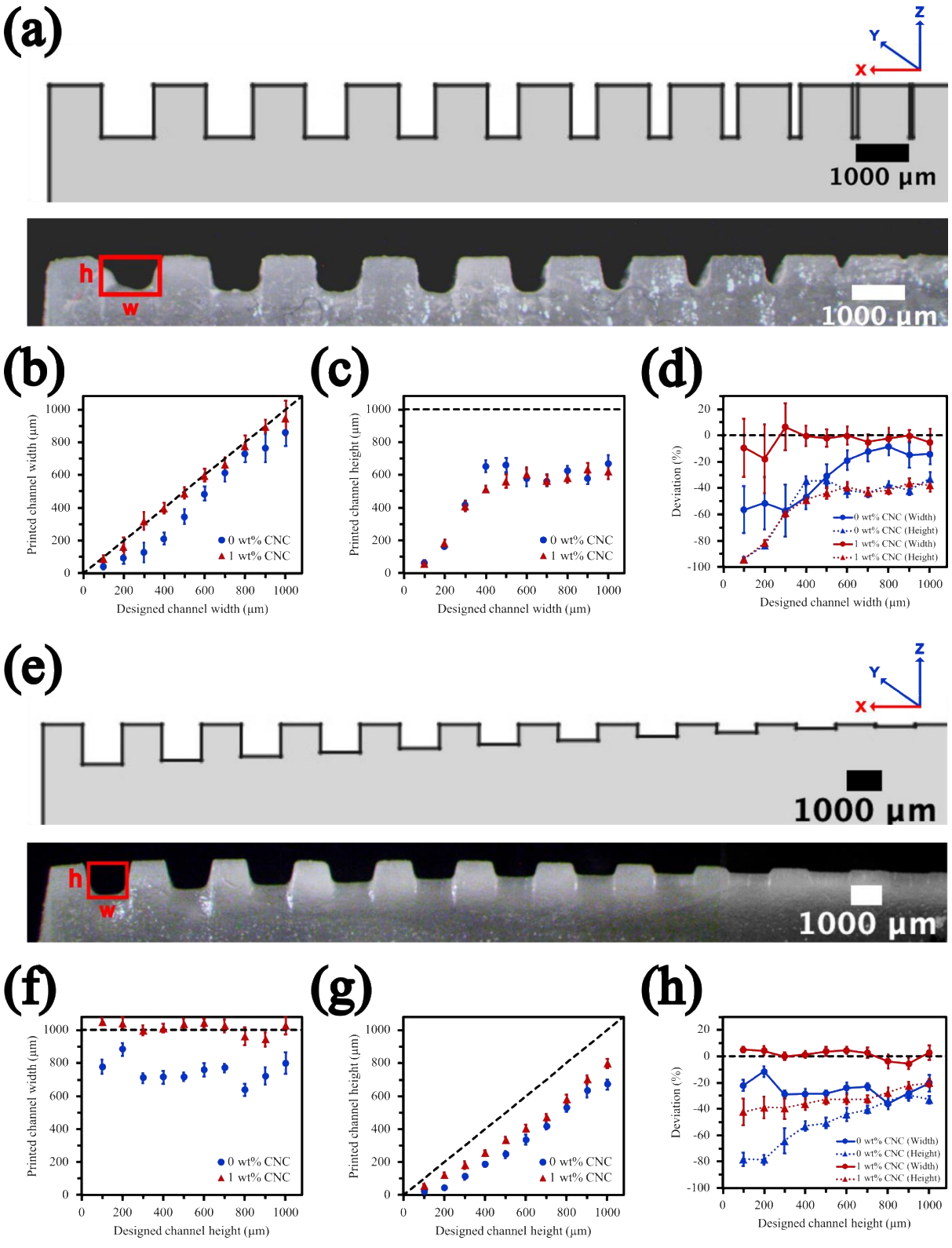


Figure 3.5: The printing resolution of the (a-d) channel width and (e-h) channel height of the silicone-based composite ink with 3D VP printing. (a) The CAD design model (top) and the 3D VP printing model (bottom) of the test model with a designed channel width ranging

from 50 to 1000 µm with a constant channel height of 1000 µm. The printing accuracy of both the **(b)** channel width (labeled w) and **(c)** channel height (labeled h) at each channel of the silicone-based composite ink with 0 and 1 wt% of CNC is illustrated and **(d)** is compared in terms of deviation in percentage. **(e-h)** The exact replica of (a-d) with a test model consisting of designed channel height ranging from 50 to 1000 µm with a constant channel width of 1000 µm. Error bar represents ± SD, n ≥ 3. Scale bar: 1000 µm.

On the contrary, the printed channel height was found to deviate at about -40 % even for the largest channel width with a dimension of 1000 µm regardless of the addition of 1 wt% of CNC **(Figure 3.5c and 3.5d)**. This reveals that 1 wt% of CNC might not be sufficient to eliminate the penetration of residual light, which causes the overcuring of trapped pre-gel solution within the microchannels as the residual light penetrates sideways through the designated pattern of the microchannels and formed cured gel within the microchannels **(Figure 3.6)**. Also, the pre-gel solution volume in the printing vat was observed to be inversely proportional to the nearly 50 % drop in accuracy of the printed channel height. This is because a higher pre-gel solution volume increases the likelihood of pre-gel entrapment in the microchannels. With regards to pre-gel entrapment, the printed channel height was also observed to reduce proportionally for the channel width below 400 µm **(Figure 3.5c and 3.5d)**. This is mainly attributed to the reduction in space within the microchannel as the channel width reduces, which results in a higher amount of trapped pre-gel solution being subjected to overcuring within the microchannels. Hence, the reduction in printed channel height is due to the presence of residual light penetrating through the designated pattern of the printed layer with the overcuring effect being amplified by the pre-gel entrapment within the microchannel with either a high pre-gel volume level in the printing vat or a small channel width in proportion to the channel height, or both.

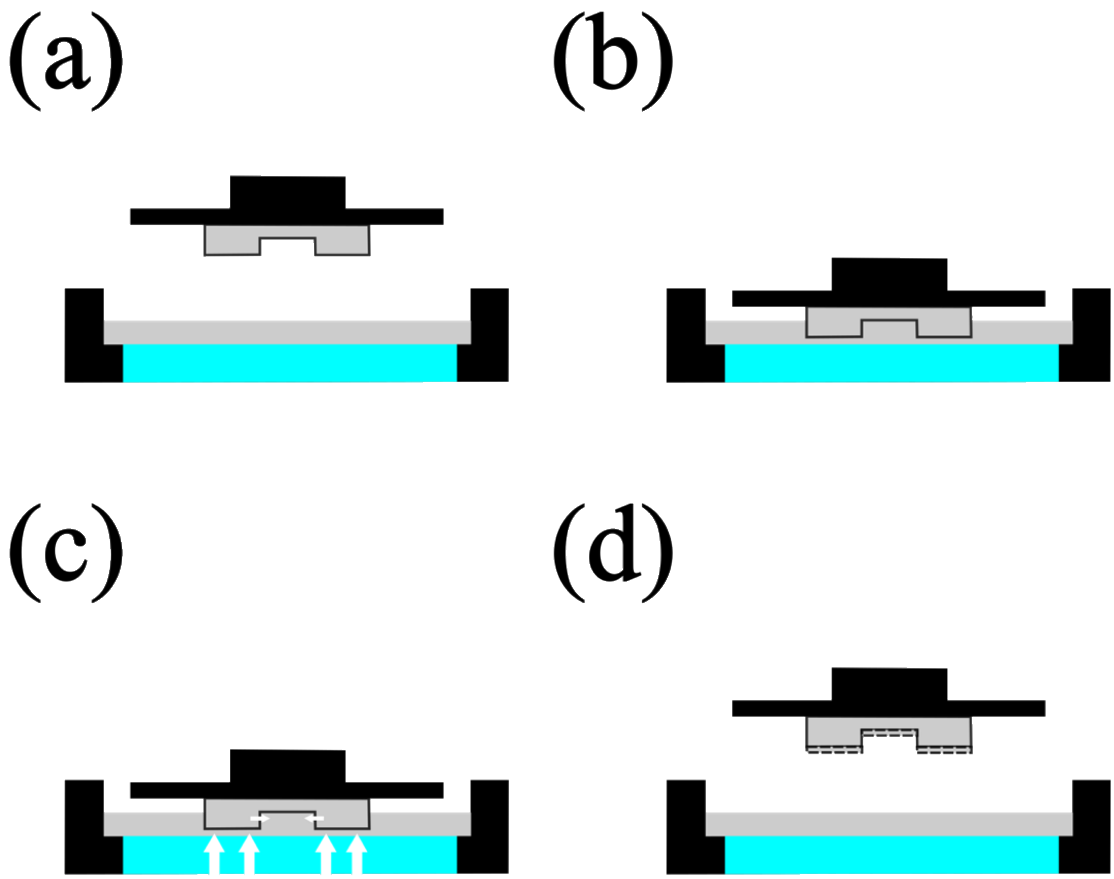


Figure 3.6: The illustration of VP printing on the overcuring of pre-gel within the microchannel. (a) Before the printing of the next layer, the build plate with the half-printed microchannel was moved out of the printing vat filled with pre-gel solution as the resin material. **(b)** The build plate with the half-printed microchannel then moved into the printing vat for the printing of next layer. **(c)** UV light with the designated pattern for the current printing layer was projected onto the half-printed channel from the bottom of the printing vat. At this stage, there might be residual light penetrating through the current printing layer and the half-printed structure, and give rise to the curing of trapped pre-gel solution within the microchannels. **(d)** The half-printed structure moved out of the printing vat with the build plate after the printing of the current layer. The printing process repeats from (a) to (d) until the printing structure is complete.

A test model was used to further evaluate the printing accuracy of the channel height. This model portrays a gradual reduction in channel height from 1000 to 50 μm while keeping the channel width constant at 1000 μm **(Figure 3.5e, top)**. Similarly, the addition of 1 wt% of CNC was observed to improve the printing accuracy of the channel width with a near zero deviation in channel width regardless of the dimension of channel height **(Figure 3.5f and 3.5h)**. This confirms that 1 wt% of CNC improves the printing precision of the channel width in the X and Y printing directions. In addition, the fact that the channel width maintains a high level of printing accuracy independent of the channel height demonstrates that the channel height has no effect on the channel width's printing accuracy. As I investigate the printed channel height, the addition of 1 wt% of CNC was found to increase the printing accuracy for the channel height ranging from 1000 to 100 μm as well **(Figure 3.5g and 3.5h)**. However, the improvement is not as significant when compared to the designed channel height. Despite that, the dimension of the printed channel height was found to align with the general trend of the designed channel height when paired with a constant channel width of 1000 μm **(Figure 3.5g)**, which is different from the observation for the dimension of printed channel height when paired with a gradually reduced channel width **(Figure 3.5c)**. This provides a key insight for the designing of dimensions for microchannels. A large enough channel width in proportion to the channel height is required to eliminate the entrapment of pre-gel solution within the microchannel as a resolution to compromise with the residual light penetrating through the designated pattern layer. Similar to the previous test model, the microchannel with a 50 μm channel height remains indistinguishable regardless of the addition of 1 wt% of CNC. It is predicted that the developed pre-gel material allows the VP printer to resolve channel features down to 100 μm. All in all, with the relatively large channel width at 1000 μm, the VP printer can generate channel height down to 100 μm with a compromised reduction in channel height

dimension ranging from 20.3 ± 2.9 % for 1000 µm up to 42.1 ± 10.1 % for 100 µm **(Figure 3.5h)**.

To examine the impact of the pre-gel volume level in the printing vat on the accuracy of the channel height, the volume level of the pre-gel solution was reduced in the second test model. Based on **Figure 3.5h**, the deviation of the printed channel height for the microchannel with the designed dimension of 1000 x 1000 µm in width and height was revealed to be -20.3 ± 2.9 %, which is 1.65 times more accurate than the deviation of -37.9 ± 4.7 % for the printed channel height with the same microchannel dimension in the first test model **(Figure 3.5d)**. This provides evidence that the lower pre-gel volume level in the printing vat can minimize the level of pre-gel entrapment within the microchannels as the printing progresses. Although attempts have been made to modify the volume level of the pre-gel in the printing vat, it is not possible to entirely prevent the excessive overcuring of the gel within the microchannels. As previously stated, a concentration of 1 wt% of CNC may not be enough to fully prevent residual light from penetrating the prescribed pattern of the printing layer. Apart from that, the nature of CNC in scattering instead of absorbing light most probably leads to the redirection of light beams across the previously printed layers as the light reflects off the surface of CNC in the formulated silicone-based composite material.[440] The redirection of light beams increases the probability for residual light to penetrate sideways across the designated pattern of the previously printed layers and overcures the trapped pre-gel solution within the microchannels. Nevertheless, the reduction in channel height is never a major concern as it does not pose any detrimental effect on the functionality of the printed channel as a microfluidic device. Instead, the targeted channel height can be achieved by factoring in the potential deviation in the printed channel height into the CAD design of the microchannel if necessary. On a side note, the printing accuracy of the channel width in the XY direction is as critical as the channel height in the Z direction. This is because a slight change in the channel dimension in the XY printing

direction may alter the flow design of the microfluidic device. Hence, the capability to generate delicate channel features with near zero deviation in the XY direction, as mentioned above upon the incorporation of 1 wt% of CNC, remains an appealing feature for the incorporation of CNC as a non-staining photoscatterer.

3.3.3 Printing of Microfluidic Devices

To prove the practicality of fabricating microfluidic devices with VP printing, I utilize the hydrophilic silicone-based composite material to print typical channel layouts for these devices. According to the initial assessment, VP printing can generate very consistent and straight microchannels using the developed material. The width of these channels ranges from 1000 to 300 µm. The linearity index for the channel width of 1000 µm was found to be approximately 0.97 ± 0.02, while for the channel width of 300 µm, it was approximately 0.90 ± 0.05 **(Figure 3.7)**.

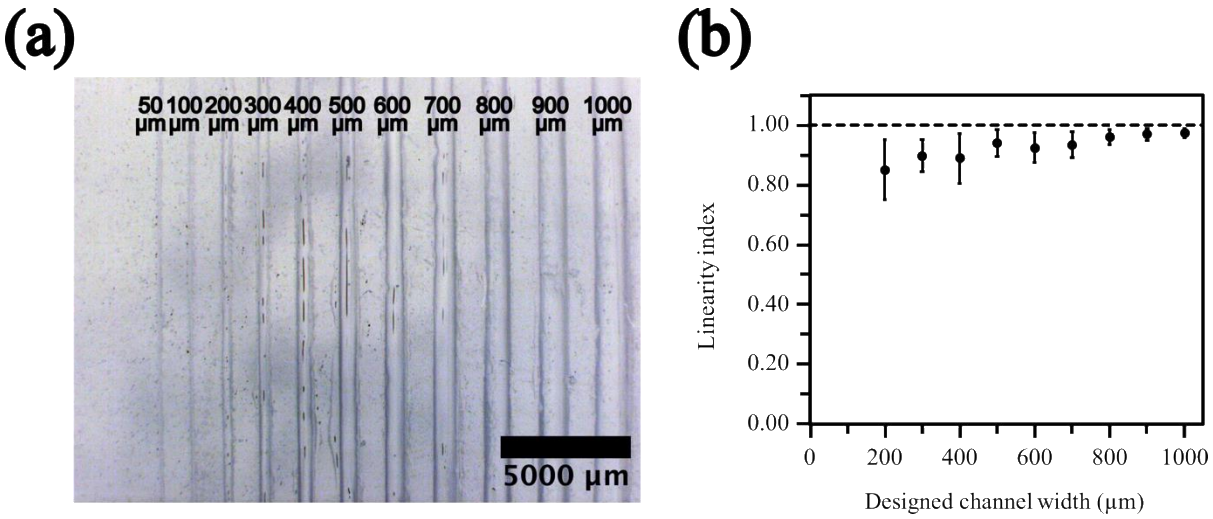


Figure 3.7: The linearity of the printed straight microchannels. (a) The micrograph and **(b)** the linearity index of the printed straight microchannels with channel width ranging from 50 to 1000 µm. The linearity index for microchannels with a channel with of 50 and 100 µm remains unmeasurable due to the difficulty in distinguishing the channel width from the micrograph.

Besides straight microchannels, a variety of channel patterns with highly accurate features as illustrated by the CAD design can be fabricated using the hydrophilic silicone-based composite material with VP printing as shown in **Figure 3.8**. For instance, I have successfully demonstrated the feasibility of fabricating simple channel patterns, such as Y-shaped channel **(Figure 3.8a)**, T-shaped channel **(Figure 3.8b)**, and serpentine channel **(Figure 3.8c)**, using the silicone-based composite material with VP printing. Furthermore, integrated channel patterns with more than one channel design element can be easily fabricated as demonstrated by the accurately printed channel patterns for columns with perpendicularly connecting channels **(Figure 3.8d)**, sample channel pattern for concentration gradient generator (CGG) **(Figure 3.8e)**, and sample channel pattern for cancer tumor cells (CTCs) capturing **(Figure 3.8f)**. Besides symmetrical channel designs, asymmetrical channels can also be accurately fabricated as shown by the vascular-like channels in **Figure 3.8g**. With the highly accurate replication of the CAD design pattern, microfluidic devices with any design of channel patterns can be effectively fabricated using the hydrophilic silicone-based composite material via VP printing.

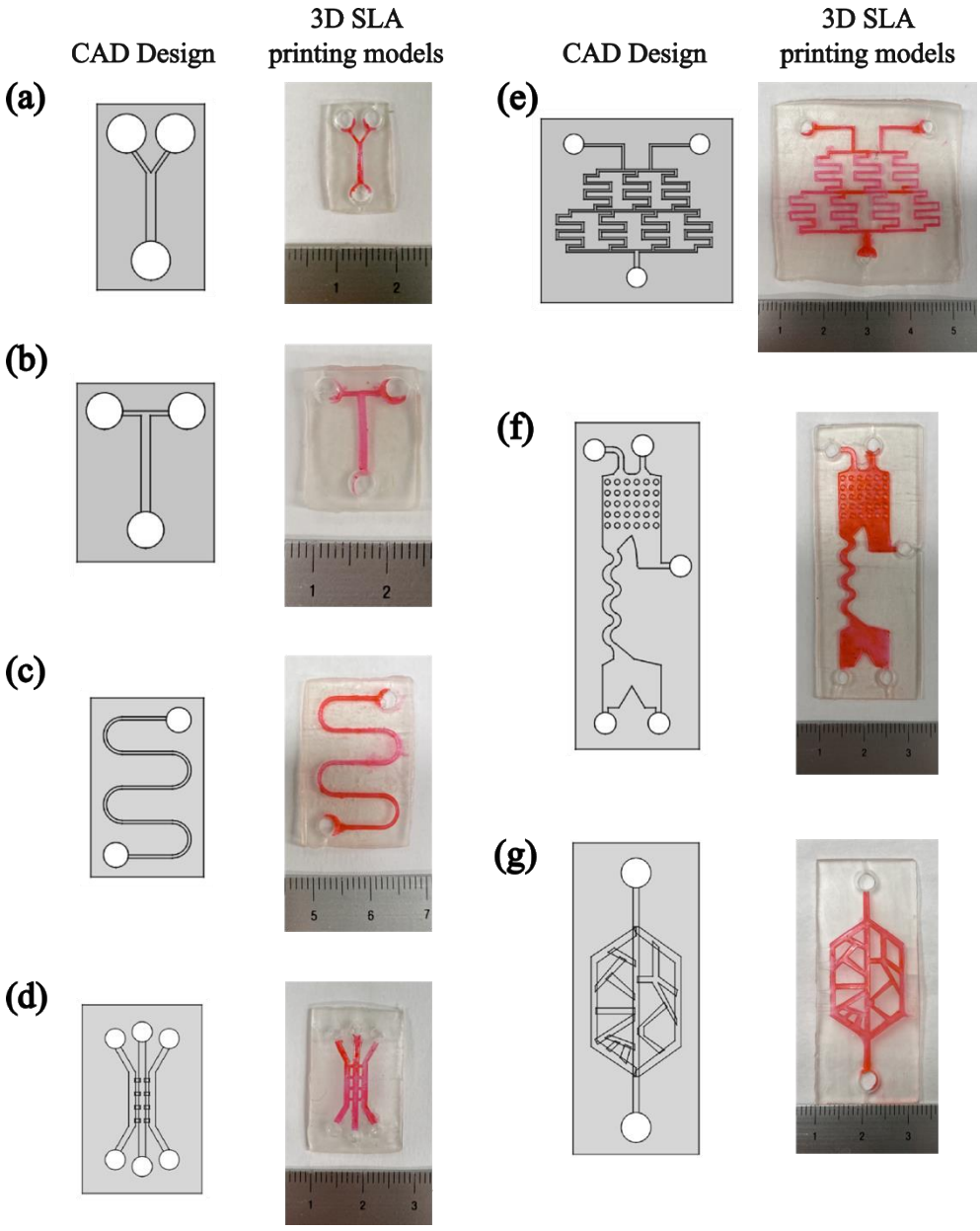


Figure 3.8: The CAD design and 3D VP printing of microfluidic devices. (a) Y-shaped channel. **(b)** T-shaped channel. **(c)** Serpentine channel. **(d)** Columns with perpendicularly connecting channels. **(e)** Sample channel pattern for concentration gradient generator. **(f)** Sample channel pattern for cancer tumor cells (CTCs) capturing. **(g)** Vascular-like channels. The microchannel dimension for channel width ranges from 500 to 1000 µm with a channel height of 500 µm. The printed microchannels are stained with red dye for better visualization; Scale photographed with 3D VP printing models: cm.

Furthermore, with the excellent printing accuracy and resolution of VP printing, the dimension of the microchannels can be further scaled down to 50 % without deteriorating the channel patterns **(Figure 3.9a and 3.9b)**. This is well represented by the Y-shaped channel pattern with a clear channel pattern showing the emergence of two smaller channels, with a channel width of 131.48 μm, into a large channel, with a channel width of 370.28 μm, upon 50 % scaling down in dimension **(Figure 3.9a)**. Besides straight channels, fine features, like circular poles and wavy curvature column, can be accurately printed with VP printing as well upon 50 % scaling down in dimension **(Figure 3.9b)**. The capability to generate fine tiny features further verifies that the test models used for the measurement of printing accuracy and resolution in **Figure 3.5** do not fully represent the capability of VP printing in generating tiny features with the formulated material and can only serve as a reference for printing accuracy. Attempting to reduce the size to 20 and 10 % did not result in the formation of a printed structure since the overall thickness of the designed microfluidic device is smaller than the thickness of a single printing layer, which is 50 μm. Besides that, microfluidic channels often consist of pole structures to aid in the manipulation of flow direction within the microchannels. Based on **Figure 3.9c**, I demonstrate the ability to print micron-sized pole structures with highly customized shapes and sizes within the microchannel. The micrographs provide more evidence that the printed pole structures made with the developed material closely match the corresponding CAD model. Typically, the designed composite material based on silicone is well-suited for use in the VP fabrication of microfluidic devices featuring fine channel characteristics.

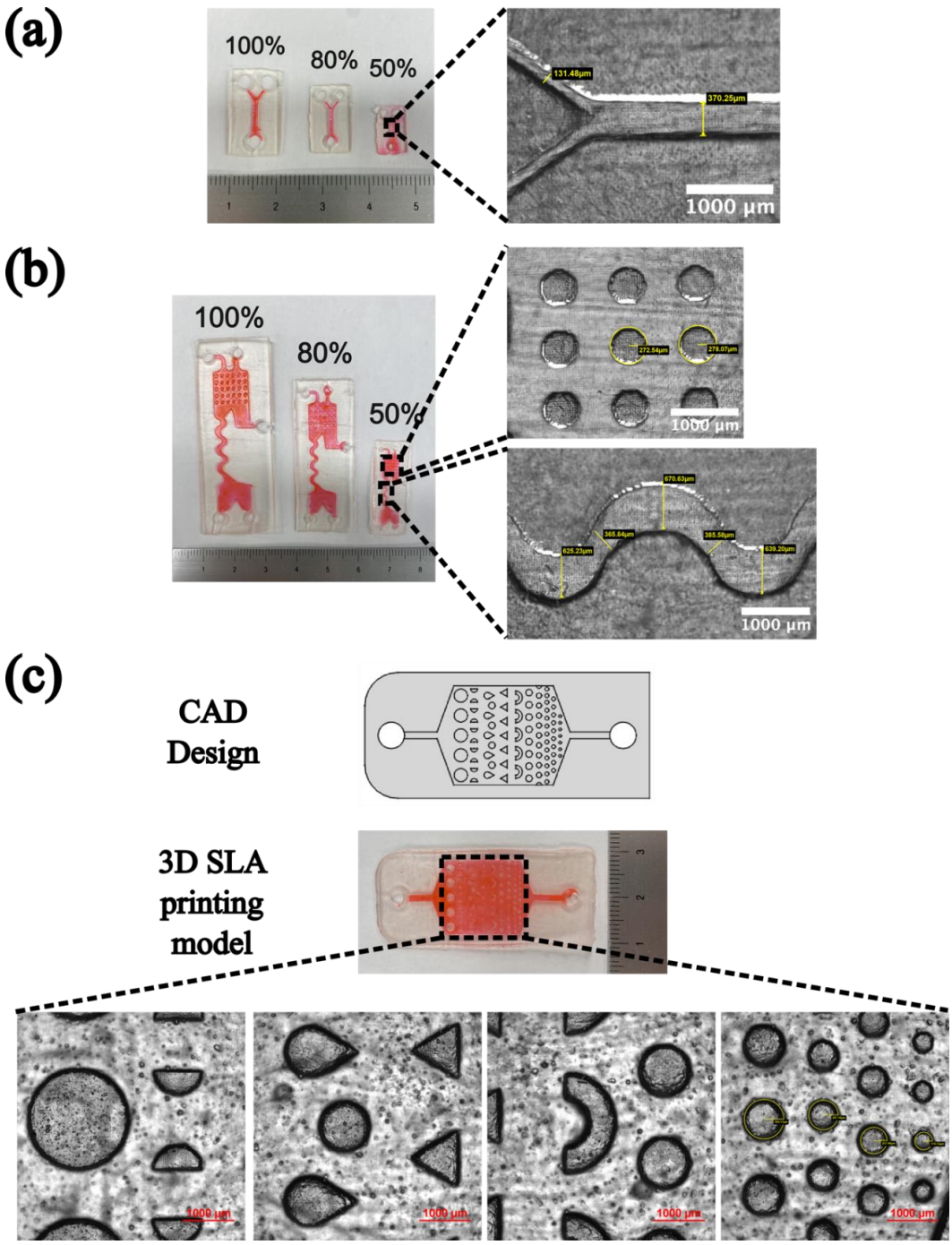


Figure 3.9: The 3D VP printing of scaled-down channel patterns. The **(a)** Y-shaped channel and **(b)** sample pattern of the fluidic device for CTCs capturing with microscope images showing the fine printing structures of the respective patterns when being scaled down to 50 %. **(c)** The CAD design (top), 3D VP printing model (middle), and microscope images (bottom) of poles with different shapes and sizes. Scale photographed with 3D VP printing models: cm; Scale bar: 1000 µm.

Aside from generating highly accurate replicates of fine channel patterns, microfluidic devices can be fabricated in a relatively short time with VP printing as opposed to the conventional soft-lithography method. As observed in this study, a microfluidic device with an overall thickness of 1.5 mm can be fabricated within 7 minutes when paired with the optimum pre-gel viscosity and rapid curing properties of the formulated silicone-based composite material. After printing, the printed microfluidic device will be subjected to washing in water at room temperature (22 ± 2 ºC) for 30 seconds to remove any uncured residual pre-gel solution on the printed structure. The printed microfluidic device can then be directly bonded to the glass slide after air drying using the pressure-sensitive double adhesive tape and is ready to be used for fluid processing once fully bonded. Despite the translucent appearance of the printed material, the absence of distinct colour aids in the clear visualization of fluid from the bottom of the printed microfluidic device **(Figure 3.10)**. The relatively simple procedure and short fabrication time of microfluidic devices with VP printing as compared to the conventional method of soft-lithography highlights the potential to prototype or mass produce microfluidic devices more efficiently via the direct printing of microfluidic devices with VP printing. To sum up, I demonstrated the feasibility of fabricating microfluidic devices consisting of excellent surface finish with fine channel structures in a comparatively short fabrication time via VP printing using the developed silicone-based composite material.

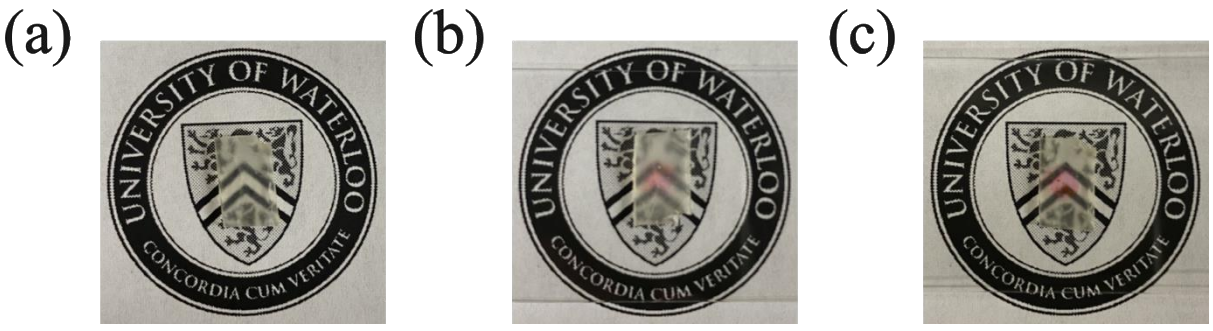


Figure 3.10: The observation on the visual appearance of hydrophilic silicone-based composite polymer with 1 wt% of CNC. (a) The printed material without bonding to glass

slide showing a translucent appearance. **(b)** The top view of the printed material (top) after bonding to glass slide (bottom) showing a blur view of red stain in between the bonded layers. **(c)** The bottom view of the printed material (bottom) after bonding to glass slide (top) showing a clear view of red stain in between the bonded layers.

3.3.4 Functionality of the Microfluidic Devices

To function as a microfluidic device, the printed channel needs to be able to flow fluid effectively without any leakages. With regards to that, both static and dynamic flow test was conducted on the printed microfluidic device consisting of four straight channels with a channel width of 1000 μm and channel height of 500 μm to observe for fluid leakages when being subjected to different conditions. Prior to the flow test, the printed microfluidic device with the open channels was attached to the glass slide with the pressure-sensitive double-adhesive tape and left at room temperature (22 ± 2 ºC) for at least 1 hour to ensure that the printed microfluidic device was well attached to the glass slide before proceeding with the flow test. Based on **Figure 3.11a**, all four printed channels remain intact and no fluid leakages were observed for 24 hours when the channels were flowed with water. The same observation of no fluid leakage was obtained with acetone, except that a separation in dye with the acetone was observed within the channels across the 24 hours due to the immiscibility of the red dye and acetone. Nonetheless, the static flow of water and acetone within the channels for a period of 24 hours highlights the capability of the printed microfluidic device to process different solvents, including organic solvents, without fluid leakage at room temperature for up to 24 hours.

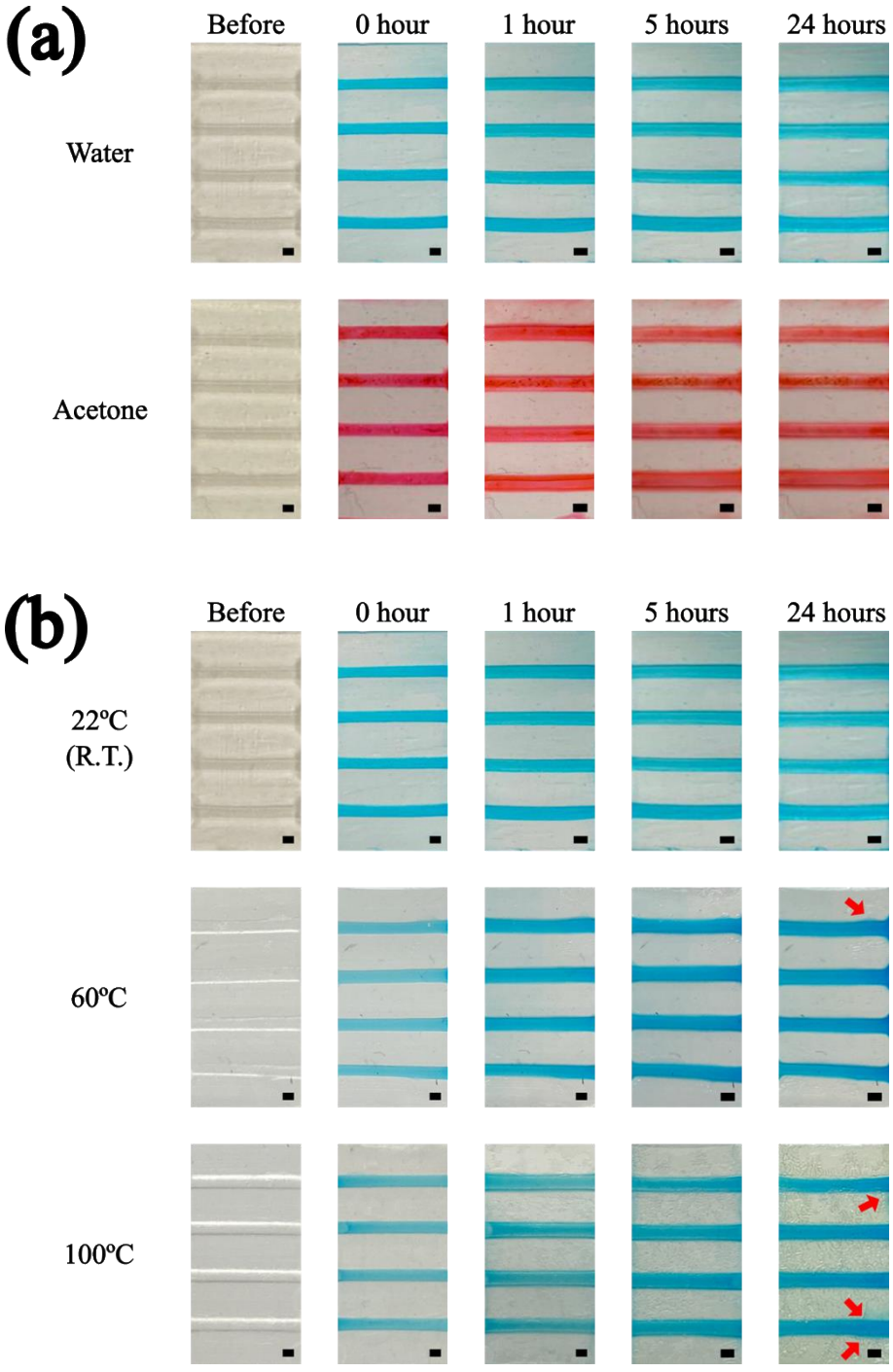


Figure 3.11: The static flow test on four straight microchannels when being subjected to different solvents and different incubation temperatures. The observation on the microchannels when being exposed to **(a)** different solvents, such as water (blue) and acetone (red), at room temperature (22 ºC) and **(b)** to different incubation temperatures, such as 22 ºC

(room temperature), 60 ºC, and 100 ºC, with water (blue) for an incubation period up to 24 hours. The fluid leakage observed was indicated by red arrows. Scale bar: 1000 µm.

Furthermore, the effect of temperature was investigated to understand the behaviour of the printed microfluidic devices with temperature and its potential to be used for applications requiring elevated temperature, such as enzyme-related [441–444] and PCR-related studies.[445,446] Based on **Figure 3.11b**, the printed channels were observed to have a compromised fluid flow with minor leakages detected when being subjected to elevated temperature for a prolonged time. No fluid leakages were observed from the straight channels for up to 5 hours for both the incubation temperature at 60 ºC and 100 ºC. Upon 24 hours of incubation, fluid leakages were observed from the straight channels for both the incubation temperature at 60 ºC and 100 ºC, with the leakages being more severe for the channels incubated at 100 ºC. It was found that the fluid leakages were caused by the pressure-sensitive double adhesive tape disintegrating when exposed to heat. The signs of disintegration were most noticeable when the incubation temperature was set at 100 ºC. After one hour of incubation at 100 ºC, the cracks found on the double-sided adhesive tape indicate that it is beginning to disintegrate. As the incubation period grows to 24 hours, the fissures widen even more. Moreover, the printed microfluidic device was observed to shrink slightly with heat, which caused the printed channels to slightly distort, particularly at the sides of the microfluidic devices. The initial indication of distortion was seen at 60 ºC after 5 hours and at 100 ºC after 1 hour. However, the channels remained undamaged and there were no instances of fluid leakage until the double-sided tape deteriorated. Therefore, the observed fluid leakage was mostly caused by the degradation of the pressure-sensitive double adhesive tape, resulting in the gradual detachment of the printed microfluidic device from the glass slide. Therefore, the printed microfluidic device has the capacity to be operated at high temperatures, as long as a different bonding technique or a heat-resistant material is used to attach the printed microfluidic device to the glass slide. With the current bonding

method, the printed microfluidic device demonstrates promising results to be used for up to 5 hours at 60 ºC and 100 ºC without any fluid leakage observed.

To further evaluate the durability of the printed microfluidic devices when being subjected to continuous fluid flow, a dynamic flow test was conducted on a straight microchannel with the experimental setup as shown in **Figure 3.12a**. A variable flow rate dosing pump, ranging from 2.5 to 20 mL/min, was employed to regulate the speed of the ongoing fluid flow within the microchannel. In order to better demonstrate the continuous fluid flow, the microchannel was first flowed with blue dye followed by an immediate interchange with red dye **(Figure 3.12b)**. The gradual transition in colour from blue to red within the microchannel over time further portrays the ability of the printed microfluidic devices to process a continuous flow of fluid without any fluid leakage. Additionally, the flow rate of the fluid across the microchannel was increased progressively from 2.5 to 20 mL/min with a 15-minute interval between each flow rate upon switching. Similarly, no fluid leakage was observed and the microchannel remains intact with the maximum flow rate of the dosing pump at 20 mL/min. Hence, the printed microfluidic device effectively demonstrates its capability to handle a continuous flow of fluid at a rate of up to 20 mL/min without any instances of fluid leakage. Specifically, the flow pressure at a flow rate of 20 mL/min flowing through the microchannel with a dimension of 1000 µm in width x 500 µm in height x 10 mm in length was calculated to be approximately 3.95 kPa based on Poiseuille's law [447,448] after taking into account the tube resistance of the tygon tubing with an internal diameter of 0.79 mm. Essentially, the silicone-based composite material demonstrates success in fabricating functional microfluidic devices with VP printing as reflected by the good fluid processibility of both static and dynamic fluid by the printed microfluidic devices when being subjected to suitable conditions.

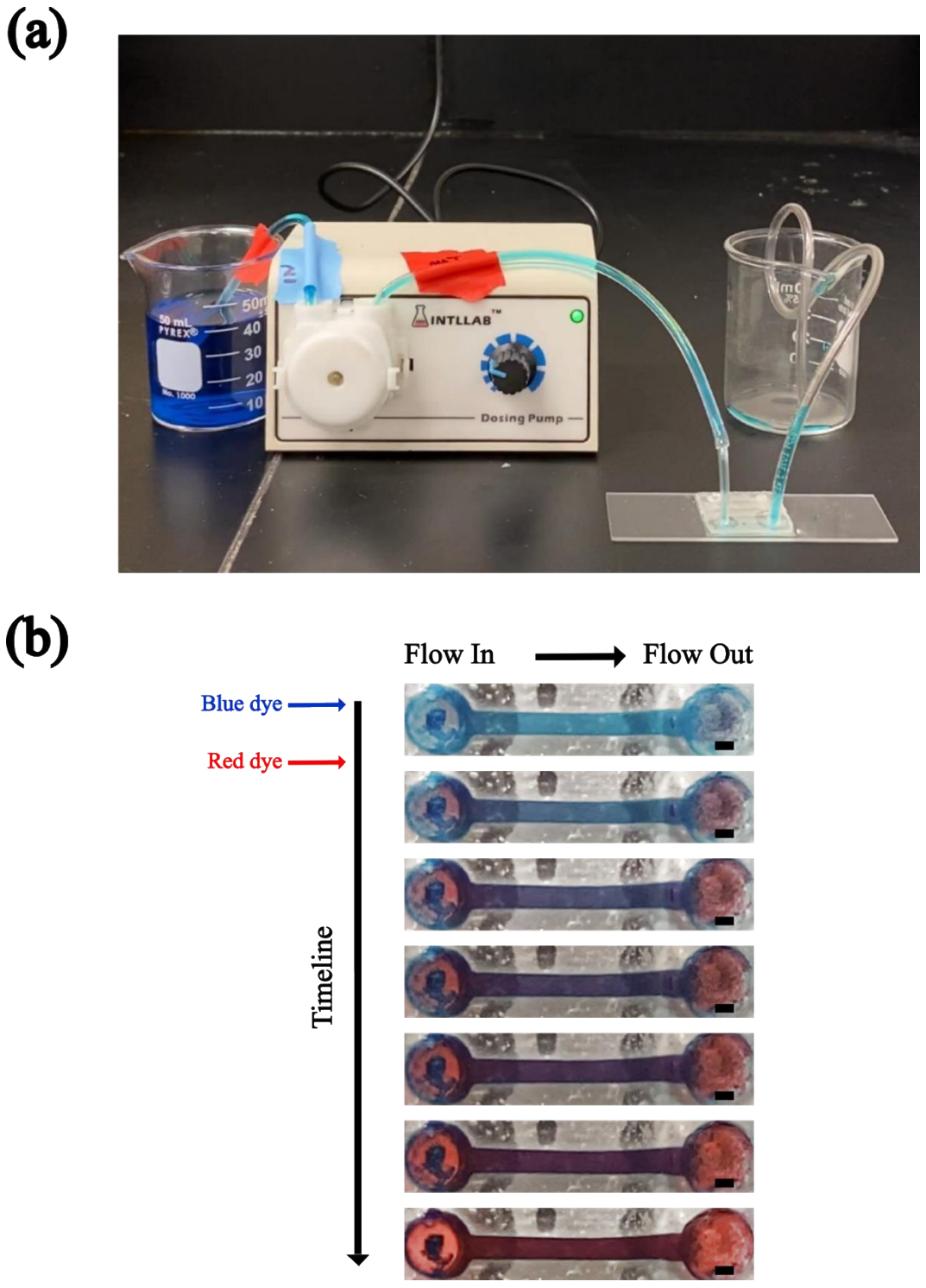


Figure 3.12: The dynamic flow test on a straight microchannel. **(a)** The setup of a dosing pump to flow fluid in and out of the microfluidic chip and **(b)** the dosing of blue dye followed by red dye to show the gradual change in colour with respect to the continuous liquid flow across the microchannel.

3.3.5 Physico-chemical Characteristics and Biocompatibility

The silicone-based composite material confers sustainable hydrophilicity throughout the monitoring period of 7 days as illustrated by **Figure 3.13a**. As shown in **Figure 3.13a**, the silicone-based composite material shows hydrophilic properties with a contact angle below 90º, which demonstrates a striking difference when compared to the contact angle of the regular PDMS with hydrophobic properties at 109.3 ± 4.9º. Upon the addition of 1 wt% of CNC, the hydrophilic properties of the formulated material further improve with a drop in contact angle from 44.9 ± 2.9º to 36.0 ± 1.9º, which is most likely contributed by the hydrophilic functional groups, such as hydroxyl groups, on the CNC surface. In addition to that, the silicone-based composite material was compared against plasma-oxidized PDMS (PDMS-O2). This is because conventional PDMS with hydrophobic properties is often treated with plasma oxidation to acquire hydrophilic properties.[449] Studies have shown that the plasma oxidation treatment can effectively transform the hydrophobic surfaces of PDMS into hydrophilic with the introduction of polar groups to the PDMS surface via surface oxidation.[449] However, based on my findings, despite achieving a super hydrophilic surface with a close to 0º contact angle upon plasma oxidation, the hydrophilicity of the PDMS-O2 is not sustainable and reverts back to a hydrophobic surface within 30 minutes of exposure to open air. On the contrary, the hydrophilicity of the silicone-based composite material was found to remain stable regardless of the addition of CNC as opposed to the PDMS-O2. Further comparisons on the formulated material were made using the formulation with 1 wt% of CNC. Unlike PDMS-O2, the contact angle of the developed silicone-based composite material remains constant from 36.0 ± 1.9º to 37.1 ± 1.8º from Day 0 to Day 7. Therefore, by using the developed silicone-based composite material, I have unlocked the potential to create a silicone-based microfluidic device that has long-lasting hydrophilicity without the requirement of an additional step to coat or modify the microchannel surface.

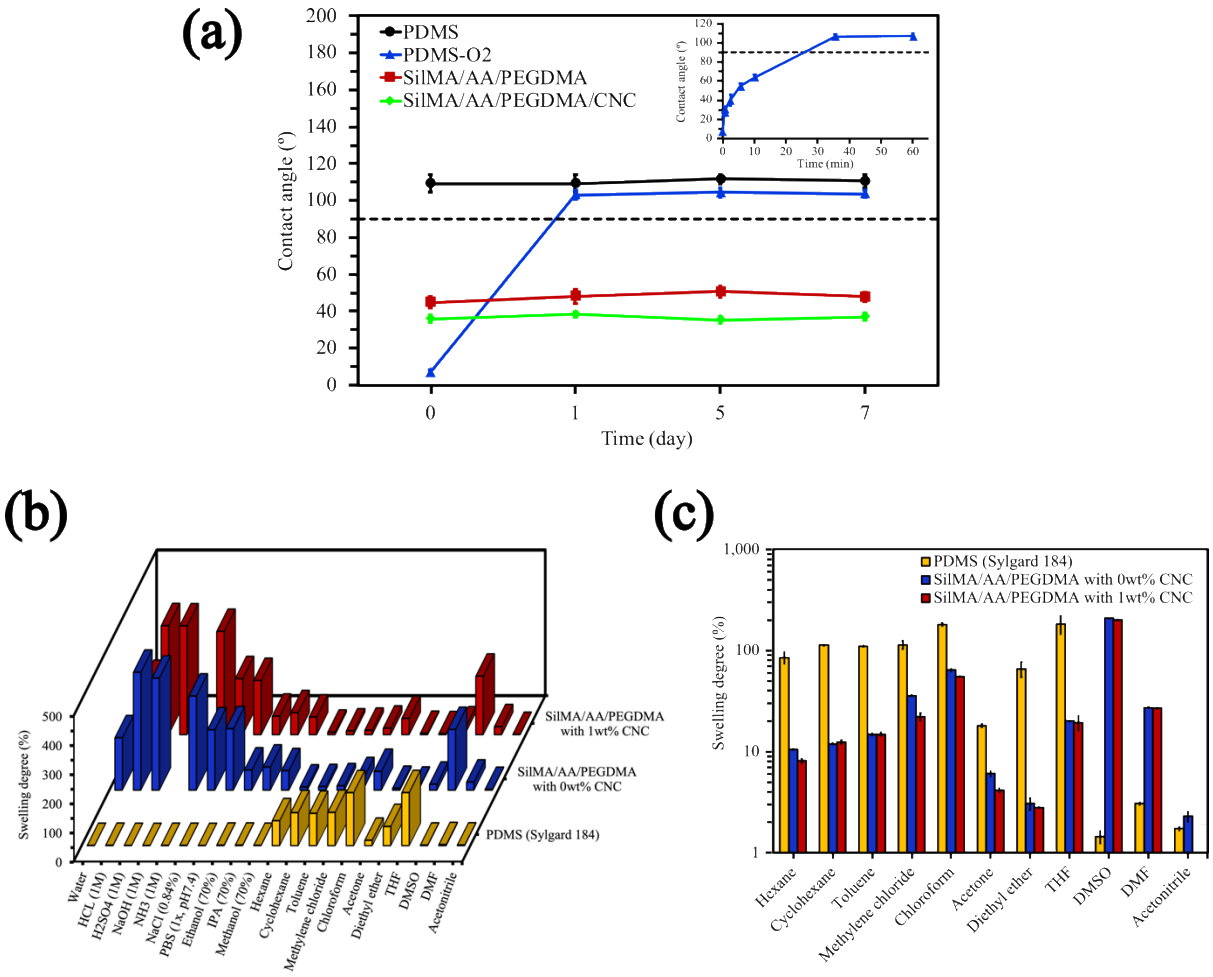


Figure 3.13: The cured gel properties of the silicone-based composite material. (a) The contact angle of PDMS, PDMS-O2, SilMA/AA/PEGDMA (silicone-based composite material with 0 wt% of CNC), and SilMA/AA/PEGDMA/CNC (silicone-based composite material with 1 wt% of CNC) for 7 days. **(b)** The swelling degree of PDMS, SilMA/AA/PEGDMA, and SilMA/AA/PEGDMA with 1 wt% of CNC with different solvents after 24 hours of incubation period, **(c)** with the swelling degree against organic solvents specifically illustrated in log scale. Error bar represents ± SD, n ≥ 3.

Moreover, the silicone-based composite material was tested with a variety of organic and inorganic solvents typically employed in chemical and biological reactions. This was done to assess the chemical compatibility of the developed material with different solvents. In conjunction with the hydrophilicity of the developed material, the developed material was

revealed to have a better resistance towards organic solvent as compared to the regular PDMS material, as reflected by its comparatively lower swelling degree with most of the organic solvents **(Figure 3.13b)**. Particularly, the swelling degree in diethyl ether was reduced by about 20-fold, and about 10-fold in hexane, cyclohexane, toluene, and THF, followed by about 3-fold in methylene chloride, chloroform, and acetone with the developed material as compared to the regular PDMS material **(Figure 3.13c)**. The addition of 1 wt% of CNC yields a small reduction in swelling degree against most of the organic solvents, with an exception improvement in chemical resistance for acetonitrile. The swelling degree of the developed material with acetonitrile was observed to reduce from 2.29 ± 0.29 to 0.38 ± 0.26 % upon the addition of 1 wt% of CNC, with an approximately 6-fold reduction in swelling degree. However, due to the hydrophilicity of the developed material, the developed material was observed to have a significantly higher swelling degree than the regular PDMS material with water, hydrochloric acid (1M HCl), sulfuric acid (1M H_2SO_4), ammonia solution (1M NH_3), 0.84 % sodium chloride (NaCl), 1x phosphate-buffer saline (PBS, pH 7.4), 70 % ethanol, 70 % isopropyl alcohol (IPA), 70 % methanol, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) **(Figure 3.13b and 3.13c)**. Despite that, the high swelling degree of the developed material with certain solvents should not be of major concern. This is because only a small volume of fluid will be in contact with the microfluidic device as it flows through the microchannels, and the effect of swelling caused by the solvent within the microchannel would have minimal to no impact on the fluid processibility of the printed microfluidic device. This is proven by the capability of the printed microfluidic channels to hold water and acetone for up to 24 hours with no visible sign of reduction in channel width due to swelling **(Figure 3.11a)**. With that being said, the swelling test does not impose any restrictions on the types of solvent to be used with the printed microfluidic device. Instead, the swelling test functions as a

reference for a better understanding of the chemical compatibility of the developed material with different types of solvents.

Among the solvents tested, the developed material was observed to dissolve completely in sodium hydroxide (1M NaOH) upon full sample immersion for 24 hours. The dissolution of the developed material suggests that the developed material might not be suitable to be used with solutions containing hydroxide ions (OH^-) for a prolonged period. This is because the presence of hydroxide ions can degrade the AA/PEGDMA polymer network,[450–452] which leads to the disentanglement of the SilMA/AA/PEGDMA interpenetrating network, and subsequently, results in the dissolution of the developed material. Based on the aforementioned findings, the printed microfluidic device fabricated from the developed silicone-based composite material was discovered to be able to process a wide range of organic and inorganic solvents without material degradation, with the exception of NaOH.

In terms of biocompatibility properties, the cytotoxicity of the silicone-based composite material was assessed by quantifying the relative cell viability as opposed to the control group after co-culturing with living cells for up to 6 days. The material would be considered non-cytotoxic when presented with a cell viability greater than 70 % throughout the monitoring period.[423] **Figure 3.14** indicates that both the silicone-based composite materials, with and without 1 wt% of CNC, exhibit a significant increase in relative cell viability, which is highly comparable to the control group. This reaffirms the excellent biocompatibility properties of the developed material. Additionally, the comparable relative cell viability of the developed material with and without 1 wt% of CNC provides evidence that the addition of 1 wt% CNC does not affect the biocompatibility of the developed material. With the non-cytotoxicity properties as revealed by the high relative cell viability, the developed material exhibits great potential for the fabrication of microfluidic devices that require a cell-friendly environment.

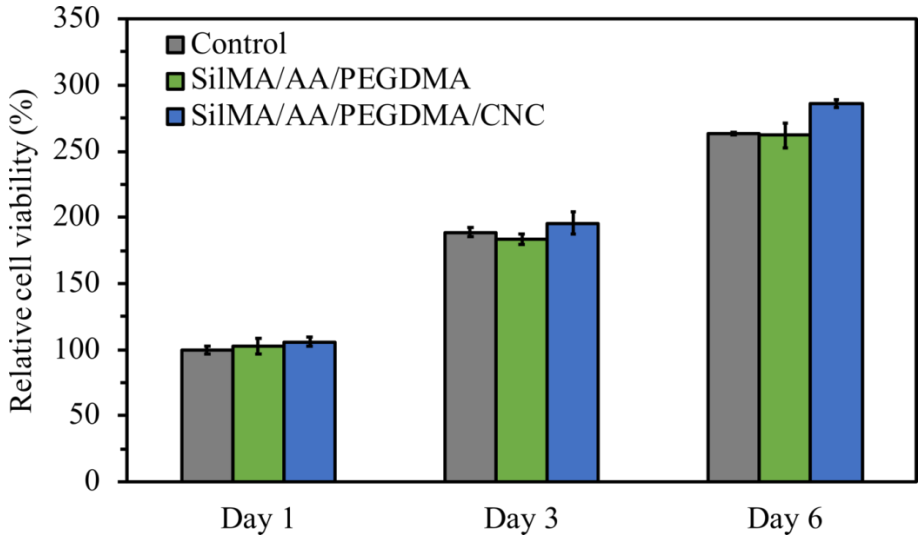


Figure 3.14: The biocompatibility properties of the silicone-based composite material. The relative cell viability of SilMA/AA/PEGDMA and SilMA/AA/PEGDMA/CNC consisting of 1 wt% of CNC for Day 1, 3, and 6. Error bar represents ± SD, $n \geq 5$.

3.4 Conclusion

In conclusion, the incorporation of 1 wt% of CNC was found to increase the printing accuracy of both the channel width and height of the microchannels, with the improvement being more prominent for channel width in the printing direction of X and Y. In terms of channel height, further adjustments are required to compromise with the residual light scattered by the 1 wt% of CNC across the previously printed layers, with measurements including but not limited to printing with a low pre-gel volume level in the printing vat, having a microchannel design with a large enough channel width in proportion to the channel height, and factoring in the potential deviation in channel height when designing the dimensions for the microchannel. Regardless, the exceptional improvement in the X and Y printing accuracy upon the integration on 1 wt% of CNC remains appealing as it leads to a near-zero deviation in the channel width dimension with no negative impact on the pre-gel properties for optimal VP printability, as proven by the successful fabrication of the direct replica of various detailed

microfluidic channel patterns down to micron scale. More importantly, CNC does not impart a distinct colour to the formulated ink material, enabling clear flow visualization when utilized in microfluidic device fabrication. In terms of functionality, the printed microfluidic devices demonstrate good fluid processibility without fluid leakages when being subjected to organic and non-organic solvents for prolonged period of up to 24 hours, elevated temperature at 60 ºC and 100 ºC for up to 5 hours, and a flow rate of up to 20 mL/min. The better organic solvent resistance than regular PDMS, sustainable hydrophilicity, and good biocompatibility of the developed hydrophilic silicone-based material further expand the potential application of the printed microfluidic device in both biological and chemical fields. Overall, the successful fabrication of a highly precise, neutral-coloured, and highly functional microfluidic device with VP printing upon the integration of CNC opens up a new frontier in the aspect of silicone printing material and fabrication method for the mass-production of silicone-based microfluidic devices in the near future.

Chapter 4 Development of Hydrophilic Silicone-based Ink with Amphiphilic Siloxane Oligomers for the 3D Printing of Embedded-channel Fluidic Devices via Vat Photopolymerization

4.1 Introduction

To enable the fabrication of embedded-channel fluidic devices, a hydrophilic silicone-based material with an even lower pre-gel viscosity and better photocuring depth tuning is preferred to avoid the overcuring of ink material within the channels during the VP printing process for the accurate generation of embedded channels. Despite the addition of AA and PEGDMA as reactive diluents in the previous formulation, the silicone-based material consisting of the high-molecular-weight SilMA remains slightly viscous with a compromised flowability that prevents the effective draining of excessive resin material through the intended voids before the printing of the next layer. Therefore, I am looking forward to formulating a new version of hydrophilic silicone-based material using low-molecular-weight oligomers and monomers for an overall lower pre-gel viscosity catering to the effective printing of void structures. Explicitly, I will be exploring the use of a linear amphiphilic siloxane oligomer with a hydrophobic siloxane chain terminated with hydrophilic poly(ethylene glycol) methacrylate (PEGMA) groups at both ends. Due to the presence of polymerizable groups at the hydrophilic PEGMA ends, these linear amphiphilic siloxane oligomers are often incorporated in small amounts as a strategy to increase the overall crosslinking density of the polymer network. To the best of my knowledge, the use of amphiphilic siloxane oligomers as the main component for resin formulation is uncommon and there is currently no study reporting on the use of the mentioned amphiphilic siloxane oligomer with an A-B-A arrangement of PEGMA-siloxane-PEGMA as the major component for the formulation of VP-printable silicone-based resin material **(Table 1.2)**. This is likely because the described siloxane oligomer was initially

considered a crosslinking monomer, and there is difficulty in dissolving the described siloxane oligomer when used in high amount due to its amphiphilic nature.

Besides, the use of 1 wt% of CNC for photocuring depth tuning in the previous chapter was revealed to be insufficient to fully limit overcuring, resulting in failure to generate embedded channels. Since the main purpose of this chapter is to highlight the use of amphiphilic siloxane oligomer as the main composition for the formulation of a hydrophilic silicone-based material, I will be adopting the conventional use of yellow dye as the photoabsorber for photocuring depth tuning. As mentioned previously, the staining of fluidic devices is not ideal for fluid flow visualization. Hence, the dosage of yellow dye needs to be carefully optimized to achieve an optimum photocuring depth while preventing heavy staining on the printing material for effective fluid flow visualization. In another aspect, as emphasized in **Section 1.3.2**, the fabrication of embedded-channel fluidic devices with VP printing remains challenging and is still in its early stage of development as most studies only managed to demonstrate simple channel geometries when printing fluidic devices with embedded channels. Moreover, most studies focused on presenting the feasibility of fabricating silicone-based fluidic devices using VP printing with a lack of investigation of the fluid processibility of the printed devices. As such, similar to **Chapter 3**, the fluid processibility of the printed devices will also be explored extensively in this chapter to prove the practicability of the printed devices, serving as evidence for the printed device to move beyond the prototyping stage for real-world practical applications.

In this chapter, I explore the use of amphiphilic siloxane oligomer as the major component for the formulation of a hydrophilic silicone-based resin material designed for the VP printing of fluidic devices with embedded channels consisting of complicated geometries. The mentioned amphiphilic siloxane oligomer will be known as silmer hereafter. The

formation of a thermosetting polymer network with only a single monomer or oligomer type often lacks flexibility for printability and mechanical properties tuning. Hence, both acrylamide (AA) and glycidyl methacrylate (GMA) are further included in small amounts as additional monomers to fine-tune the printability and mechanical properties of the thermosetting polymer network. Herein, I will first provide an overview of the formation of the silmer/AA/GMA polymer network. Then, I proceed to investigate the effect of solvent on the solubility and hydrophilicity of silmer followed by solvent ratio optimization for the formulation of resin material with ideal pre-gel properties for VP printing. Subsequently, I evaluate the impact of varying AA and GMA monomer ratios with respect to silmer in dictating the properties of the cured material, including its mechanical, chemical, biological, and printing properties. After that, I proceed with demonstrating the printing of fluidic devices with embedded channels consisting of multiple geometries using the developed material. Thereafter, the printed fluidic devices are tested for fluid leakage against different temperature and flow rate conditions with static and dynamic flow measurements, respectively. Furthermore, I investigate the performance of the printed fluidic device under actual experimental circumstances for hydrogel particle synthesis, which further enhances the potential use of the hydrophilic silicone-based fluidic device for biomedical applications.

4.2 Materials and Methods

4.2.1 Materials

Silmer (ACR Di2510) was provided by Siltech Corporation, Canada. Acrylamide (AA), glycidyl methacrylate (GMA), ethylene glycol, sodium hydroxide, chloroform, acetone, acetonitrile, N-N-dimethylformamide (DMF), hydrochloric acid, sulfuric acid, hexane, toluene, methylene chloride, diethyl ether, gelatin, amoxicillin, and soybean oil were purchased from Sigma-Aldrich Canada Ltd., Canada. Diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO)

and sorbitan monooleate (SPAN80) were purchased from TCI Chemicals, United States. Cyclohexane, tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) were purchased from Caledon Laboratories Ltd., Canada. Sylgard 184 silicone elastomer kit was purchased from Dow Silicones Corporation, United States. Ethanol was purchased from Greenfield Global Inc., Canada. Ammonium hydroxide, 0.05 % trypsin-EDTA (1X), and fluorescein-5-isothiocyanate (FITC) were purchased from Thermo Scientific Chemicals, Canada. Isopropyl alcohol (IPA) and penicillin/streptomycin were purchased from Wisent Inc., Canada. Dulbecco's Modified Eagle's Medium with 4.5 g/L glucose and L-glutamine (DMEM) was purchased from Lonza Inc., USA. Fetal Bovine Serum (FBS) was purchased from Avantor Inc., USA. MTT cell proliferation assay kit was purchased from ATCC Bioproducts, USA. All the chemicals were laboratory-grade and used as received. All the aqueous solutions were prepared using Milli-Q water (18.2 MΩ·cm).

4.2.2 Molecular Dynamics Simulation and FTIR Characterization

The simulation of the possible arrangement of the silmer in different solvents was conducted using Polymer Builder in CHARMM-GUI to perform equilibrium simulation using coarse-grained model (https://charmm-gui.org/?doc=input/polymer). An amphiphilic oligomer chain with similar characteristics to silmer with 5 monomer units of polyethylene oxide (hydrophilic), 30 monomer units of polyethylene (hydrophobic), and 5 monomer units of polyethylene oxide (hydrophilic) capped with a hydrogen atom at both ends was employed in the simulation system. The arrangement of the designed polymer chain was simulated in a polymer-solvent system with X = 54 Å, Y = 54 Å, and Z = 54 Å with a number of 20 polymer chains and 128 solvent chains against water, propanol, acetone, and THF, for which both water and propanol was noted as good solvent for the hydrophilic monomer and poor solvent for the hydrophobic monomer while both acetone and THF was noted as good solvent for both

hydrophilic and hydrophobic monomer based on the simulated solvent indicator. The specific parameters of the settings keyed into the simulation system are listed below in **Table 4.1**.

Table 4.1: The parameters for molecular dynamic simulation using Polymer Builder.

Steps	Parameters	Settings
Step 1	System Type	Solution
	Building Block(s) of Polymer	As specified above
Step 2	Box Type	Cubic
	Length of XYZ	54.4
	Solvent	Any solvent type
	#Chain	20 - 50
Subsequent steps	All the subsequent parameters	Use default settings

The change in oligomer arrangement of silmer with different solvents was further verified with Fourier transform infrared spectroscopy, FTIR (Tensor 27 FTIR, Bruker, Germany).

4.2.3 Preparation of Silmer/AA/GMA Pre-gel Solution

In brief, silmer was dispersed in a solvent mixture consisting of ethanol, ethylene glycol, and water followed by the addition of AA and GMA monomers. Firstly, a solvent mixture with varying ratios of ethanol, ethylene glycol, and water was prepared. Then, silmer was dispersed in the solvent mixture with a 1:1 ratio by weight at room temperature (22 ± 2 °C) until a homogeneous mixture was obtained. After that, a varying dosage of AA and GMA with a ratio ranging from 0.04:0.01 to 0.01:0.04 with respect to silmer was added into the pre-gel solution and stirred at room temperature (22 ± 2 °C) until complete dissolution. Finally, 3 wt% of TPO was added and stirred at room temperature for 1 hour in the dark before proceeding with printing. 3 wt% of TPO was adopted as the optimum dosage as further increment in TPO dosage does not contribute to a significant decrease in gel point with the developed material **(Figure 4.1)**. The dosage in wt% mentioned in this section was calculated based on the total monomer content of the pre-gel solution.

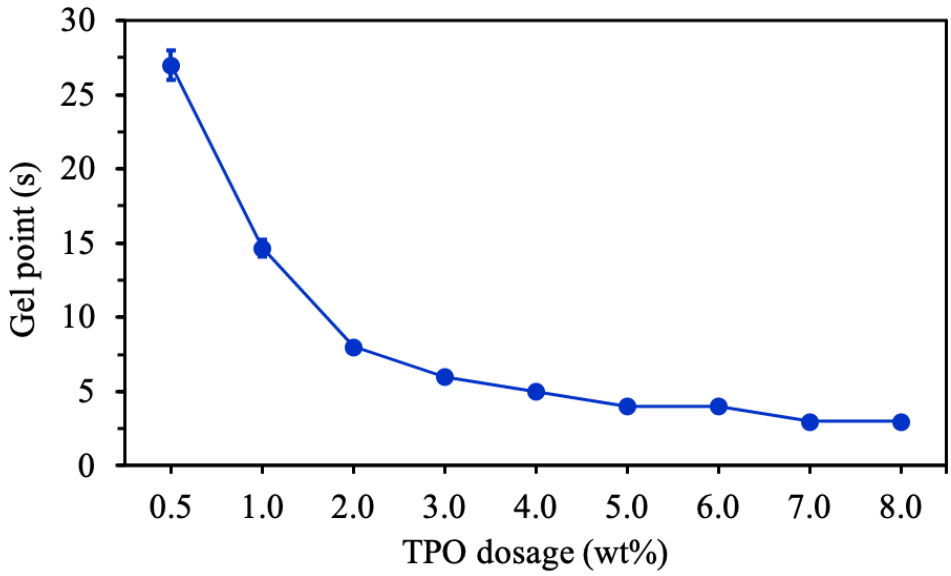


Figure 4.1: The gel point of the silmer-based material with increasing TPO dosage. The material composition used for this preliminary investigation consists of 1 silmer: 0.2 AA formulated in 1:1 ratio with ethanol. Error bar represents ± SD, n ≥ 5.

4.2.4 Pre-gel Solution Properties

The optical transmittance of the pre-gel solution at 700 nm was obtained by loading 200 µL of sample solution into the wells of a 96 well-plate followed by measurement using the UV-vis spectrophotometer (Molecular Devices SpectraMax M2, Marshall Scientific, USA). The loaded samples were further subjected to UV curing in a UVP crosslinker (Analytik jena, Germany) at 4000 µJ cm^{-2} for about 1 minute or until the samples were fully cured. The 96 well-plate was returned to the UV-vis spectrophotometer for the measurement of the optical transmittance of the cured polymer samples. The shear viscosity of the pre-gel solution was measured at a constant shear rate of 1 s^{-1} consisting of 10 samples per decade for 5 minutes at 25 ºC with the rheometer (Kinexus Ultra+, Malvern, United Kingdom) using spindle DG25 L0381 SS. The shear viscosity values obtained across the 5 minutes were reported as average.

The curing depth of the pre-gel solution was determined by measuring the thickness of the film formed with the digital caliper after being subjected to UV light (~3 mW/cm^2 at 405 nm) at different UV exposure times ranging from 0 to 60 seconds in the VP printer (Photon Mono 4K, Anycubic, China).

4.2.5 Contact Angle

A 10 µL water drop was dispensed onto the cured polymer surface followed by photographing with a digital camera. After that, the water contact angle was measured using ImageJ with 20 readings recorded from the same sample to avoid any measurement inaccuracies. The measurements were replicated on different samples and values were reported as average.

4.2.6 Rheological Properties

The storage modulus (G′), loss modulus (G″), and phase angle (δ) of the cured polymer were measured with constant shear stress at 1 Pa and constant frequency of 1 Hz for up to 5 minutes using the rheometer (Kinexus Ultra+, Malvern, United Kingdom). The values obtained across the 5 minutes were reported as average. The test was conducted at 25 ºC with 10 sample readings per decade using spindle CP2/20 L0219 SS.

4.2.7 Mechanical Properties

Both the ultimate compressive strength and ultimate tensile strength of the cured polymer were evaluated using the universal tensile machine (CETR-UMT-2MT Tribological Tester, Bruker, Germany). In terms of compression testing, a cylindrical sample with a 7 mm diameter and 4 mm height of the cured polymer was compressed at a speed of 0.05 mm s^{-1} with a 1000 N load until the sample was fractured. In terms of tensile test, a rectangular strip with 3

mm length, 1 mm width, and 2 mm thickness was pulled at a speed of 0.05 mm s^{-1} with a 100 N load until the sample fractured.

4.2.8 Chemical Compatibility Test

The cured samples were fully immersed in the respective solvent at room temperature (22 ± 2 °C) for 24 hours. Then, the swelling degree (SD) of the samples after 24 hours was calculated using the following equation:

$$SD\ \% = \frac{W_t - W_0}{W_0} \times 100\% \qquad \text{Equation 4.1}$$

where W_0 and W_t represent the weight of the cured polymer before and after swelling, respectively.

4.2.9 Biocompatibility Test

The cell viability of the NIH-3T3 fibroblast cells with the cured polymer samples was evaluated on Day 4 of culturing. NIH-3T3 fibroblast cells were selected due to it well-characterized cell behaviour, and thus, is a common cell line used for cytotoxicity testing. Firstly, the cells were cultured in DMEM supplemented with 10 % (v/v) of FBS and 1 % (v/v) of penicillin/streptomycin at 37 ºC with 5% CO_2. Before the test, the cured gel samples were soaked in 70 % ethanol for 24 hours followed by soaking, washing, and dialyzed with MilliQ water and PBS solution, respectively, for at least 1 week. The cured gel samples were cultured with cells using 6 well-plates. Subsequently, the cell viability of the respective samples on Day 4 was quantified using the MTT test based on the manufacturer's protocol. In brief, 100 µL of cell media was added with 10 µL of MTT reagent and incubated at 37 ºC for 4 hours followed by the addition of 100 µL of detergent solution and incubated at room temperature for 2 hours. Finally, the incubated cell media was transferred to a 96 well-plate for absorbance

measurement at 570 nm using the UV-vis spectrophotometer (Molecular Devices SpectraMax M2, Marshall Scientific, USA).

4.2.10 Gel point determination

The printer vat was filled with 10 mL of pre-gel solution followed by exposing the pre-gel solution with the built-in UV light source of the VP printer (Photon Mono 4k, Anycubic, China) from the bottom of the vat. The physical state of the UV-exposed pre-gel solution was checked with a scraper upon every second of UV exposure. Once a solid layer of cured gel was observed to begin to form, the minimum UV exposure time required to transform the liquid pre-gel solution to solid cured gel was recorded as the gel point for the formulated material. The content in the vat was then emptied and repeated with replicates formulated with the same material composition.

4.2.11 Three-dimensional Printing

3D structures were fabricated with the VP printer (Photon Mono 4K, Anycubic, China). Prior to printing, the 3D models were designed using FreeCAD followed by slicing with Photon workshop (Anycubic, China). Then, the structure was printed with a 100 % UV power of ~3 mW/cm^2 at 405 nm using the printing parameters as detailed in **Table 4.2**. After printing, the printed structure was removed and washed in 50 % ethanol at 800 to 900 rpm for 30 seconds, followed by air-dried before subjecting it to post-curing in a UVP crosslinker (Analytik jena, Germany) at 4000 μJ cm^{-2} for 0 to 5 minutes. Finally, the cured polymer was characterized with Fourier transform infrared spectroscopy, FTIR (Tensor 27 FTIR, Bruker, Germany).

Table 4.2: The 3D VP printing parameters and settings for all printed structures.

Parameters	Settings
Layer thickness (mm)	0.05
Exposure time (s)	20 to 60*
Off time (s)	5.0
Z Lift height [0]** (mm)	1.5
Z Lift speed [0]** (mm/s)	2.0
Z Retract speed [0]** (mm/s)	3.0
Z Lift height [1]** (mm)	4.5
Z Lift speed [1]** (mm/s)	2.0
Z Retract speed [1]** (mm/s)	3.0

**Exposure time depends on the gel time of the pre-gel solution with varying composition.*
***[0] = initial lift distance; [1] = subsequent lift distance after the initial lift distance*

4.2.12 Printing Resolution

The printing resolution of the channel in terms of width and height was evaluated in reference to the test models developed by Gensler et al., 2020 [388] with modifications to suit the purpose of channel fabrication. In terms of channel width, a test model with a gradual reduction in channel width from 1000 to 50 μm and a constant channel height of 1000 μm was employed. In terms of channel height, a test model with a gradual reduction in channel height from 1000 to 50 μm and a constant channel width of 1000 μm was employed. The printed test models were photographed and measured using ImageJ.

4.2.13 Preparation of PDMS

PDMS sample was prepared using Sylgard 184 silicone elastomer as a control material. Sylgard 184 was prepared according to the manufacturer's instruction with a 10 to 1 mix ratio of base to curing agent by weight. Then, the mixture was cured in moulds at room temperature (22 ± 2 °C) for 72 hours.

4.2.14 Synthesis of Amoxicillin Drug-encapsulated Gelatin Hydrogel Beads

The 4 % gelatin solution was prepared by dissolving the gelatin powder in water at 50 ºC for at least 30 minutes. The FITC-labelled amoxicillin drug solution was prepared following the manufacturer's protocol by first dissolving 10 mg of amoxicillin in 1 mL of 0.1 M sodium bicarbonate buffer at pH 8.3 followed by slowly adding in 10 mg of DMSO per mL of the drug solution while stirring and left to incubate at room temperature for at least 1 hour in the dark before purification. Both the gelatin and FITC-amoxicillin solution were mixed and extruded into the oil bath for the formation of hydrogel beads. The oil bath consists of soybean oil with 3 wt% of SPAN80 mixed for at least 3h and stored at 4 ºC prior to use.

4.3 Results and Discussion

4.3.1 Silmer/AA/GMA Polymer Network

Silmer is an amphiphilic siloxane oligomer with an A-B-A linear chain arrangement of PEGMA-siloxane-PEGMA **(Figure 4.2a)**, for which PEGMA and siloxane contribute to the hydrophilic and hydrophobic properties of silmer, respectively. The siloxane chain was calculated to have an average chain length of about 33 to 34 Si-O monomer units based on the average molecular weight of 2,800 g/mol. Further FTIR characterization confirms the presence of siloxane chains in silmer with the emergence of peaks at 1260, 1010, and 800 cm^{-1} representing Si-$\underline{CH_3}$, Si-O-Si, and $\underline{Si\text{-}C}H_3$, accordingly **(Figure 4.2b)**. [412] On the other hand, the presence of the PEGMA group in silmer was justified by the emergence of peaks at 1720, 1638, 1188, and 1088 cm^{-1} representing the C=O,[453] C=C,[454,455] C-O-C in ester,[456] and C-O-C in ether,[456] respectively. Among the functional groups mentioned, the presence of the C=C bond of the methacrylate group in PEGMA is vital for the formation of a crosslinked silicone polymer network upon photoinitiation. This is because the C=C bond often serves as the growth

point for polymerization owing to its ability to form radicals for chain-growth polymerization upon initiation. Therefore, due to the presence of growth points at both ends, silmer is often included as a crosslinking monomer in a small amount to form branches connecting linear polymer chains for an optimally crosslinked polymer network.

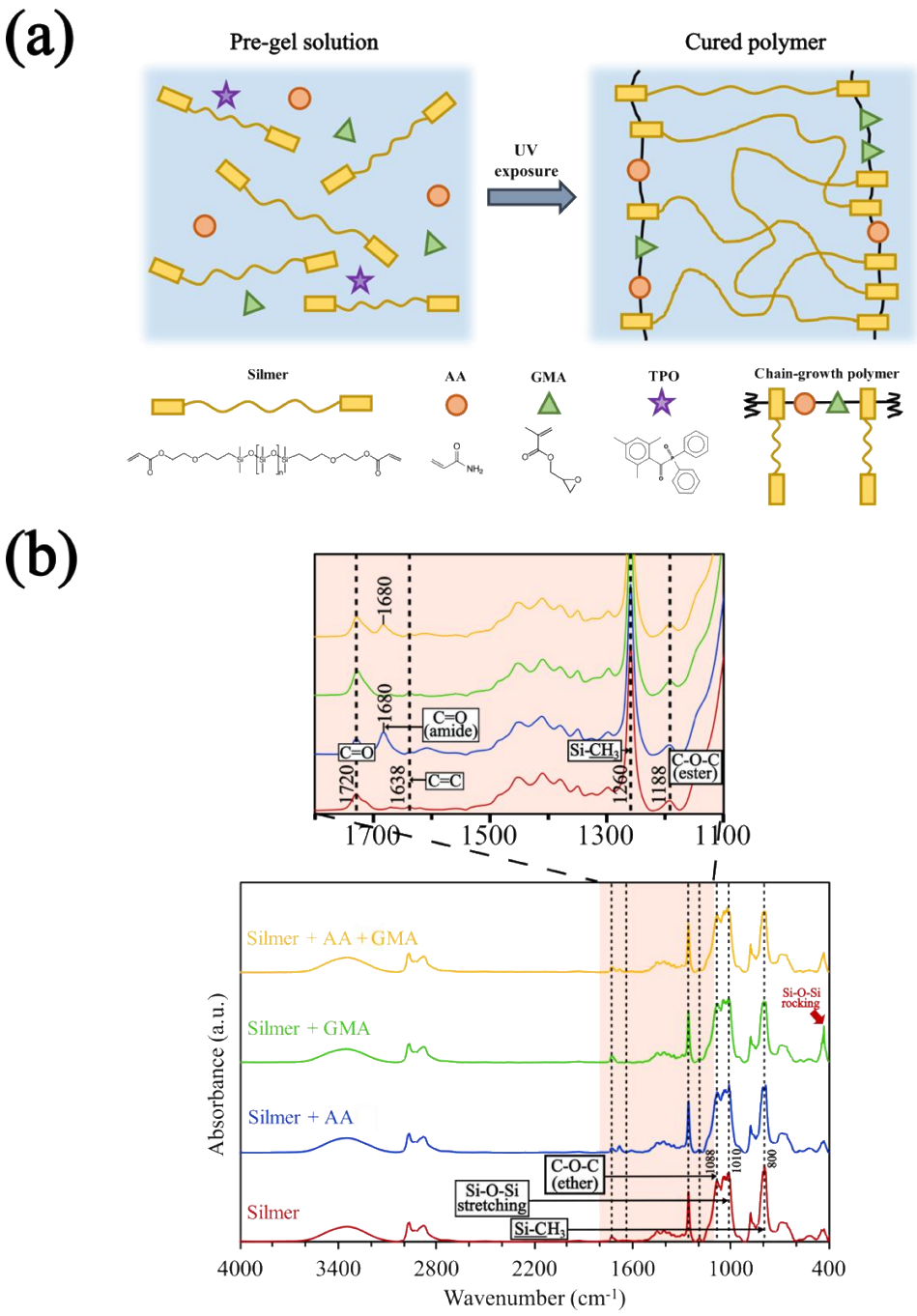


Figure 4.2: The illustration and characterization of the silmer, acrylamide (AA), and glycidyl methacrylate (GMA) polymer network. (a) The schematic diagram for the

formation of silmer, AA, and GMA polymer network based on chain growth polymerization upon UV exposure in the presence of TPO as the photoinitiator. The chemical structure of silmer, AA, GMA, and TPO are shown below their respective legend keys. **(b)** The FTIR spectra of silmer (S), silmer with AA (S: A), silmer with GMA (S:G), and silmer with AA and GMA (S:A:G) formulated with the respective monomer ratio of S = 1, S:A = 1:0.05, S:G = 1:0.05, and S:A:G = 1:0.025:0.025.

Differing from the usual approach, this study proceeds with investigating the utilization of silmer as the major monomer composition for the formulation of a hydrophilic silicone-based polymer network. However, silmer was revealed to have a comparatively slow curing rate when used solely with a high amount of photoinitiator (~10 wt%) required for rapid photocuring. The slow photocuring rate of silmer might be due to the presence of less reactive side groups that hinders the formation of silmer radicals at the growth point. Hence, additional monomers with better reactivity in radical formation are incorporated as a strategy to enhance the overall photocuring speed of the silmer polymer network. Specifically, acrylamide (AA) monomer was well-known to polymerize quickly upon photoinitiation due to the presence of its amide side group in favoring the formation of AA radicals **(Figure 4.2a)**. Additionally, AA is a common building block for hydrophilic polymers intended for biomedical use, which aligns with my purpose in designing a hydrophilic silicone-based material for biomedical applications. As such, AA was selected for inclusion into the silmer polymer system to elevate the overall photocuring speed of the silmer polymer network. The further inclusion of AA into the silmer polymer network was characterized by the emergence of an FTIR peak at 1680 cm^{-1} representing the C=O of the amide group **(Figure 4.2b)**. [413,457]

Despite the faster photocuring speed upon the inclusion of AA, the cured silmer polymer was found to be very brittle with no improvement in elasticity based on preliminary

investigations. This likely infers that a dense polymer network of silmer/AA is formed upon photopolymerization, resulting in a polymer network with high crystallinity that fractures easily upon stress applied. Hence, glycidyl methacrylate (GMA) is incorporated as the third monomer in hopes of inducing a slight disorder in the highly packed silmer/AA polymer network with the presence of its epoxy side group **(Figure 4.2a)**. The slight disruption in the highly ordered arrangement of the dense polymer network would essentially allow the polymer chains to slide past each other more easily, leading to an increase in elasticity and flexibility. The successful interruption of the highly packed silmer/AA polymer network with GMA is further evidenced by the emergence of peak at 438 cm^{-1} representing Si-O-Si rocking upon the addition of GMA as the emergence of Si-O-Si rocking indicates the change in siloxane chain conformation in the presence of GMA **(Figure 4.2b)**.[458] Thus, aside from elevating the photocuring speed, the incorporation of additional monomers provides evidence of altering the polymer network arrangement, and therefore the mechanical properties of the final polymer material, offering the flexibility to fine-tune polymer characteristics by varying the monomer composition. The effect of the different AA and GMA monomer compositions with respect to silmer on the cured polymer properties will be further discussed in the following section. Henceforth, I proceed with the formulation of a hydrophilic silicone-based resin material with silmer as the major monomer composition complemented with AA and GMA for the formation of a thermosetting silicone-based polymer network based on chain growth polymerization upon UV exposure as illustrated in **Figure 4.2a**.

4.3.2 Solvent Effect on Pre-gel and Surface Properties

Following the selection of monomer precursor, I further proceed with investigating the effect of solvent on silmer followed by the optimization of solvent blend for optimum pre-gel and surface properties. The dissolution of monomers with a suitable solvent is an essential step

for the formulation of a pre-gel solution. As silmer appears to be the major component of the silicone polymer network, the dissolution of silmer will be prioritized over AA and GMA when considering the selection of a suitable solvent for monomer dissolution. Then, the final selected solvent will be tested against AA and GMA to ensure the complete dissolution of all components for a homogeneous distribution of the monomers within the pre-gel solution. Due to the nature of silmer being an oligomer, the behaviour of silmer aligns more closely with polymers rather than individual monomers when exposed to solvents. Generally, the arrangement of polymers in the solvent depends highly on their interaction with the surrounding solvent molecules.[402,403,459] Consequently, when a good solvent is used, the polymer chains expand due to polymer-solvent interactions, resulting in a clear solution appearance. On the contrary, when a poor solvent is used, the polymer chains tend to collapse as the polymer-polymer interactions are promoted, which usually leads to an opaque appearance as the polymer aggregates scatter light within the suspension. Therefore, the choice of an appropriate solvent is crucial to facilitate the expansion of silmer within the solvent, resulting in a clear solution appearance. Nevertheless, the fact that silmer is amphiphilic adds an additional layer of complexity to the task of finding an appropriate solvent that can dissolve silmer without causing the creation of silmer aggregates.

Based on **Figure 4.3**, silmer was revealed to have a clear appearance when dissolved in ethanol and isopropyl alcohol (IPA) with 1:1 ratio of silmer to solvent, which is most likely attributed to the good interaction between silmer and the amphiphilic solvent molecules due to their similarity in chemical composition. Conversely, silmer was observed to exhibit an opaque appearance when dissolved in water, which is most likely due to the inability of the highly hydrophilic water molecules to interact with the hydrophobic section of the amphiphilic silmer, leading to the formation of silmer aggregates. Additionally, it was noted that the pre-gel viscosity of silmer exhibited a substantial rise, resulting in the formation of a gel-like

consistency, upon dissolution in water. The increase in pre-gel viscosity rules out water as a choice of solvent when used solely for silmer dissolution as VP printing prefers ink with low pre-gel viscosity. [43,85] Interestingly, silmer presents a translucent appearance when dissolved in hexane instead of solid white as with water. Similarly, the hydrophilic portion of the amphiphilic silmer has limited interaction with the hydrophobic hexane molecules, leading to the formation of silmer aggregates. However, the less opaque appearance of silmer with hexane further reaffirms that silmer has a higher composition of hydrophobic siloxane chains than hydrophilic PEGMA groups. This is because the hydrophobic siloxane chain is capable of interacting and expanding seamlessly while the hydrophilic PEGMA group forms aggregate in the presence of non-polar solvent. As such, the translucent appearance reflected by the low amount of silmer aggregate suggests that silmer has an overall lower composition of the hydrophilic PEGMA group. To provide a clear interface for fluidics application, the silicone ink containing silmer was further formulated with amphiphilic solvents for a clear pre-gel solution. Particularly, I chose to proceed with ethanol as silmer formulated with IPA was revealed to cure significantly slower owing to the chain transfer properties of IPA. [460,461]

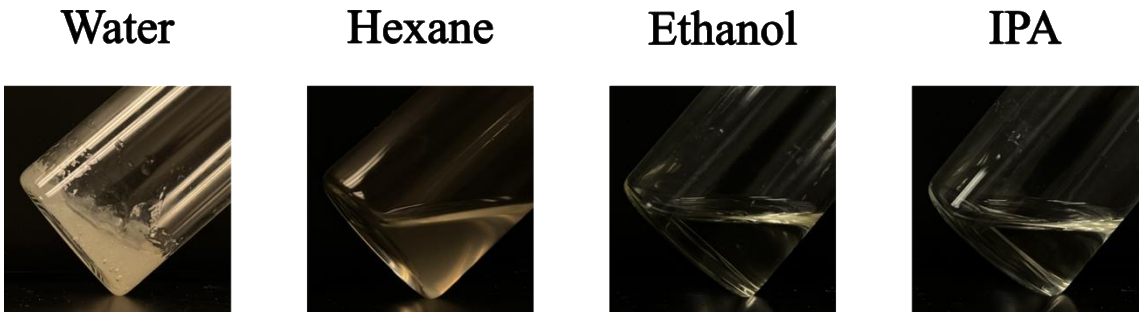


Figure 4.3: The effect of solvent on the solubility of silmer. The pre-gel appearance of silmer with water, hexane, ethanol, and isopropyl alcohol (IPA).

Besides having a clear device interface, the final printed structure will need to acquire hydrophilic surface properties to cope with the aqueous solutions used for biomedical

applications. Typically, polymers with a water contact angle below 90º are regarded as hydrophilic, while those with a water contact angle above 90º are considered to have hydrophobic surface properties. Based on **Figure 4.4,** despite the presence of hydrophilic PEGMA groups in silmer, the cured silmer polymer formulated with ethanol was found to have hydrophobic surface properties with a water contact angle of 102.6 ± 3.0º. There have been studies showing that solvents with different solvent qualities can induce conformational changes in amphiphilic polymers, and thus, possibly altering the surface properties of the amphiphilic polymer by varying the proportion of polar and non-polar groups on the surface of the polymer. [402,403] Therefore, a number of amphiphilic solvents were further investigated in a 1:1 ratio mix with ethanol in hopes of altering the surface properties of silmer to have a higher portion of PEGMA groups on the silmer polymer surface for hydrophilic surface properties. The incorporation of ethylene glycol, diethylene glycol, ethylhexanoic acid, and dibenzyl ether with ethanol, respectively, were revealed to aid in the formation of silmer polymer with hydrophilic surfaces **(Figure 4.4)**. However, silmer that was prepared using a combination of ethanol with acetone, methyl ethyl ketone (MEK), ethyl acetate, and tetrahydrofuran (THF), accordingly, were observed to retain their hydrophobic properties.

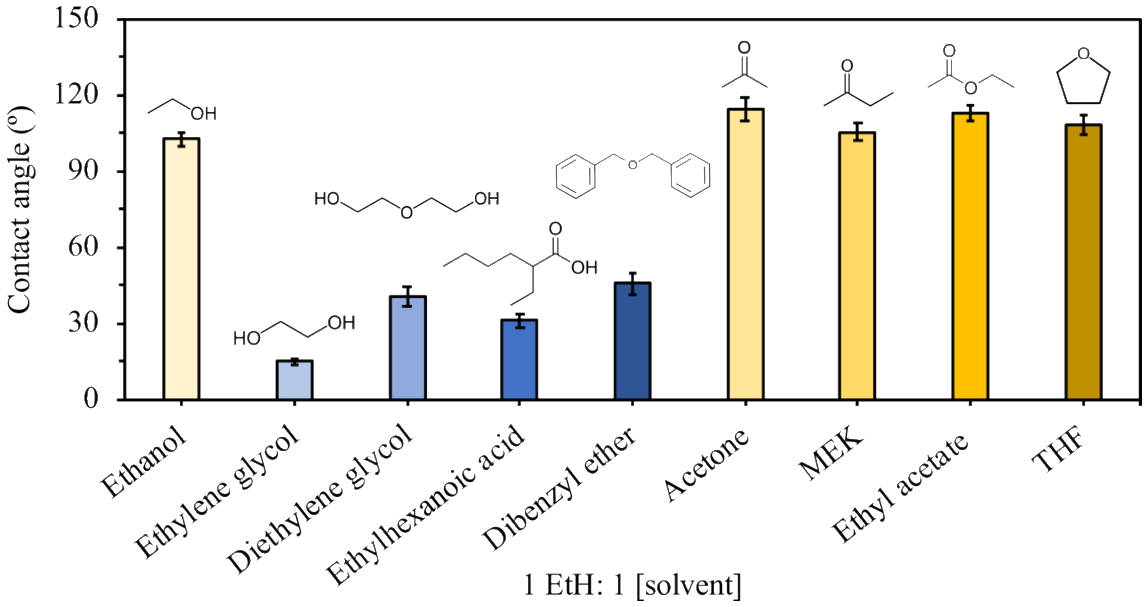


Figure 4.4: The effect of solvent on the surface properties of silmer. The water contact angle of cured silmer polymer formulated with 1:1 solvent ratio of ethanol to different amphiphilic solvents. Error bar represents ± SD, n ≥ 5.

Further molecular dynamic (MD) simulation suggests that solvents that facilitate the creation of hydrophilic surfaces may possess unique solvent properties in relation to the polar and non-polar components of silmer. The MD simulated polymer/solvent system consists of amphiphilic polymers with PA (pink sphere) representing hydrogen atoms, PB (blue sphere) representing hydrophilic blocks, and PC (yellow sphere) representing hydrophobic blocks, together with solvent molecules represented by white spheres **(Figure 4.5)**. Specifically, the solvents that help with the creation of hydrophilic surfaces were observed to exhibit characteristics of being a low-quality solvent for hydrophobic siloxane chains, while being a high-quality solvent for the hydrophilic PEGDMA groups. With that, the amphiphilic polymer results in a conformation where the hydrophobic section is sandwiched between the hydrophilic groups as the solvent favors interaction with the hydrophilic groups and not the hydrophobic groups. In contrast, the use of an equally good solvent for both the polar and non-polar composition of silmer encourages the random arrangement of silmer as there is no formation

of polymer aggregates. Subsequently, the initially higher composition of the siloxane chain than the PEGMA group in silmer further contributes to the hydrophobic surface properties when arranged randomly.

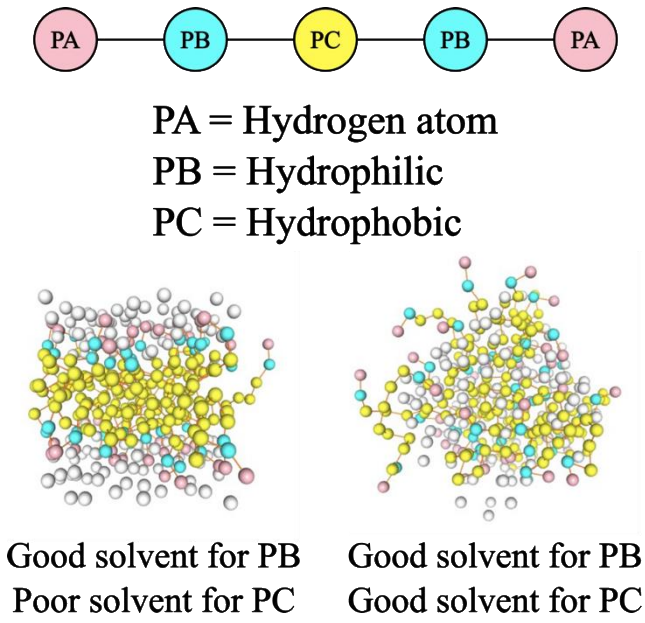


Figure 4.5: The molecular dynamic (MD) simulation of silmer-solvent interaction. The MD simulation on the amphiphilic polymer arrangement when subjected to two different solvent types.

The change in silmer conformation with solvent is further evidenced by the FTIR spectra shown in **Figure 4.6**. Upon the inclusion of ethylene glycol to ethanol, the absorbance at 1010 cm^{-1} representing Si-O-Si stretching was revealed to increase with a significant reduction in the absorbance at 438 cm^{-1} representing Si-O-Si rocking. [458] The peaks at 1010 and 438 cm^{-1} are marked in blue and green, respectively. The significant reduction in Si-O-Si rocking implies the collapse of the siloxane chains upon the inclusion of ethylene glycol, which aligns with the MD simulation where the siloxane chains fold compactly to form distinct layers of polymer with hydrophobic siloxane chains being sandwiched between the hydrophilic

PEGMA groups. Therefore, it is evident that the change in solvent can alter the silmer conformation for a change in surface properties. Additionally, the inclusion of a poor solvent with respect to hydrophobic groups can help structure the hydrophilic groups of the silmer to the surface of the cured polymer for hydrophilic surface properties. Among the solvents investigated, ethylene glycol was found to generate the most hydrophilic surface with a water contact angle of 14.8 ± 0.9 º when mixed with ethanol **(Figure 4.4)** and was further selected to proceed with the further optimization of the formulation.

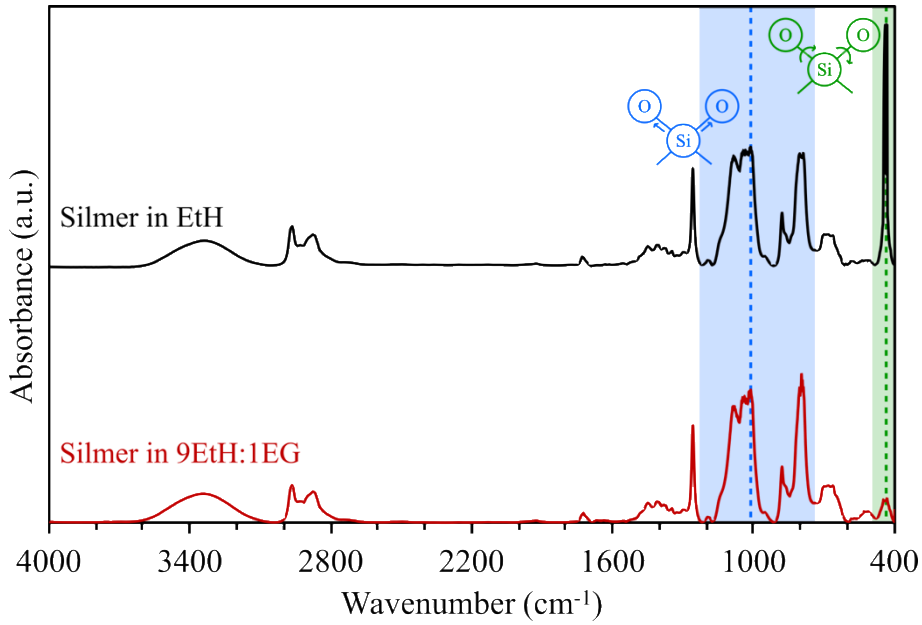


Figure 4.6: The FTIR spectra of silmer with different solvent blend. The FTIR spectra of silmer with ethanol (EtH) and with 9:1 ratio of EtH to ethylene glycol (EG) with the peaks at 100 and 438 cm^{-1} representing Si-O-Si stretching and Si-O-Si rocking are marked in blue and green, respectively.

Prior to the further optimization of the solvent ratio, a monomer ratio of silmer, AA, and GMA of 1:0.04:0.01 was selected to proceed with the optimization of the solvent ratio. The optimization of the monomer ratio will be discussed further in detail in the subsequent section. Based on **Figure 4.7a**, the water contact angle of silmer was found to lower from 34.5

± 2.3 to 14.8 ± 1.9º as the ethylene glycol (EG) content in the solvent mixture increases relative to ethanol (EtH) from 9 EtH:1 EG to 2 EtH:8 EG, accordingly. The water contact angle of silmer was observed to further reduce down to 11.2 ± 1.1º with the use of EG only as the solvent. This stands in contrast to the hydrophobic surface properties of conventional PDMS material as reflected by the water contact angle at 109.3 ± 4.9º. However, the pre-gel viscosity was found to increase with the increasing content of EG **(Figure 4.7b)**. Theoretically, the pre-gel viscosity of the resin material is recommended to be less than 5 Pa·s for a stable VP printing process. [85,86] In this study, I further benchmarked the pre-gel viscosity of the developed resin material against that of the commercial acrylate-based resin material from Anycubic at 186 ± 3 mPa·s. Therefore, any value of pre-gel viscosity above that of the commercial resin material will be deemed as less suitable to proceed with VP printing. Furthermore, the increase in EG content results in a slight reduction in the transparency of both the pre-gel solution and cured polymer, with the effect being amplified when formulated solely with EG as the solvent, leading to an opaque appearance with 12.9 ± 8.4 % and 17.6 ± 6.5 % of light transmitted through the pre-gel solution and cured polymer, respectively **(Figure 4.7c)**. It is worth noting that the behaviour of silmer when dissolved in water is very similar to this occurrence when combined with EG **(Figure 4.3)**. The increase in pre-gel viscosity and reduction in transparency with EG further implies EG as a poor solvent with respect to the hydrophobic siloxane chain, which causes the formation of a high amount of silmer aggregates as reflected by the opaque appearance of both the pre-gel solution and cured polymer. As indicated previously, silmer aggregation is necessary for the organization of hydrophilic groups to the surface of cured silmer polymer for hydrophilic surface qualities. However, excessive silmer aggregation would result in an opaque appearance accompanied by a surge in pre-gel viscosity. For this reason, it is of utmost importance to only induce an ideal amount of silmer aggregation

for the generation of hydrophilic surfaces while maintaining the transparent appearance and low pre-gel viscosity of the formulated material.

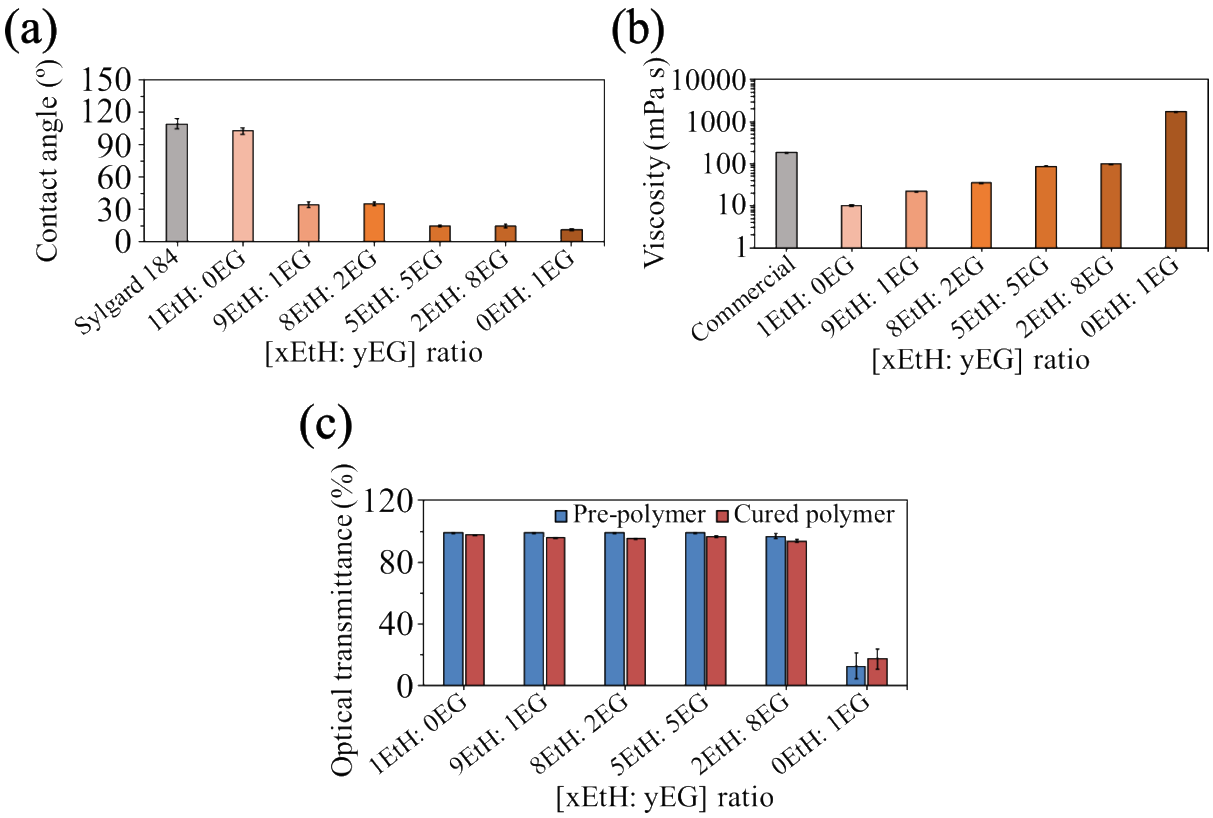


Figure 4.7: The effect of increasing ethylene glycol content in the ethanol (EtH): ethylene glycol (EG) solvent blend on the material properties of silmer/AA/GMA polymer. (a) The contact angle of the cured polymer. **(b)** The viscosity of the pre-polymer solution. **(c)** The optical transmittance of the pre-polymer and cured polymer at 700nm. The control commercial resin material used for comparison is an acrylate-based resin material from Anycubic. Error bar represents ± SD, $n \geq 3$.

Moving on, the effect of EG content on the rheological properties of the silmer/AA/GMA polymer was investigated **(Figure 4.8)**. The silmer/AA/GMA polymer was revealed to increase in stiffness with the EG content. This is reflected by the values of tan δ approaching 0 as the loss modulus (G″) representing the viscous component in the viscoelastic

material reduces steadily with the increasing EG content. The increase in stiffness with EG might be due to the increase in hydrogen bond formation between the silmer polymer with the hydroxyl groups (-OH) in EG. By considering all the possible criteria, the solvent mixture of 9:1 of EtH:EG appears to be the optimum ratio for the generation of cured silmer polymer with hydrophilic surfaces without much impact on the pre-gel viscosity, transparency, and viscoelastic properties.

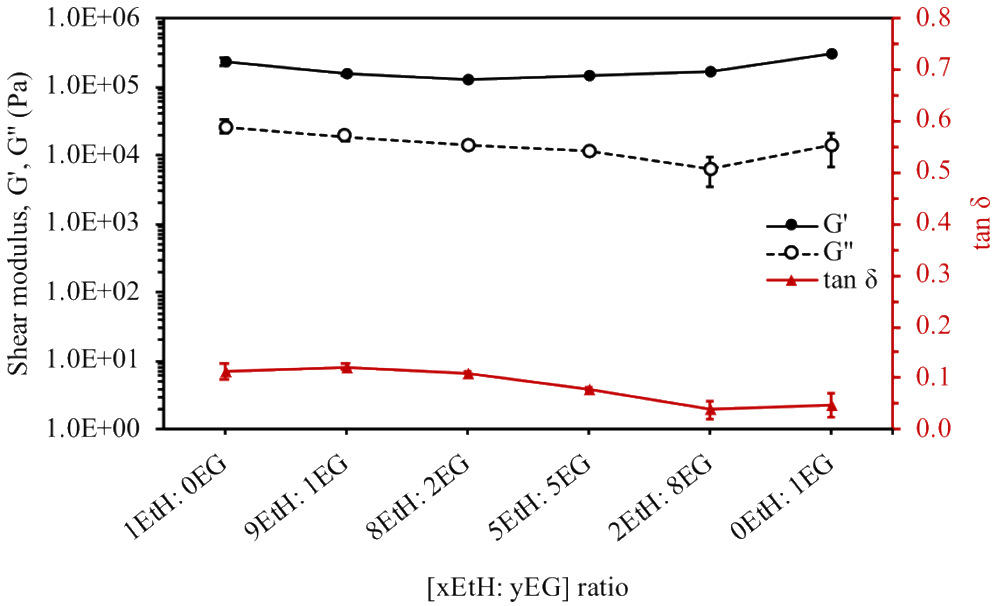


Figure 4.8: The effect of increasing ethylene glycol content in the ethanol (EtH): ethylene glycol (EG) solvent blend on the rheological properties of silmer/AA/GMA polymer. The storage modulus, G′, loss modulus, G″, and tan δ of the silmer/AA/GMA cured polymer with varying EG content in the EtH: EG solvent blend. Error bar represents ± SD, n ≥ 3.

Despite achieving the targeted properties, the pre-gel solution formulated with 9 EtH:1 EG was observed to have relatively slow photocuring properties. There have been studies showing that solvent plays a critical role in affecting the rate of free radical polymerization of monomers. [462,463] For instance, N,N-dimethylacrylamide was revealed to have a 2.7 and 8.5 times slower polymerization rate when formulated with ethylene glycol and methanol as the

solvent, respectively, instead of water. [463] This aligns with my observation on the slow polymerization rate of silmer pre-gel solution containing AA and GMA monomers when formulated with a 9:1 ratio of EtH:EG solvent mixture. As AA monomer demonstrates a higher reactivity than silmer and GMA for polymerization due to the nature of its side group, further solvent formulation will focus on increasing the polymerization rate of AA monomer as a strategy to increase the overall polymerization rate of the silmer pre-gel solution. Studies have revealed that both AA and methacrylamide (MAA) monomers were found to polymerize quickly in the presence of water. [462,463] Specifically, the water molecules were found to aid in the reorientation of the bond-forming group as the water molecules formed hydrogen bonding with both the carbonyl (-C=O) and amino ($-NH_2$) groups of the respective monomers. [462] Upon the reorientation of the bond-forming group, both AA and MAA can polymerize more rapidly as the bond-forming group gains increased exposure to the surrounding medium for better access to monomers for polymerization. Concerning that, further investigations were conducted by including water as part of solvent formulation. Based on **Figure 4.9**, the addition of 1-part of water to the EtH:EG solvent mixture was found to increase the curing rate significantly with the overall curve of curing depth against exposure time shifting towards the left, demonstrating a shorter exposure time required for a designated curing depth. Despite the increase in curing rate with the ratio of water included, further addition of water was observed to elevate the pre-gel viscosity and reduce transparency, which aligns with the observation made on silmer with water in **Figure 4.3**. Hence, a final solvent ratio of 8:1:1 of EtH:EG:H_2O was employed for a relatively fast curing rate without severely impacting the other targeted properties of the silmer pre-gel solution and cured polymer.

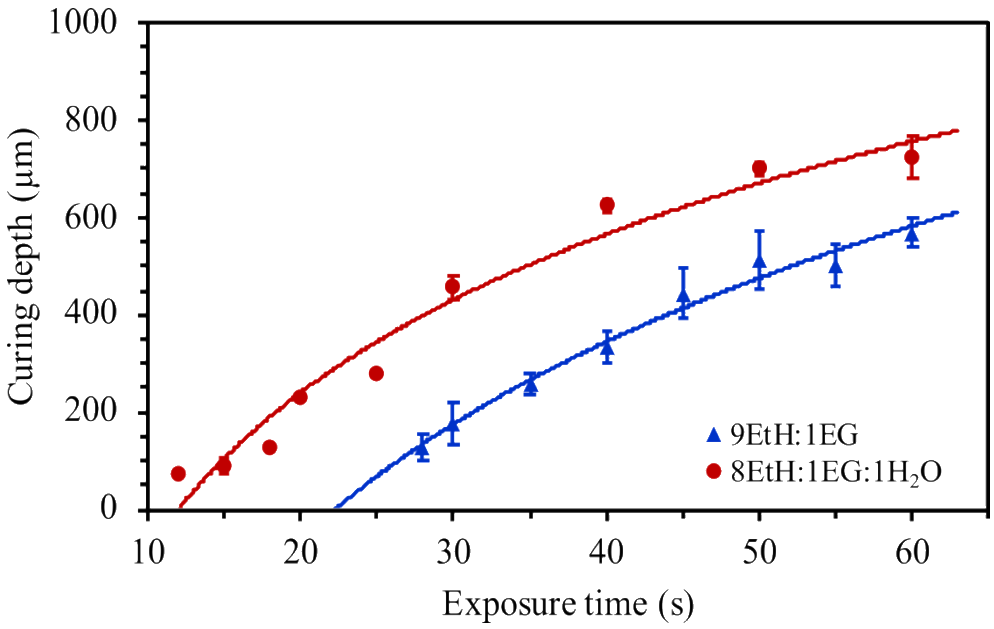


Figure 4.9: The curing depth of the composite polymer. The curing depth of the composite polymer when dissolute in 9 EtH:1 EG and 8 EtH:1 EG: 1 H_2O solvent blend across a range of exposure times. Error bar represents ± SD, n ≥ 3.

4.3.3 Monomer Ratio Effect on Cured Polymer Properties

After identifying the optimum solvent blend ratio for the developed material, I further proceed to investigate the effect of different AA and GMA monomer ratio with respect to silmer on the cured polymer properties before identifying an optimum monomer ratio to proceed with printing. In terms of rheological properties, the silmer polymer demonstrates elastomeric properties resembling that of viscoelastic solids as reflected by the higher storage modulus (G′) as opposed to the loss modulus (G″) for all the respective samples, regardless of the dosage of AA and GMA **(Figure 4.10)**. Upon the sole inclusion of 0.05-part of AA to 1-part of silmer, the strength of the silmer polymer was observed to increase as reflected by the proportional increase in G′ and G″. This further provides evidence of the role of AA in imparting strength to the silmer polymer due to its ability to increase the crosslinking density within the silmer polymer network. On the other hand, further incorporation of GMA in a small

amount with respect to AA (0.04 AA:0.01 GMA) was found to aid in improving the elasticity of silmer polymer as demonstrated by the slight drop in tan δ as a result of the increase in elastic component (G′) with respect to viscous component (G″), as tan δ represents the ratio of G″:G′. [411,419,420] The similar rheological profile of silmer polymer with an equal proportion of AA and GMA (0.025 AA:0.025 GMA) further confirms the role of GMA in imparting elasticity to the silmer polymer. These observations on the rheological properties of silmer polymer upon the incorporation of GMA align with the discussion in **Section 4.3.1** on the capability of GMA in improving the elasticity of the silmer polymer network by interfering with the arrangement of the highly packed silmer polymer network as evidenced by the FTIR spectrum in **Figure 4.2b**. However, the further increase in GMA with respect to AA (0.01 AA:0.04 GMA) was revealed to result in a silmer polymer with low strength and less elasticity as implied by the drop in G′ and G″ followed by the reduction in elastic component represented by the rise in tan δ, respectively **(Figure 4.10)**. The sharp drop in G′ and G″ along with the surge in tan δ upon the sole inclusion of 0.05-part of GMA to 1-part of silmer further implies the creation of a weak silmer polymer when a high dose of GMA is used. Hence, GMA should be incorporated in small amounts with respect to AA for the best results in terms of rheological properties. In conjunction with that, both silmer with an additional monomer ratio of 0.04 AA:0.01 GMA and 0.025 AA:0.025 GMA appear to be within the range for the formulation of an ideal silicone-based polymer with silmer, AA, and GMA due to the optimum strength and elasticity as reflected by the relatively high G′ and G″, and the low tan δ value, accordingly.

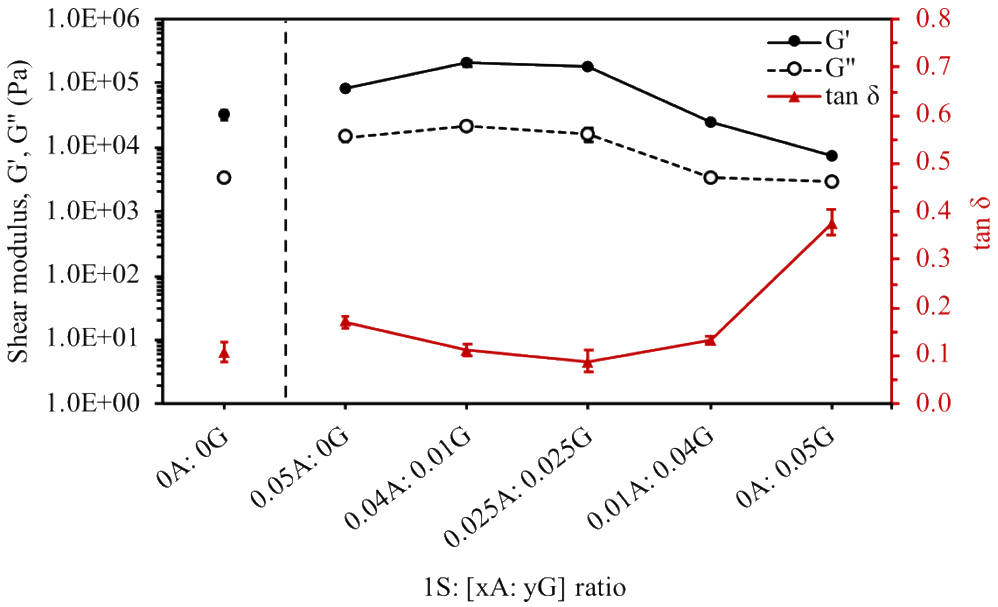


Figure 4.10: The rheological properties of silmer/AA/GMA cured polymer with varying AA and GMA monomer ratio. The storage modulus, G′, loss modulus, G″, and tan δ, of the silmer/AA/GMA cured polymer with different proportion of AA and GMA monomer content. Error bar represents ± SD, n ≥ 5.

Next, I investigated the compression and tensile properties of silmer/AA/GMA polymers with different AA and GMA monomer ratios relative to silmer. Based on **Figure 4.11a** and **4.11b**, the gradual increase in compressive modulus at 10 and 30 % with the increasing content of AA with respect to GMA further confirms the role of AA in imparting strength. Interestingly, the compression at break of the silmer/AA/GMA polymer remains comparatively similar within the range of 54 to 57 %, regardless of the AA and GMA monomer ratio. This suggests that the compressibility of the silmer/AA/GMA polymer is largely influenced by the constant silmer content within the polymer, with the amount of both AA and GMA being too small to significantly influence the compressibility of the silmer/AA/GMA polymer.

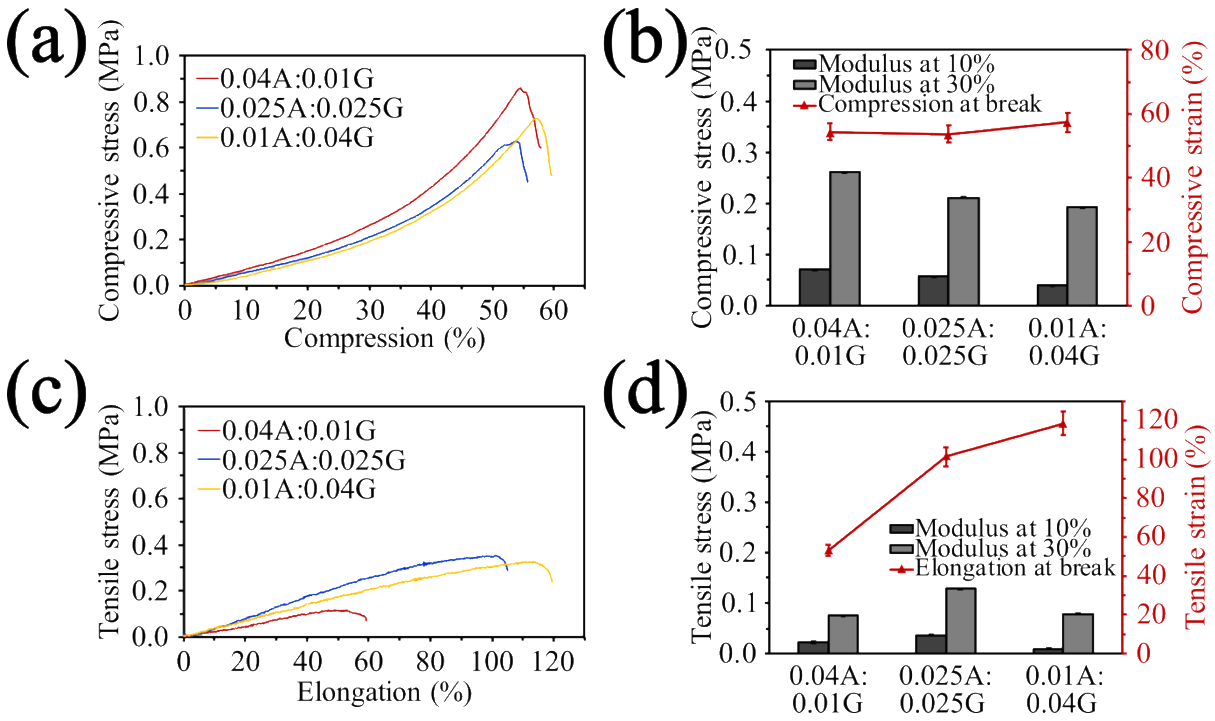


Figure 4.11: The mechanical properties of the silmer/AA/GMA cured polymer with varying AA and GMA monomer ratio. (a) The compressive stress-strain curve, **(b)** the compressive modulus at 10 % and 30 %, and the compression at break. **(c)** The tensile stress-strain curve, **(d)** the tensile modulus at 10 % and 30 %, and the elongation at break. Error bar represents ± SD, n ≥ 5.

On the contrary, the varying AA to GMA monomer ratio with respect to silmer was observed to have a significant impact on the elasticity of the silmer/AA/GMA polymer as reflected by the tremendous increase in elongation at break from 53 to 118 % as the GMA content increases from 0.01- to 0.04-part with respect to 0.04- to 0.01-part of AA **(Figure 4.11c** and **4.11d)**. This aligns closely with all the previous analyses regarding the role of GMA in imparting elasticity to the silmer polymer upon its inclusion. As for the AA monomer, a high AA content relative to GMA (0.04 AA: 0.01 GMA) was observed to produce a relatively brittle silmer polymer, resulting in a lower tensile modulus that stands out as an outlier among the three sets of samples. Further increase in GMA content from 0.025- to 0.04-part with respect

to the reduction in AA content from 0.025- to 0.01-part, respectively, was found to result in a gradual reduction in tensile modulus, which closely resembles the trend observed for compressive moduli. Moreover, the change in AA:GMA monomer ratio with respect to silmer has no significant impact on the hydrophilicity, viscosity, and transparency of the silmer/AA/GMA polymer **(Figure 4.12)**.

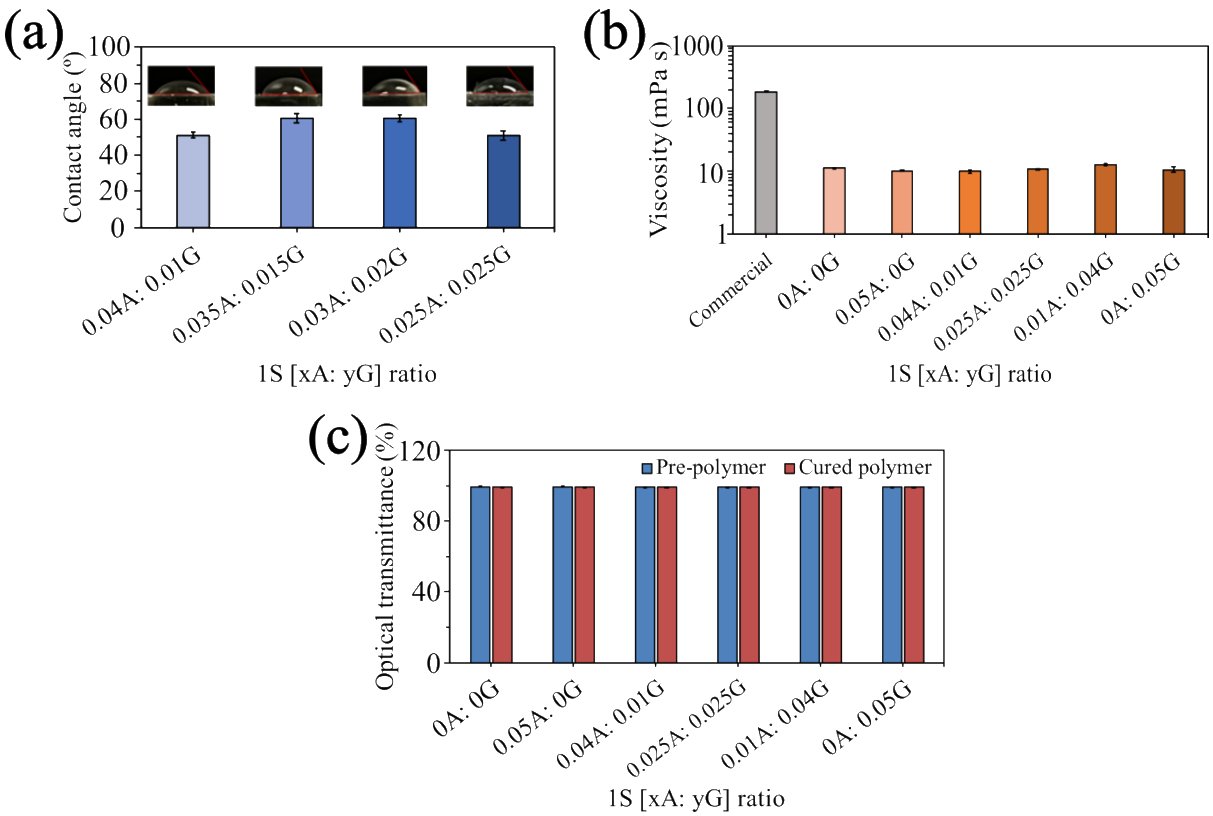


Figure 4.12: The effect of different AA and GMA monomer ratio on the material properties of silmer/AA/GMA polymer. (a) The contact angle of cured polymer, **(b)** pre-gel viscosity, and **(c)** optical transmittance of pre-polymer and cured polymer at 700 nm of the silmer/AA/GMA polymer with varying monomer ratio of AA:GMA with respect to silmer. The control commercial resin material used for comparison is an acrylate-based resin material from Anycubic. Error bar represents ± SD, $n \geq 3$.

In general, the developed material demonstrates mechanical properties in the range of elastomeric materials upon comparison with the Ashby modulus-density chart [464] as shown in **Figure 4.13**. However, high elasticity is not a necessary material characteristic for fluid processibility when fabricating fluidic devices with the developed material. Therefore, when considering the formulation of silmer/AA/GMA polymer for the VP printing of fluidic devices, it is important to understand that a final polymer material with sufficient strength and elasticity to withstand the required fluid pressure is adequate for the fabrication of fluidic device with effective fluid processibility.

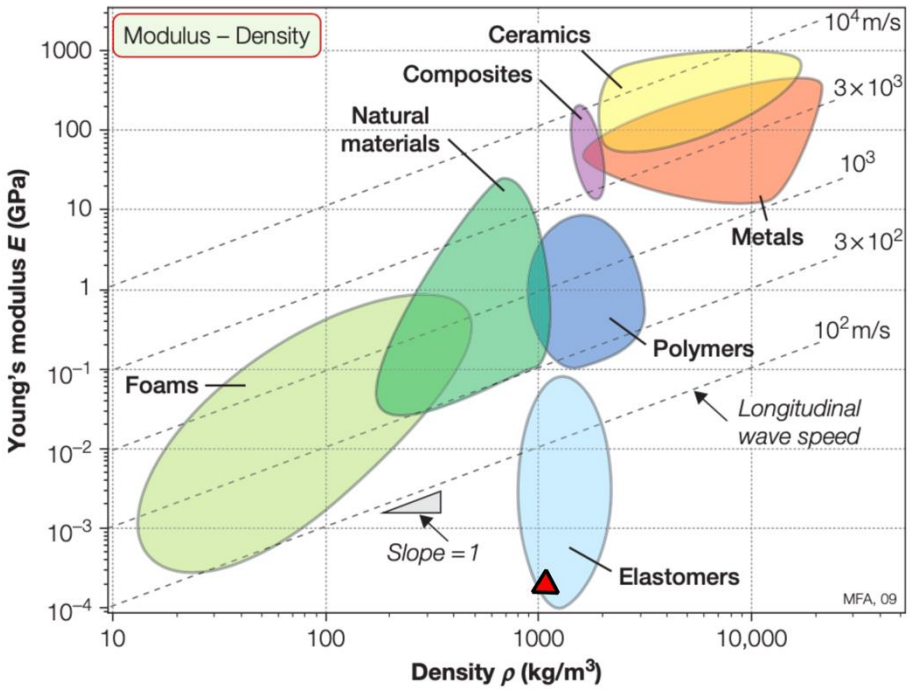


Figure 4.13: The modulus-density chart of the general range of material derived from Ashby 2011. The silmer/AA/GMA material is marked by a red triangle for comparison.

As for the chemical compatibility properties, the silmer/AA/GMA polymer was evaluated in terms of swelling degree against a variety of polar and non-polar solvents for up to 24 hours. Based on **Figure 4.14**, the silmer polymer was revealed to have a lower swelling degree for most solvents upon the inclusion of AA and GMA monomers, except for ammonia

and tetrahydrofuran (THF). The lower swelling degree of silmer polymer upon the inclusion of AA and GMA is most likely due to the increase in crosslinking density with AA and GMA monomers. This is because an increase in crosslinking density often indicates an increase in the number of crosslinking points connecting the polymer chains, which in turn, helps restrict the expansion of the crosslinked polymer, resulting in less swelling when exposed to solvents for an extended time.

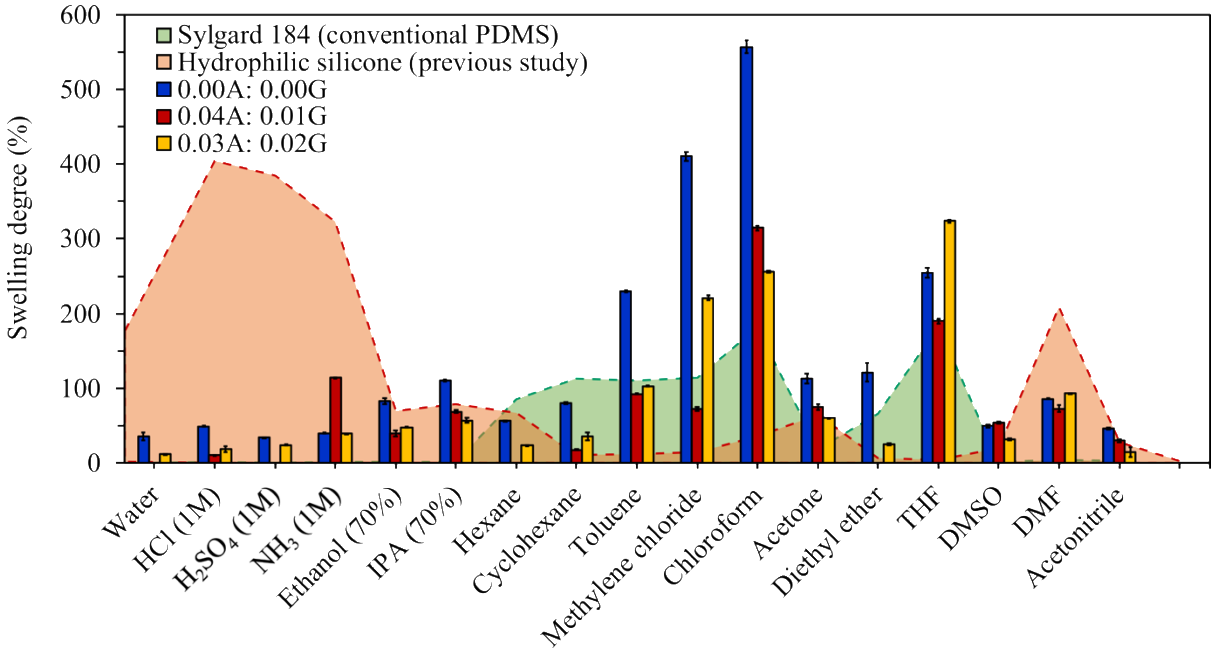


Figure 4.14: The chemical compatibility properties of silmer/AA/GMA cured polymer. The swelling degree of the silmer/AA/GMA cured polymer compared against Sylgard 184 and the hydrophilic silicone material reported in Chapter 2 and 3 with different solvents upon 24 hours of incubation. Error bar represents ± SD, n ≥ 3.

As for the exception with ammonia and THF, the higher swelling degree of silmer with 0.04 AA: 0.01 GMA and 0.03 AA: 0.02 GMA as opposed to silmer itself in ammonia and THF is most probably attributed to the similar chemical structure of AA with ammonia and GMA with THF, respectively **(Figure 4.14)**. This is because polymer tends to attract solvent molecules with similar chemical composition. When a high AA content (0.04 AA: 0.01 GMA)

is employed, the strong presence of the amine group in AA encourages the absorption of ammonia sharing the same amine structure **(Figure 4.15)**. Similarly, with the increasing GMA content (0.03 AA: 0.02 GMA), the stronger presence of the cyclic ether group in GMA encourages the absorption of THF sharing the identical cyclic structure.

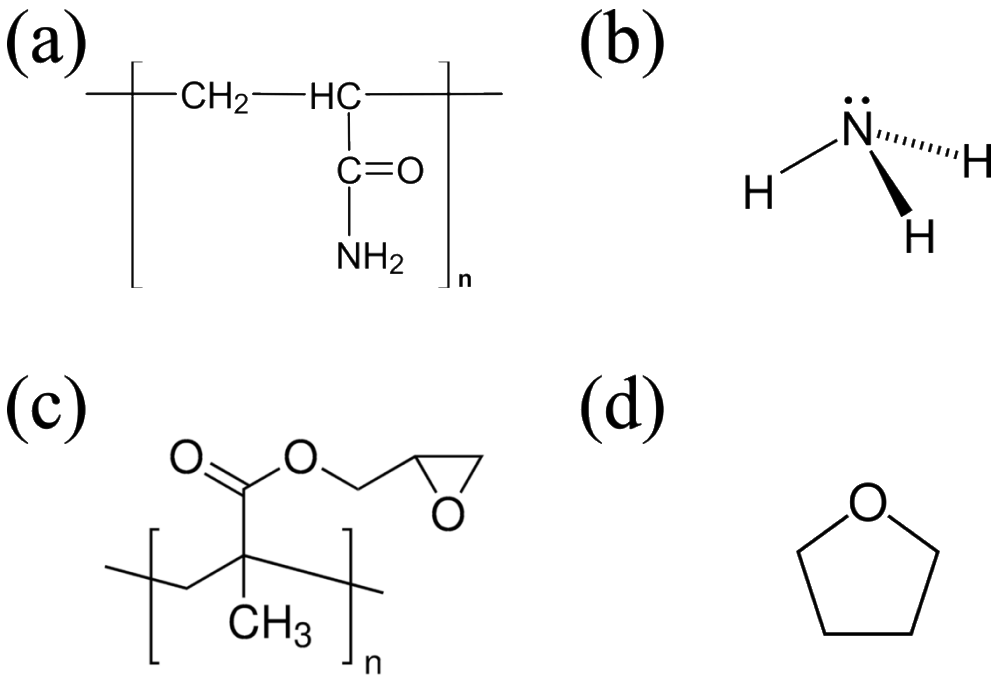


Figure 4.15: The chemical structure of polyacrylamide, ammonia, poly(glycidyl methacrylate), and tetrahydrofuran. (a) Polyacrylamide. **(b)** Ammonia. **(c)** Poly(glycidyl methacrylate). **(d)** Tetrahydrofuran.

Furthermore, the inclusion of a high AA content (0.04 AA: 0.01 GMA) was revealed to demonstrate a better chemical resistance towards most of the solvent, with the exception for isopropyl alcohol (IPA), chloroform, acetone, dimethyl sulfoxide (DMSO), and acetonitrile, for which an increase in GMA content (0.03 AA: 0.02 GMA) has a better chemical resistance towards the mentioned solvents **(Figure 4.14)**. Interestingly, the mentioned solvents demonstrating a higher reduction in swelling degree with increasing GMA content (0.03 AA: 0.02 GMA) were observed to have a similar chemical structure with a single functional group

differing from the remaining two or three functional groups attaching to the fully occupied central carbon atom **(Figure 4.16)**. The increased resistance to solvent molecules with a fully occupied central carbon consisting of a singular distinct functional group may have been caused, in part, by the cyclic ether in GMA. In any case, the chemical resistance towards the range of solvent tested does not vary much with respect to the AA:GMA ratio, except for chlorine-containing organic solvents, where a higher AA content results in a 4-fold decrease in swelling with methylene chloride while an increasing GMA content results in a 1.5-fold decrease in swelling with chloroform.

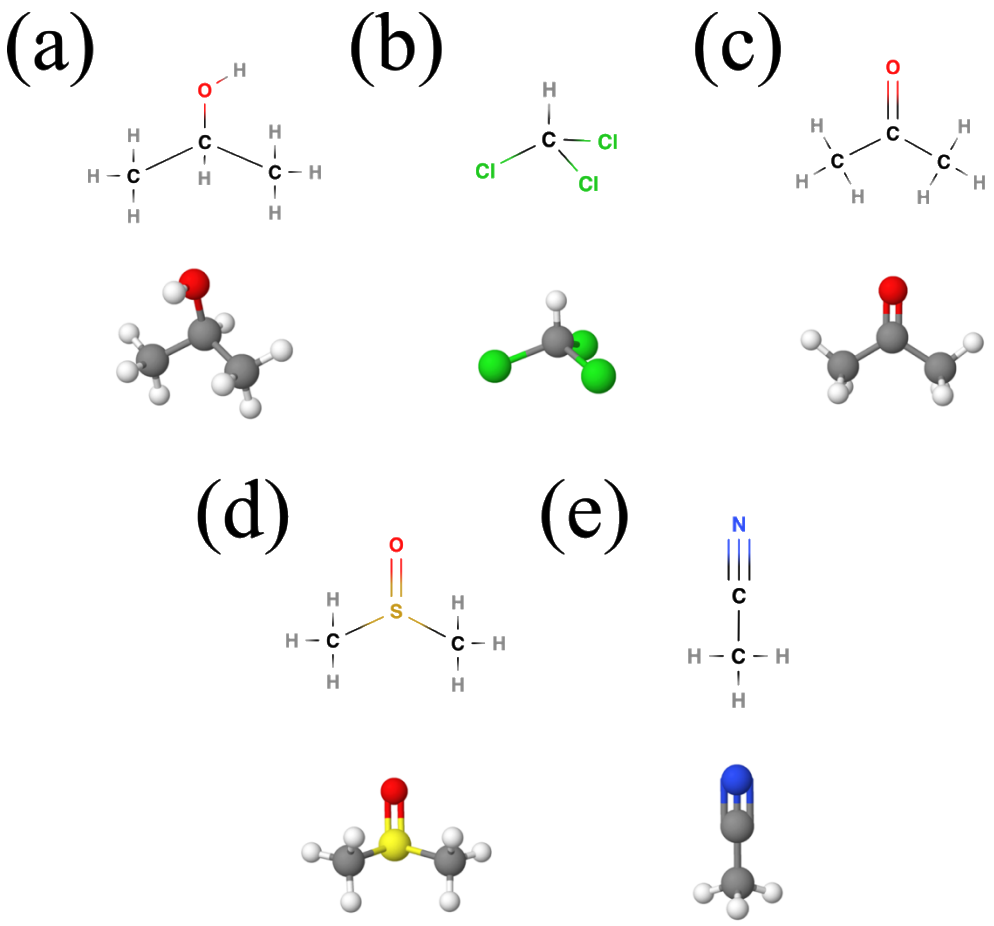


Figure 4.16: The 2D and 3D model of solvent molecules. (a) Isopropyl alcohol (IPA). **(b)** Chloroform. **(c)** Acetone. **(d)** Dimethyl sulfoxide (DMSO). **(e)** Acetonitrile. All the models are generated from MolView.org.

In general, the silmer/AA/GMA polymer demonstrates a similar chemical compatibility profile as the conventional hydrophobic PDMS material, regardless of the monomer ratio of AA:GMA **(Figure 4.14)**. The silmer/AA/GMA polymer was found to have better resistance towards polar solvents than non-polar solvents as reflected by its lower swelling degree with polar solvents as opposed to non-polar solvents. This is most likely due to the higher proportion of hydrophobic siloxane chains compared to the combined presence of hydrophilic groups contributed by the PEGMA group, AA monomer, and GMA monomer in the overall silmer/AA/GMA polymer. This differs significantly from the chemical compatibility profile of the hydrophilic silicone-based material developed in the previous chapters **(Chapter 2 and 3)**, where a reverse pattern of chemical compatibility was obtained as opposed to the conventional PDMS material with hydrophobic surface properties. Despite acquiring the hydrophilic properties, the hydrophilic silicone-based material reported previously exhibits a poor resistance towards polar solvents due to the higher proportion of hydrophilic groups. With the use of silmer in the current formulation, a new class of hydrophilic silicone-based materials with good resistance towards polar solvents is created. This highly benefits the fabrication of fluidic devices catering to biomedical applications as both the hydrophilic surface properties and good resistance towards polar solvents allow the fluidic devices fabricated with the silmer/AA/GMA polymer to process aqueous solutions without swelling upon contact. Moreover, the hydrophilic properties of silmer/AA/GMA polymer have effectively removed the need for an extra post-processing step to convert the hydrophobic surfaces to hydrophilic, as opposed to the conventional PDMS material.

Aside from the swelling degree, the appearance of the silmer/AA/GMA polymer after subjecting to solvent swelling was investigated. Based on **Figure 4.17**, the silmer/AA/GMA polymer was revealed to have good compatibility with acid as reflected by the clear interface of the polymer after being exposed to hydrochloric acid and sulfuric acid. This is in line with

the low swelling degree of the polymer when being subjected to acid as illustrated by **Figure 4.14**. On the contrary, despite the relatively low swelling degree with base **(Figure 4.14)**, the silmer/AA/GMA polymer was found to discolour with base as demonstrated by its pinkish-brown appearance upon exposure to sodium hydroxide and ammonia for a prolonged period **(Figure 4.17)**. This implies that the silmer/AA/GMA polymer might not be suitable to be used with basic solutions for a prolonged period as polymer discolouration often indicates polymer degradation. Particularly, the silmer/AA/GMA polymer was observed to form a weak gummy paste that partially dissolves in the soaking medium when subjected to sodium hydroxide. Due to the difficulty in obtaining the final polymer mass after swelling, the swelling degree of the silmer/AA/GMA polymer with sodium hydroxide is not recorded.

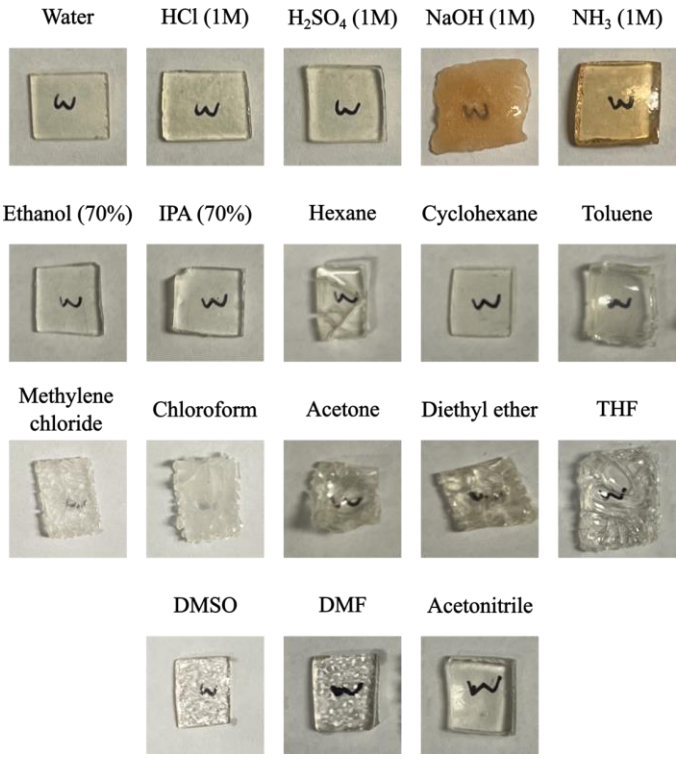


Figure 4.17: The appearance of the silmer/AA/GMA cured polymer after swelling test with different solvent. The observation on the appearance of the silmer/AA/GMA cured polymer with a monomer ratio of 1 silmer: 0.04 AA:0.01 GMA after 24 hours of incubation with different solvents.

Moving on, the silmer/AA/GMA polymer was found to rapidly form a network of surface cracks upon removal from certain organic solvents **(Figure 4.17)**. The formation of surface cracks upon removal from organic solvent is a common phenomenon with solvent-based polymer, termed solvent crazing.[465] This phenomenon is attributed to the evaporation, or desorption, of solvent from the polymer surface. The evaporation of solvent from the polymer surface generates tensile stress close to the polymer surface, which when it reaches or exceeds the critical stress required to initiate surface cracks, would cause cracks to form on the surface of the polymer. Also, the molecular weight of the solvent molecule is a major factor in surface crack development. The solvent molecules may disperse into the polymer and possibly supplant the existing solvent molecules as the polymer swells. Thus, higher-molecular-weight solvent molecules would extend the space that lower-molecular-weight solvent molecules formerly occupied, putting the polymer under tensile stress that could further encourage surface crack formation. This aligns with the observation on the clear appearance of silmer/AA/GMA polymer without any crack formed when being subjected to solvents with a lower molecular weight, namely water, ethanol, IPA, and acetonitrile, than the existing solvent used for the ink formulation **(Table 4.3)**. On the contrary, solvents with a higher molecular weight than the existing solvent used for ink formulation, such as hexane, methylene chloride, chloroform, diethyl ether, and THF, were discovered to induce surface crack on the silmer/AA/GMA polymer upon removal from the soaking medium. However, silmer/AA/GMA polymer was observed to retain its clear interface without cracks with cyclohexane, toluene, DMSO, and dimethylformamide (DMF), despite the higher molecular weight of the solvent mentioned as opposed to the solvent used for ink formulation. This might be due to the possible reaction between the silmer/AA/GMA polymer and the mentioned solvents, which helps retain the solvent molecules within the polymer matrix to prevent the formation of stress-induced localized crack upon rapid solvent desorption from the polymer surface. Upon comparison,

both cyclohexane and toluene were found to have similarities in terms of cyclic functional groups. As for DMSO and DMF, both of these solvents were revealed to have similarities in terms of carbonyl functional group. Additionally, despite the absence of surface crack, the silmer/AA/GMA polymer was observed to develop an uneven polymer surface covered with a droplet-like pattern upon removal from DMSO and DMF. In contrast, acetone with a similar carbonyl functional group identical to DMSO and DMF was revealed to induce surface crack on silmer/AA/GMA polymer upon removal from the soaking medium. This is most probably due to the lower dipole moment of acetone as compared to both DMSO and DMF, which in turn, results in lesser hydrogen bond formation to help retain the acetone molecule within the polymer matrix. Further studies are required to understand the detailed mechanism of the mentioned solvents with the silmer/AA/GMA cured polymer. In general, all three sets of silmer/AA/GMA polymer with varying AA:GMA dosages were revealed to display the same appearance after subjecting to swelling with the range of tested solvents. Thus, it is safe to conclude that the occurrence of solvent crazing is most likely attributed to the reaction between the silmer and the solvent molecules, with little impact contributed by the minor composition of AA and GMA. Since the primary concerned was to understand the chemical compatibility of the developed material for biomedical applications, the fact that the silmer/AA/GMA polymer exhibits no surface cracks and a relatively low swelling degree after being exposed to water, ethanol, and IPA further implies the high suitability of the developed material to be used as a fabrication material for fluidic devices that mainly deal with aqueous solutions in biomedical applications.

Table 4.3: The molecular formula and molecular weight of solvents arranged in the increasing order of molecular weight.

Solvent	Molecular formula	Molecular weight (g/mol)
Water	H_2O	18.02
Acetonitrile	C_2H_3N	41.05
Ethanol	C_2H_6O	46.07
Acetone	C_3H_6O	58.08
Isopropyl alcohol (IPA)	C_3H_8O	60.10
Ethylene glycol	$C_2H_6O_2$	62.07
Tetrahydrofuran (THF)	C_4H_8O	72.11
Dimethylformamide (DMF)	C_3H_7NO	73.09
Diethyl ether	$(C_2H_5)_2O$	74.12
Dimethyl sulfoxide (DMSO)	C_2H_6OS	78.13
Cyclohexane	C_6H_{12}	84.16
Methylene chloride	CH_2Cl_2	84.93
Hexane	C_6H_{14}	86.18
Toluene	$C_6H_5CH_3$	92.14
Chloroform	$CHCl_3$	119.38

In addition to the excellent chemical compatibility with aqueous solutions, the silmer/AA/GMA polymer needs to have good biocompatibility properties to be qualified for its application involving or related to biomedical processes. In parallel to that, the silmer/AA/GMA polymer will need to achieve a relative cell viability greater than 70 % upon co-culturing with living cells to be regarded as non-cytotoxic.[423] Based on **Figure 4.18**, the silmer/AA/GMA polymer, regardless of the AA and GMA content, was revealed to be non-cytotoxic as reflected by its highly comparable relative cell viability when compared against the control group at Day 4 of cell culturing. The non-cytotoxic properties of the silmer/AA/GMA polymer are further reaffirmed by the similar cell distribution and cell morphology as the control group as demonstrated by the microscope images of the cells for the respective experimental sets in **Figure 4.18**. With its non-cytotoxic properties, the silmer/AA/GMA polymer represents a new class of silicone-based ink materials catering to biomedical applications.

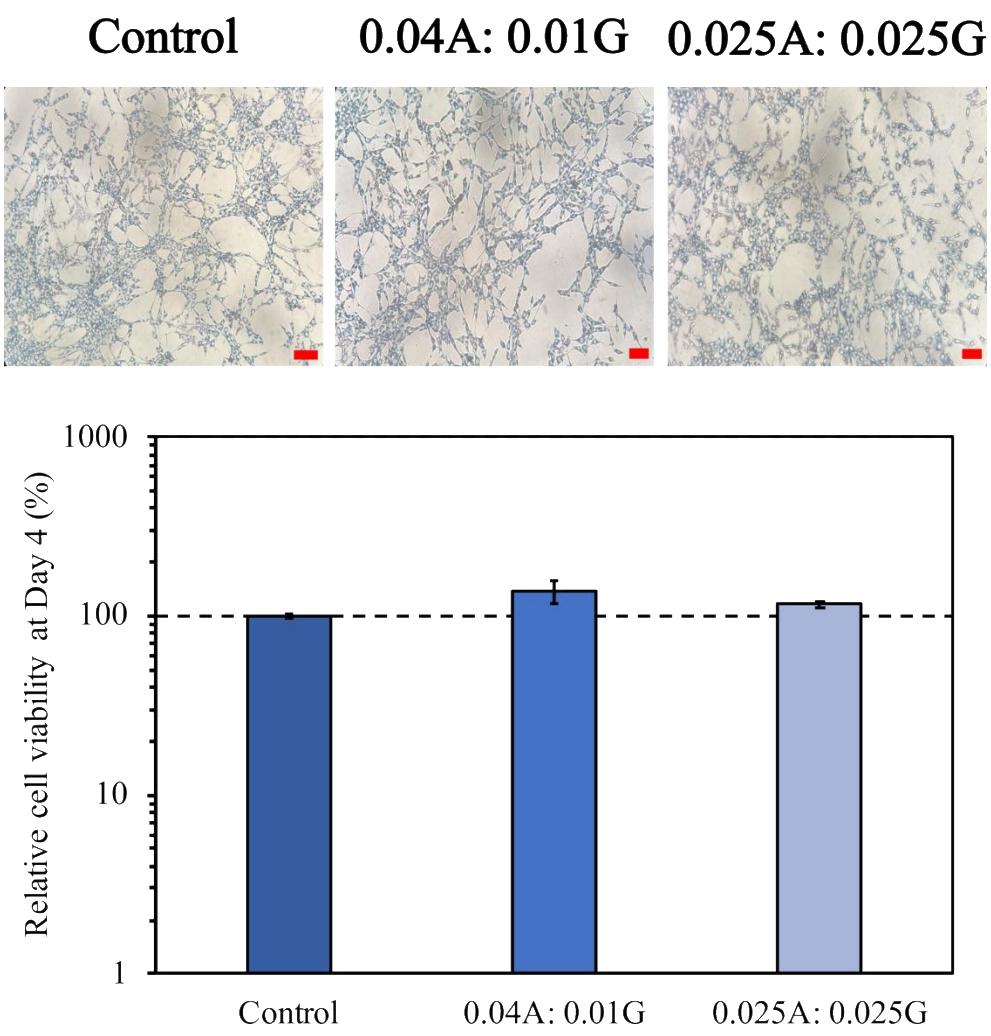


Figure 4.18: The biocompatibility properties of the silmer/AA/GMA cured polymer. The relative cell viability of silmer/AA/GMA polymer at Day 4 with the respective light microscope images of cells after staining with MTT indicator taken at 10x magnification. Scale bar: 100 µm. Error bar represents ± SD, n ≥ 5.

4.3.4 Printing of Silmer/AA/GMA Polymer

Prior to printing, the gel point of the silmer/AA/GMA polymer was evaluated using the VP printer itself. The gel point is identified as the minimum time required to transform the liquid pre-gel solution to solid cured gel when being exposed to the UV light emitted from the bottom of the printing vat. This is to serve as a reference for the optimization of the UV exposure time required per printing layer. Based on **Figure 4.19a**, the silmer/AA/GMA

polymer was revealed to require a longer gelation time with a higher gel point as the AA content reduces with the increase in GMA content.

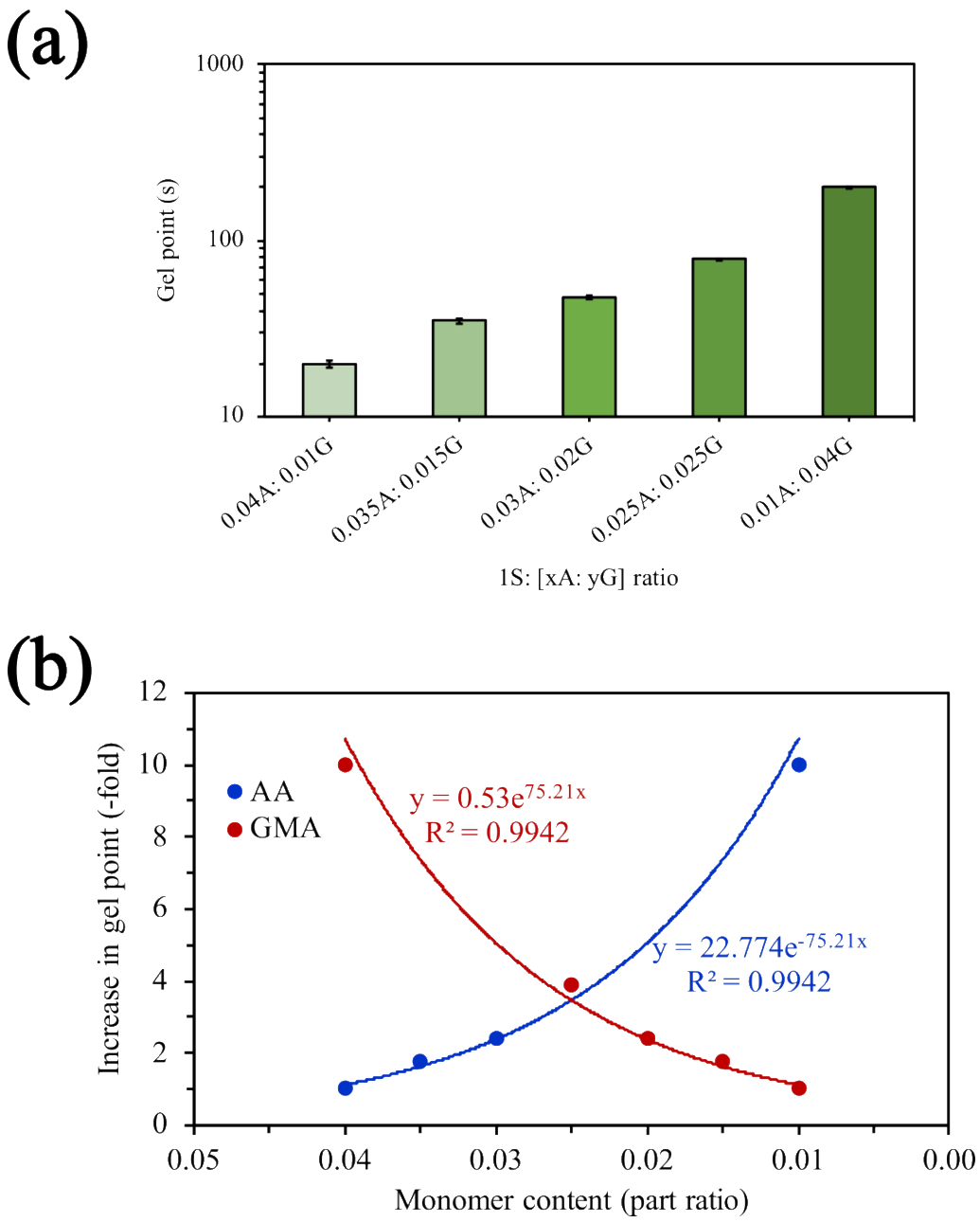


Figure 4.19: The gel point of silmer/AA/GMA polymer. (a) The gel point and **(b)** the fold increase in gel point of silmer/AA/GMA polymer with varying AA to GMA monomer ratios with respect to 1 part of silmer. Error bar represents ± SD, n ≥ 3.

Specifically, the gel point of the silmer/AA/GMA polymer was found to increase exponentially with the reduction of AA content as the GMA content increases, leading to a 10-fold increase in gelation time as the AA content reduces from 0.04- to 0.01-part with respect to the increase in GMA content from 0.01- to 0.04-part **(Figure 4.19b)**. The slower polymerization rate with GMA is most probably attributed to steric hindrance contributed by the extra methyl group bound to the alpha carbon of the -C=C bond.[466–468] Despite that, methacrylates are often included as part of the formulation for acrylate-based resin material for better distortion resistance owing to their relatively slow polymerization rate.[50] It is also important to note that the use of solvent as resin medium often results in some degree of volumetric shrinkage after printing as the monomers polymerizes[469] and the solvent evaporates from the printed structure.[470] The incorporation of methacrylates, like GMA, was revealed to help with the reduction of volumetric shrinkage after printing **(Figure 4.20)**.

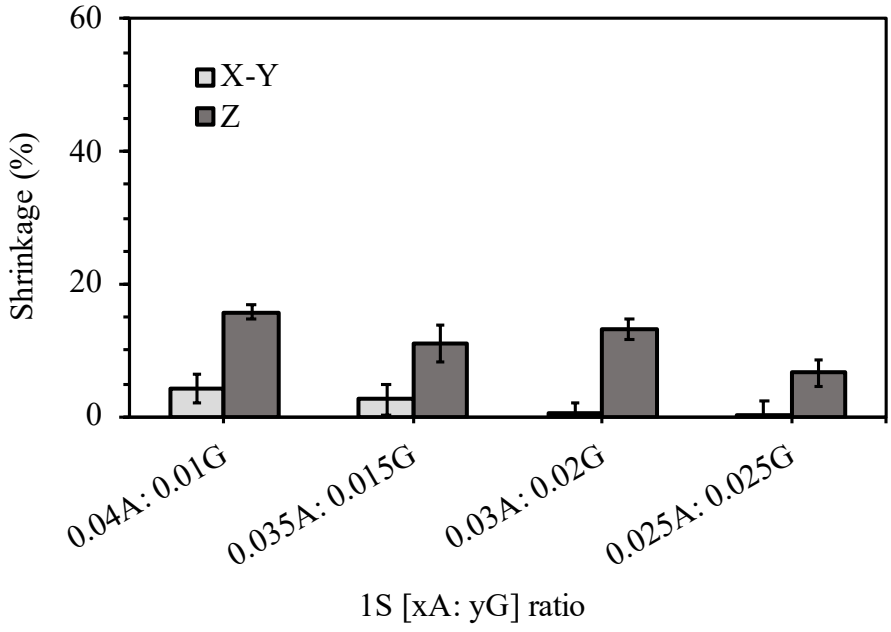


Figure 4.20: The volumetric shrinkage of silmer/AA/GMA polymer. The volumetric shrinkage of silmer/AA/GMA polymer with different AA and GMA monomer ratio with respect to silmer after printing in the XY and Z direction. Error bar represents ± SD, n ≥ 20.

Following the identification of the gel point, further adjustment is required to optimize the UV exposure time per printing layer. Oftentimes, the solid gel formed at the gel point is mechanically fragile, making it unsuitable for printing as it fails to survive the printing process.[471] As such, a longer UV exposure time than the gelation time, as specified by the gel point, is necessary to further crosslink the polymer for sufficient green strength to withstand the printing process. Based on my findings, an additional 2 to 4 seconds of exposure time on top of the gel point is adequate to provide the silmer/AA/GMA polymer with sufficient green strength to withstand the printing process. According to Jacob's working curve **(Figure 4.21)**, the critical energy (E_c) required to reach gel point with the developed material was calculated to be 36 mJ/cm^2. An additional 2 to 4 seconds of exposure time further results in a higher exposure energy (E_0) ranging from 42 to 48 mJ/cm^2, leading to an increased curing depth (C_d) at 72.6 and 135.4 μm, respectively. To achieve a good integration between the layers, I proceed with printing the silmer/AA/GMA polymer with a UV exposure time per printing layer of 4 seconds in addition to the gelation time as specified by the gel point. Upon optimization, all the silmer/AA/GMA polymers with varying AA and GMA content were successfully printed with VP printing. I further proceed with optimizing the printing resolution of the silmer/AA/GMA polymer with 0.04-part of AA and 0.01-part of GMA with respect to 1-part of silmer, owing to its shorter gelation time as indicated by the lower gel point for a faster printing process.

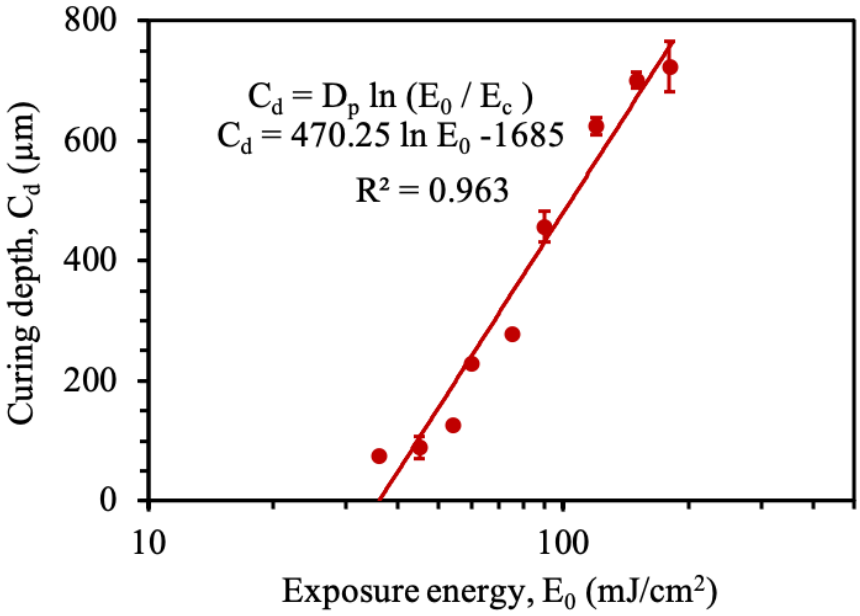


Figure 4.21: The Jacob's working curve of silmer/AA/GMA polymer. The Jacob's working curve of the developed material with Jacob's equation shown. The pre-polymer consists of 1 silmer: 0.04 AA: 0.02 GMA formulated with 8 EtOH: 1 EG: 1 H_2O. Error bar represents ± SD, $n \geq 3$.

The printing resolution of the silmer/AA/GMA polymer was further optimized with the addition of colouring dye as the photoabsorber. The approach to fine-tuning the printing resolution of the resin material with colouring dye is common and widely adopted by various resin formulations. In fact, several studies have reported on the successful tuning of printing resolution with colouring dye for the printing of fine features down to the micro-scale.[74,271,383,409,424–428] The improvement in printing resolution with coloring dye is mainly attributed to its ability to limit the amount of light penetrating through the highly transparent resin material. This helps to prevent the overcuring of additional areas, which is a major cause of poor printing resolution. In parallel to that, yellow dye is well-known to have excellent light absorption properties near 405 nm and is often included as photoabsorber for VP printing resins.[383,409,472,473] The ability of yellow dye to fine-tune the printing accuracy and resolution is further

evidenced by the Jacob's working curve showing the proportional reduction in C_d of the developed material when subjected to the same E_0 with increasing dosage of yellow dye **(Figure 4.22)**. I further proceed with optimizing the printing resolution of silmer/AA/GMA polymer using yellow dye.

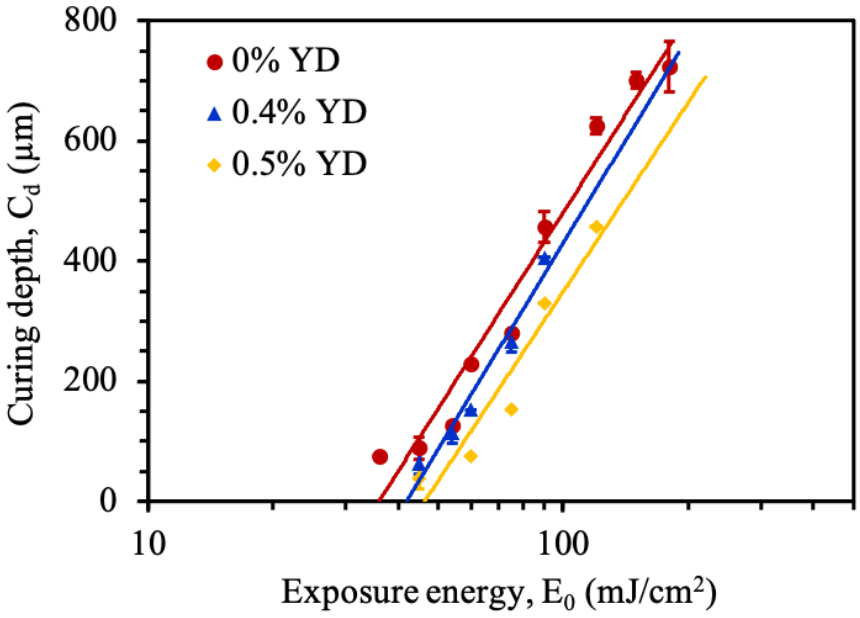


Figure 4.22: The Jacob's working curve of silmer/AA/GMA polymer with yellow dye. The Jacob's working curve of silmer/AA/GMA when added with different yellow dye (YD) dosage. The pre-polymer consists of 1 silmer: 0.04 AA: 0.02 GMA formulated with 8 EtOH: 1 EG: 1 H_2O. Error bar represents ± SD, n ≥ 3.

To begin with, the printing resolution of the silmer/AA/GMA polymer in terms of channel width and height was evaluated with the test models as shown in **Figure 4.23a** and **4.23d**, respectively. For channel width, a test model with a gradual reduction in channel width from 1000 to 50 µm paired with a constant channel height at 1000 µm was used to evaluate the resolution of printed channel width **(Figure 4.23a)**. Based on **Figure 4.23b** and **4.23c**, the addition of 0.5 % yellow dye was observed to generate a highly accurate channel width down

to 200 μm without affecting the accuracy of the channel height. Both the channel width at 100 and 50 μm remain indistinguishable regardless of the dosage of yellow dye, and thus, are not recorded in the data presented. However, this does not represent the incapability of VP printing to generate features below 100 μm with the silmer/AA/GMA polymer as the test models often only served as references for the evaluation of printing resolution. On the other hand, without the incorporation of yellow dye, the VP printer fails to generate channels with accurate channel width below 600 μm when printing with the silmer/AA/GMA polymer **(Figure 4.23b)**. Additionally, despite the successful printing of channels with a channel width of 600 μm and above, the printed channels were observed to experience a compromised channel height at about 40 % reduction in dimension as compared to the targeted height **(Figure 4.23c).** The failure to generate accurate channel width below 600 μm and the significant deviation in channel height of the printed channels are highly attributed to the overcuring of pre-gel solution trapped within the channel as the excessive light penetrates through the designated layer thickness in the absence of yellow dye to function as the photoabsorber. Hence, the addition of 0.5 % of yellow dye plays a vital role in reducing the photocuring depth for a better printing accuracy of channel width down to 200 μm without affecting the accuracy of channel height.

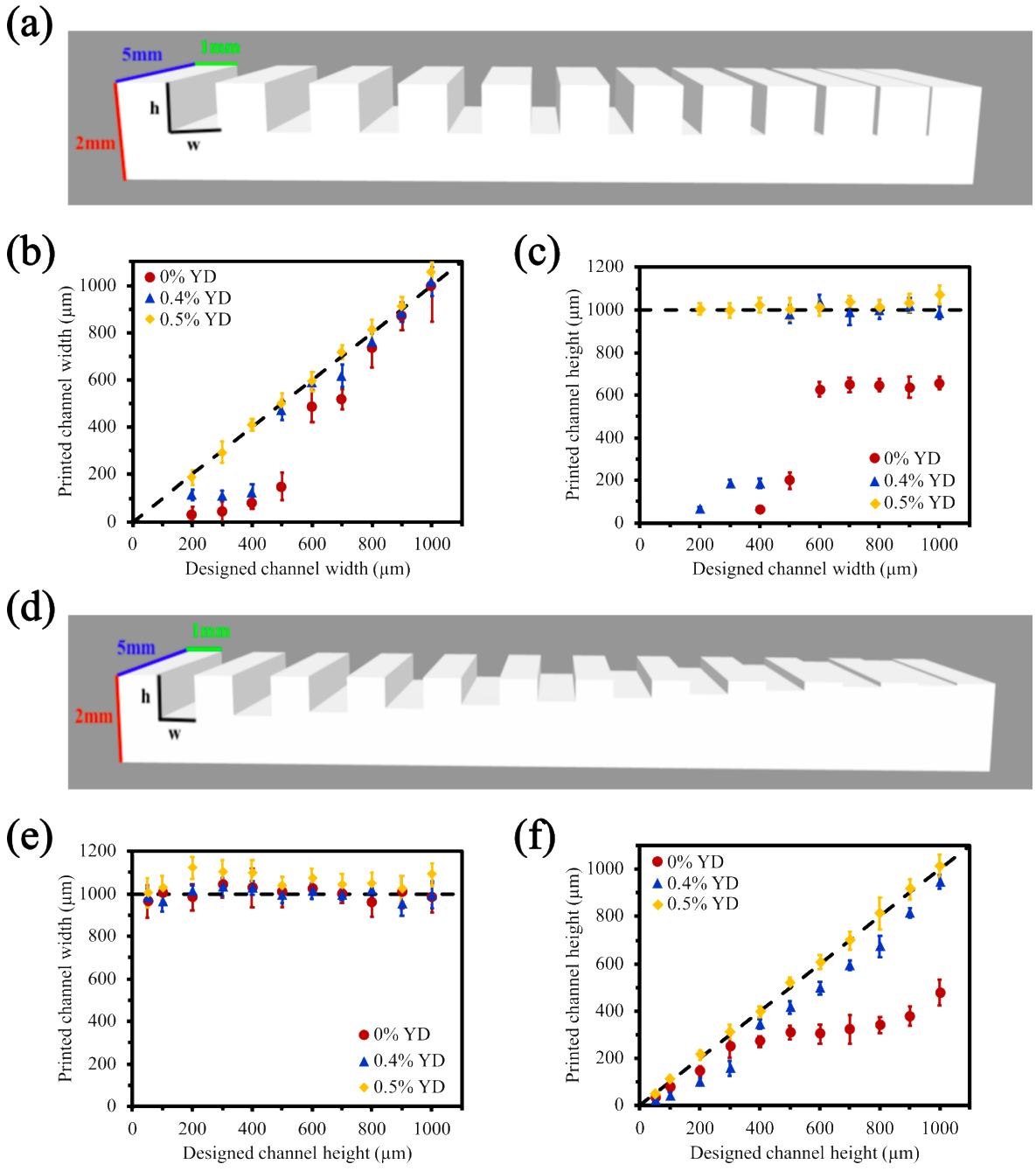


Figure 4.23: The printing resolution of the silmer/AA/GMA polymer upon photocuring depth tuning with yellow dye. The printing resolution of **(a-c)** channel width and **(d-f)** channel height of the silmer/AA/GMA polymer with different dosages of yellow dye (YD) based on the printing accuracy of the **(b)** increasing channel width and **(c)** and constant channel height of the **(a)** first test model and the **(e)** constant channel width and **(f)** increasing channel height of the **(d)** second test model, respectively. Error bar represents ± SD, n ≥ 20.

For channel height, a test model with a gradual reduction in channel height from 1000 to 50 μm paired with a constant channel width at 1000 μm was employed to evaluate the resolution of the printed channel height **(Figure 4.23d)**. Similarly, the addition of 0.5 % of yellow dye was revealed to generate a channel height highly matching that of the targeted height down to 50 μm with no impact on the accuracy of the channel width **(Figure 4.23e** and **4.23f)**. Differing from the results shown for the evaluation of the printing resolution for channel width, all the channel widths were accurately printed regardless of the channel height dimension **(Figure 4.23e)**. This provides further evidence that there is no direct correlation between the printing accuracy of the channel width and the channel height. Additionally, the accurate channel width generated regardless of the dosage of yellow dye suggests that the effect of yellow dye is more prominent with smaller channel width dimension and that a large enough channel width can be printed accurately without the need for extra photocuring depth tuning. On the contrary, without the incorporation of yellow dye, the dimension of the printed channel height was reduced by approximately half of the targeted height for channels with a targeted channel height of 1000 to 400 μm **(Figure 4.23f)**. Interestingly, the channels with a targeted height of 300μm and below were revealed to be relatively accurate even without the incorporation of yellow dye. This might be due to the lesser number of times exposing the trapped pre-gel solution within the channel with UV light as a channel with a shorter height would have a lesser number of printed layers following the creation of the channel. For instance, with a setting of 50μm in thickness per printing layer, the channel with a channel height of 1000μm will be subjected to 20 times UV exposure for the printing of the remaining 20 layers after the creation of the channel, while the channel with a channel height of 50μm will only be subjected to 1 time UV exposure for the printing of the remaining 1 layer following the creation of the channel. Thus, this significantly minimizes the effect of overcuring as the number of times of UV exposure following the creation of channel reduces with the channel height.

Regardless, the addition of 0.5 % of yellow dye was found to improve the printing accuracy of channel height down to 50 µm without impacting the accuracy of the channel width.

Overall, the addition of 0.5 % of yellow dye was revealed to be the optimum dosage for a high printing resolution with the silmer/AA/GMA polymer. Furthermore, the addition of 0.5 % of yellow dye was proven to have minimal impact on the appearance of the printed structure as shown by the highly transparent interface of the printed structure in **Figure 4.24**. Besides, the printed structure exhibits excellent layer integration with good adhesion between the printed layers. This is critical as printed structures with poor layer integration would result in poor mechanical properties that can be easily deformed when applied with mechanical stress. Aside from the excellent layer integration, the printed structure was discovered to have a smooth surface with no obvious signs of staircase effect at the edge. This further suggests the high surface quality of the printed structure generated by VP printing with the silmer/AA/GMA polymer. With the excellent printing accuracy and resolution, clear appearance, and high surface quality of the printed structure, I proceed with incorporating 0.5 % of yellow dye as part of the resin formulation for the VP printing of 3D structures using the silmer/AA/GMA polymer.

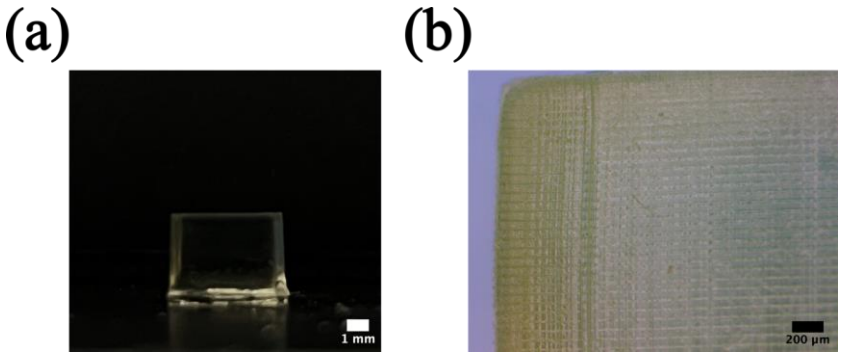


Figure 4.24: The silmer/AA/GMA polymer printed structure. (a) The printed structure with a clear transparent appearance. Scale: 1 mm. **(b)** The microscope image of the printed structure showing the layerwise structure. Scale: 200 µm.

Following the optimization of printing parameters, the potential to fabricate embedded-channel fluidic devices with the silmer/AA/GMA polymer via VP printing were further investigated. In addition to the pre-gel properties, the position of the channel within the printed device was discovered to be crucial for the successful direct printing of fluidic devices with embedded channels. [63,381] The embedded channels will need to be positioned near the top of the printed structure. This is to prevent the overcuring of pre-gel solution trapped within the channel for the successful direct printing of embedded channels. Besides, the layer enclosing the roof of the embedded channel needs to be sufficiently thick to withstand the pressure of the fluid flowing through the channel. Preliminary investigation suggests that an embedded channel with a roof thickness of 200 μm is optimum for the printing of embedded channels with the finalized silmer/AA/GMA polymer resin formulation. In conjunction with that, the printing of an embedded serpentine channel was demonstrated as shown in **Figure 4.25a**. The top view of the printed device displayed the potential of VP printing in generating the replica of fluidic channels according to the CAD design with silmer/AA/GMA polymer. The side views of the printed device further reveal the features of the embedded channel enclosed within the printed structure. Aside from the simple channel geometries, the printing of embedded-channel fluidic devices with multiple geometries was explored as well. Based on **Figure 4.25b**, I demonstrated the potential to fabricate embedded-channel fluidic devices with multiple geometries. In the example for parallel lamination mixing, I demonstrated the potential to generate a fluidic device with curved channels featuring a combination of the U-shaped channel and the serpentine channel. On the other hand, in the example for barrier structures mixing and deterministic lateral displacement (DLD) separating, I revealed the capability to print poles with different shapes and sizes. Furthermore, in the example for channels with wells, I displayed the possibility of generating irregular-shaped channels with horizontal wells. All the printed devices were revealed to demonstrate excellent functionality according to their

respective application as shown in **Figure 4.25b**. Both the parallel lamination mixer and barrier structures mixer demonstrate excellent fluid mixing properties as reflected by the homogeneous mixing of red and blue dye that results in a purple solution near the output. As for the DLD separator, the distinct separation of red and blue dye by the circular poles positioned in the middle of the device further reaffirms the function of the DLD separator in flowing the fluids in two separate streams while allowing some fluid diffusion to occur as the streams converge near the poles. Moving on, the flowing of fluids through the channels with wells demonstrates its potential application in continuous-flow cell culturing for disease modeling and drug testing. It is important to note that all the fluidic channels reported here are in milli-scale to cater to the potential use of the printed device for biomedical applications requiring milli-scale channels, such as cell culturing and hydrogel particle synthesis for cell and drug encapsulation. This does not rule out the capability to generate micro-scale embedded-channel fluidic devices with the formulated material as demonstrated by **Figure 4.25c** upon the optimization of printing parameters. In general, I revealed the potential to replicate any fluidic devices that are highly functional as per the CAD design with the silmer/AA/GMA polymer via VP printing.

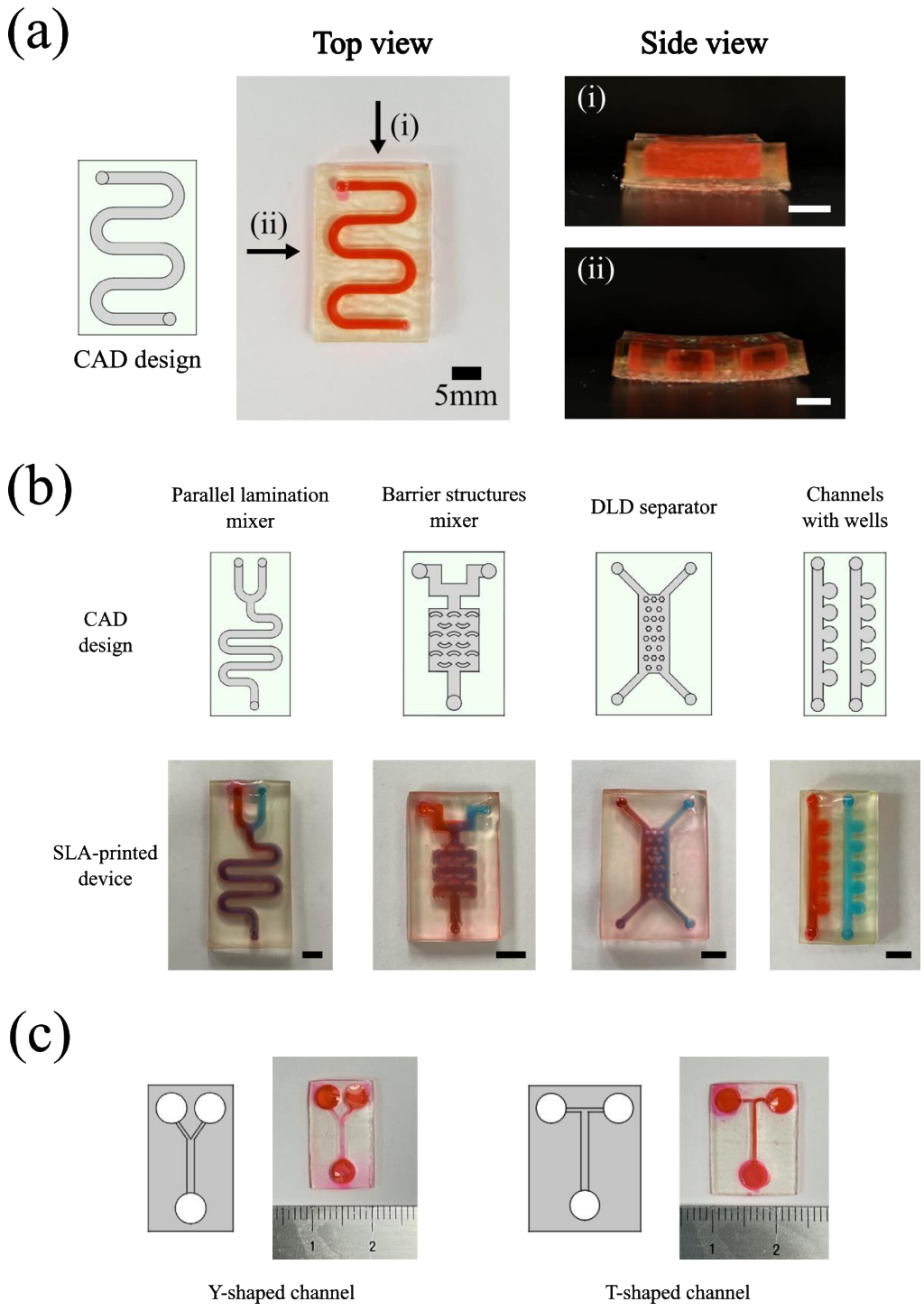


Figure 4.25: The printing of embedded channel fluidic devices with silmer/AA/GMA polymer. (a) The printing of a serpentine channel with the top view and side view showing the features of the printed embedded channel flowed with red dye. Scale: 5 mm. **(b)** The printing of fluidic devices with multiple geometries functioning as parallel lamination mixer, barrier structure mixer, deterministic lateral displacement (DLD) separator, and channels with wells

flowed with red and blue dye. All the printed structures are complemented with their respective CAD design. Scale bar: 5 mm. **(c)** The printing of micro-scale embedded Y-shaped channel and T-shaped channel. Scale: cm.

4.3.5 Functionality of Printed Fluidic Devices

To operate as fluidic devices, the printed channels must possess the capability to process fluids efficiently without any instances of leakage. The fluidic channel's ability to process fluid was assessed through static and dynamic flow testing. Based on **Figure 4.26a**, the fluidic channel was observed to remain intact with no fluid leakage for up to 24 hours at room temperature (22 ºC) when subjected to static flow. Besides, I also investigated the effect of temperature on the functionality of the printed channel. This is to explore the potential of the printed device in conducting experiments involving elevated temperatures. In conjunction with that, **Figure 4.26a** shows that the printed channel is capable of handling temperatures up to 100 ºC for 24 hours with no fluid leakages detected. Moreover, the printed device was observed to have no signs of yellowing when subjected to elevated heat up to 100 ºC for 24 hours. In contrast, the printed device was observed to exhibit significant yellowing upon 1 hour of incubation at 200 ºC. The yellowing of polymer materials is generally indicative of thermal degradation, which occurs when the components in the polymer breakdown and undergo oxidation due to exposure to high temperatures. [474,475] Yet, the printed channel was observed to remain functional with no fluid leakages detected. Further heating at 200 ºC was revealed to brown and char the printed device at the 6-hour and 24-hour mark of incubation, respectively, and the channels are no longer functional as the channel roof degrades. Overall, the printed device demonstrates promising results in processing fluid at elevated temperatures up to 100 ºC without signs of material degradation and fluid leakages.

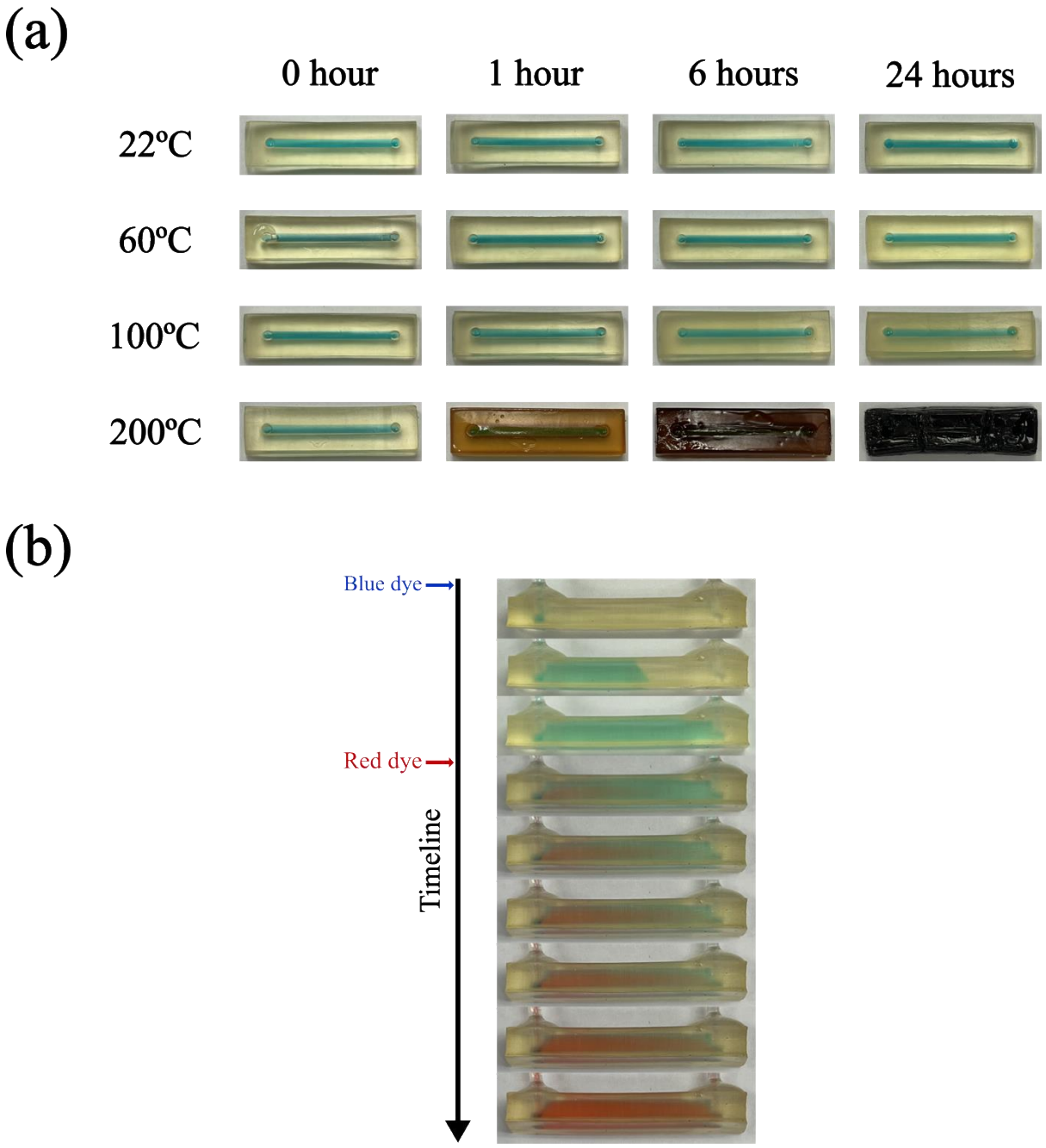


Figure 4.26: The functionality of the printed fluidic devices in fluid processing. The fluid processibility of the printed fluidic devices when subjected to **(a)** static flow at different temperatures up to 24 hours and **(b)** dynamic flow with the flow of blue dye followed by red dye to demonstrate continuous fluid flow. The printed channel dimension is 2 mm in width, 4 mm in height, and 30 mm in length.

Furthermore, I proceed to investigate the durability of the printed channel in handling continuous fluid flow with the dynamic flow test. The printed channel was first flowed with blue dye followed by red dye to better visualize the continuous flow of fluid within the fluidic channel. Based on **Figure 4.26b**, the printed channel portrays high functionality in processing the continuous flow of fluid as reflected by the gradual transition in fluid color from blue to red over time without any fluid leakages. Additionally, the durability of the fluidic channel with different flow rates was tested by simultaneously increasing the flow rate from 0.1 to 20 mL/min with a 15-minute interval between each flow rate upon switching. Likewise, the printed channel remains intact with no fluid leakage observed up to the maximum flow rate of the dosing pump at 20 mL/min. This provides further evidence of the capability of the printed device to handle continuous fluid at a relatively high flow rate. Essentially, the printed fluidic devices fabricated with the silmer/AA/GMA polymer are highly functional as reflected by its excellent fluid processibility in terms of static and dynamic flow.

4.3.6 Sample Application: Hydrogel beads Synthesis for Drug Encapsulation

Over the years, hydrogel beads have found their use in various biomedical applications, including drug delivery, cell delivery, and scaffold building.[476] As such, it is vital to be able to generate large quantities of hydrogel beads efficiently catering to their respective application in the biomedical field. In this particular example, I demonstrate the potential to synthesize drug-encapsulated hydrogel beads for drug delivery as I utilize the printed device for effective fluid mixing **(Figure 4.27a)**. Specifically, gelatin is employed as the hydrogel solution, while amoxicillin serves as the medication solution. Gelatin was chosen for its thermo-reversible qualities, which enable the production of a solid gel when the temperature decreases below its gelling point. On the other hand, amoxicillin was chosen as the sample medication because it contains an amine group that can be labeled with fluorescein isothiocyanate (FITC), allowing

for the visualization of the drug encapsulation within the hydrogel beads. Both the hydrogel and drug solution were then flowed through the printed device for a homogeneous mix. Particularly, a parallel lamination mixer with serpentine mixing channels was used. **Figure 4.27b** further revealed the capability of the printed device to effectively mix the hydrogel and drug solution for a homogeneous distribution of drugs within the hydrogel solution. Besides, both the hydrogel and drug solution were observed to have maximum contact with the fluidic channel, facilitating the effective fluid flow across the fluidic channel, owing to the hydrophilic surface of the developed material. Subsequently, the homogeneously mixed hydrogel and drug solution was extruded through a needle nozzle capped at the end of the output channel into the oil bath for hydrogel bead formation **(Figure 4.27a)**. The oil bath was added with SPAN 80, a lipophilic surfactant, to help with the formation of perfectly round hydrogel beads as the hydrogel solution extruded from the needle nozzle. Moreover, the oil bath was maintained at a low temperature of approximately 4 ºC. This is because gelatin has a gelling temperature within the range of 22 to 25 ºC. [477,478] Hence, the temperature of the oil bath needs to be below the gelling temperature of gelatin to encourage gelation for the formation of solid gelatin hydrogel beads. **Figure 4.27c** further revealed the successful synthesis of drug-encapsulated hydrogel beads as reflected by the homogeneous green fluorescent appearance of each hydrogel bead. It is important to note that the size of the hydrogel beads can be further controlled by manipulating the flow rate of solution extruding out into the oil bath and the size of the needle nozzle head. The experiment reported here on the synthesis of hydrogel beads is to serve as a proof-of-concept on the practicability of the printed fluidic device when being applied for real-world biomedical applications. Nevertheless, the successful synthesis of drug-encapsulated hydrogel beads provides further evidence for the feasibility of the printed device fabricated with the novel hydrophilic silicone-based material for biomedical applications.

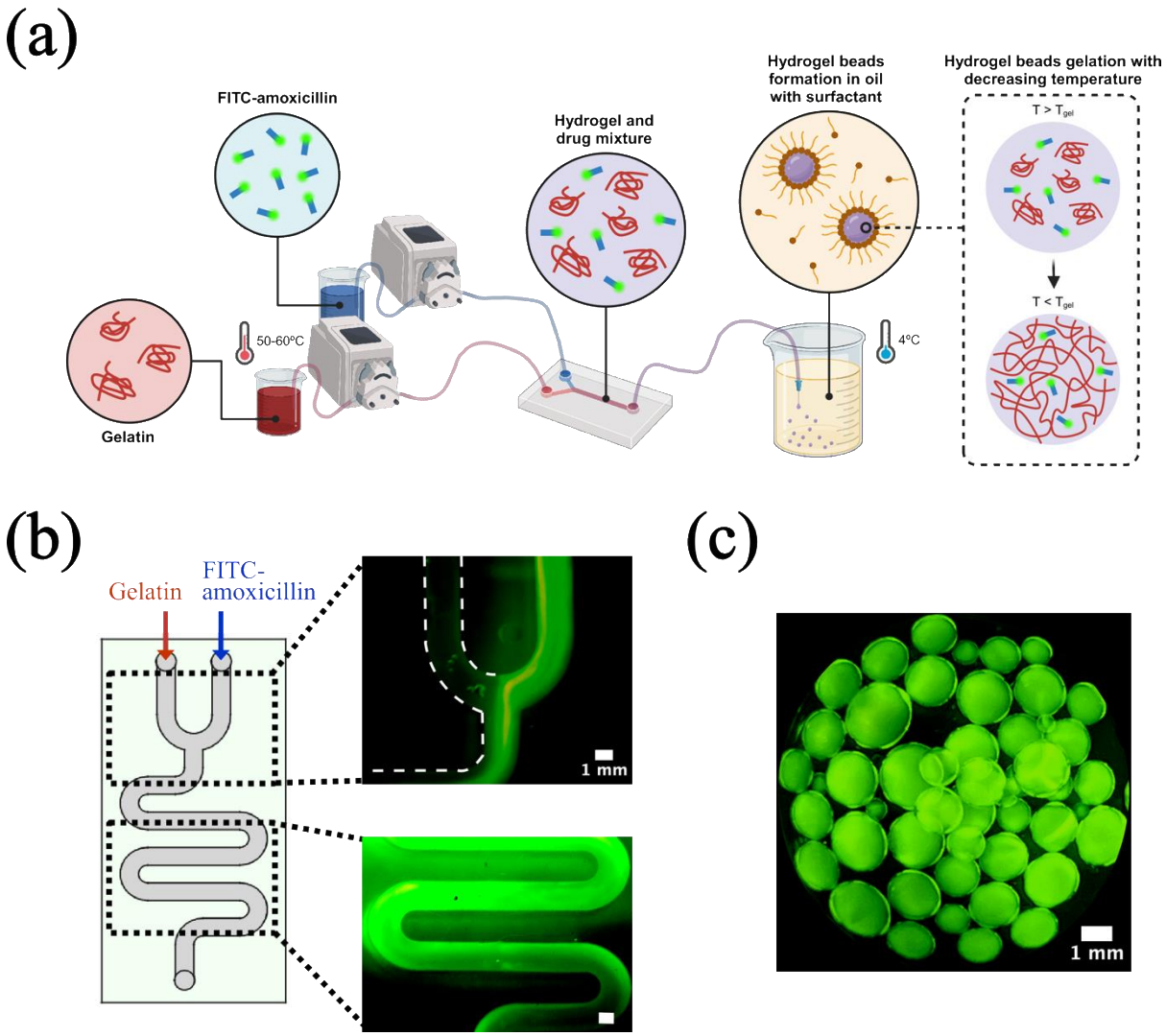


Figure 4.27: The synthesis of drug-encapsulated hydrogel beads. **(a)** The setup of the printed fluidic mixing device for the synthesis of drug-encapsulated hydrogel beads. The illustration is produced with Biorender.com. **(b)** The microscope images on the mixing of gelatin and FITC-amoxicillin drug solution within the parallel lamination mixer with serpentine channel. **(c)** The FITC-amoxicillin drug-encapsulated gelatin hydrogel beads. Scale: 1 mm.

4.4 Conclusion

In conclusion, the strategy to alter the conformation of silmer, or amphiphilic siloxane oligomer, with solvent blend has successfully enabled the development of a novel hydrophilic

silicone-based resin material for the VP printing of biomedical fluidic devices. Upon solvent optimization, the developed material demonstrates low pre-gel viscosity, high transparency, and optimal hydrophilicity for the effective VP printing of biomedical devices. Besides, the developed material possesses flexibility for mechanical properties tuning with monomer ratio variation, owing to the role of AA in imparting strength and GMA in inducing elasticity in the overall silmer/AA/GMA polymer. Furthermore, the developed material presents excellent resistance towards polar solvent despite its hydrophilic properties, rendering it highly suitable for biomedical application by allowing the processing of aqueous solution without swelling upon contact. The non-cytotoxic properties of the developed material further established its potential for biomedical use. Upon photocuring depth tuning, the developed material shows high printing accuracy down to 200 μm in channel width and 50 μm in channel height. This further enables the successful printing of embedded-channel fluidic devices consisting of highly detailed and complicated channel features with the developed material. More importantly, the printed devices are highly functional as demonstrated by their capability to process both static and dynamic fluids with no fluid leakage up to a temperature of 100 ºC for 24 hours and a flow rate of 20 mL/min, respectively. The successful combination of hydrogel and drug solution for the production of drug-encapsulated hydrogel beads further reveals the strong potential of the printed device for practical biomedical uses. Overall, the silmer/AA/GMA polymer shows significant promise as a hydrophilic silicone-based resin material for the fabrication of biomedical fluidic devices. Moreover, the ability to generate embedded-channel fluidic devices in a one-step VP printing process as reported in this chapter provides invaluable insights for the fabrication of fluidic devices with VP printing.

Chapter 5 Conclusions and Future work

5.1 Conclusions

The capability to fabricate elastic biomedical devices with VP printing has been long desired due to its low setup cost, quick turnaround time, and ability to generate high-quality features. Particularly, silicone demonstrates excellent elasticity, high optical transparency, good biocompatibility, and exceptional chemical inertness to be used as the fabrication material for a wide range of elastic biomedical devices. However, the VP printing of silicone material is especially challenging owing to the high viscosity and the lack of photocurability of the conventional silicone material. Besides, the conventional silicone material is hydrophobic in nature and demands further post-fabrication processing for the acquisition of hydrophilic surface properties prior to biomedical use. In this thesis, a series of strategies have been employed to develop a VP-printable hydrophilic silicone-based material for the fabrication of biomedical devices.

In **Chapter 2**, I discussed the formulation of a VP-printable hydrophilic silicone-based material with SilMA upon the incorporation of AA and PEGDMA as reactive diluents. The incorporation of AA and PEGDMA into SilMA has successfully resolved the issue of high pre-gel viscosity and slow curing rate of SilMA for VP printing. The SilMA/AA/PEGDMA material was revealed to possess excellent VP printability with the ability to generate high-quality features down to 100 μm. Differing from conventional silicone material, the SilMA/AA/PEGDMA material presents distinct characteristics, including hydrophilicity and good swelling properties, to be used for the construction of biomimetic structures. In another aspect, the high strength and elasticity of the developed material due to the formation of an IPN address the prominent challenge regarding the use of weak hydrogel materials for biomimetic structure fabrication. With tuneable mechanical properties, excellent shape

recovery, and good biocompatibility, the developed material represents a new class of silicone-based materials for the fabrication of elastic biomimetic structures requiring high strength, further expanding the scope of biomimetic structures that can be fabricated with VP printing.

In **Chapter 3**, I presented the improvement of the printing accuracy and resolution of the SilMA-derived hydrophilic silicone-based material upon the incorporation of CNC for photocuring depth tuning. To better portray the improvement in printing accuracy and resolution, I proceed to investigate the fabrication of biomedical fluidic devices instead. Upon the incorporation of 1 wt% of CNC, the material demonstrated high printing accuracy and resolution, achieving a minimum feature size of 100 μm with near-zero deviation in the X and Y directions. This accuracy was further validated by the successful fabrication of intricate open fluidic channel patterns at micron scale. Most importantly, no heavy colour-staining was observed upon the incorporation of CNC, which is crucial for the fabrication of fluidic devices. Furthermore, the printed devices exhibit excellent fluid processibility with both organic and inorganic solvents. Additionally, the printed devices were tested to be able to handle fluids at a relatively high flow rate of up to 20 mL/min and at elevated temperatures of up to 100 ºC. This further demonstrate the potential of the VP-printed fluidic devices, fabricated using the developed material, for practical biological and chemical applications.

In **Chapter 4**, I outlined the formulation of another version of VP-printable hydrophilic silicone-based material with amphiphilic siloxane oligomer (silmer), complemented with AA and GMA monomers. This formulation aimed to create a hydrophilic silicone-based material with an even lower pre-gel viscosity, facilitating the more effective fabrication of void structures for the creation of fluidic devices with embedded channels in one-step printing. The solvent was found to have a significant impact on the pre-gel properties and surface characteristics of the silmer-derived hydrophilic silicone-based material. Upon the adjustment

of silmer conformation with the appropriate solvent blend, the developed material exhibits favourable characteristics, such as low pre-gel viscosity, high transparency, and optimum hydrophilicity, for the effective VP printing of biomedical fluidic devices. In addition to the tuneable elastic properties, excellent polar solvent resistance, and good biocompatibility, the developed material demonstrates excellent capability in generating void structures, enabling the accurate replication of embedded fluidic channels with diverse shapes in one-step printing. Likewise, the printed devices were revealed to be highly functional with the capability to process fluid at an elevated temperature of up to 100 ºC for 24 hours and a continuous flow rate of up to 20 mL/min. Further demonstration of the hydrogel beads synthesis for drug encapsulation reveals the feasibility of the printed device for real-world biomedical applications, providing evidence for the VP-printed hydrophilic silicone-based fluidic device to move beyond the prototyping stage.

Overall, both the strategies to dilute the siloxane polymer with reactive diluents and to formulate with lower-molecular-weight siloxane oligomers revealed success in generating a new class of silicone-based elastic resin materials with low pre-gel viscosity, optimum photocurability, good hydrophilicity, superior elasticity, excellent biocompatibility, and high transparency for the VP printing of elastic biomedical devices, such as biomimetic implants and biomedical fluidic devices. This further paves the way for the high-throughput manufacturing of high-quality silicone-based biomedical devices using VP printing.

5.2 Future Work

This thesis details the development of a new class of silicone-based materials for the fabrication of biomedical devices using VP printing, along with an investigation into the feasibility of fabricating 3D structural devices using VP printing and the functionality of the VP-printed devices in relation to their respective applications. In addition to the comprehensive

studies as reported in this thesis, there are still many aspects to be explored for the VP printing of elastic biomedical devices in terms of the VP printing techniques, material formulation, and application of the printed devices.

1. For fabrication techniques, the current use of a single vat for VP printing further restricts the fabrication of multi-material structures in a single printing step. The ability to fabricate multi-material structures is fairly attractive as it enables the integration of different materials into a single structural product. In the aspect of biomimetic scaffolds, the presence of material with different mechanical and chemical properties in a single structure would enable a better replication of the function of the replacement tissue or organ upon implantation. In the aspect of fluidic devices, the potential to generate multi-material structures in a single step enables the integration of multiple fluidic components in a single device. Currently, despite the capability to fabricate elastic fluidic components, the use of a single material results in a fully elastic fluidic device, which would otherwise fit into a wider range of applications if provided with the option to integrate the outer layer with a different material, potentially a rigid material, based on the intended application. To date, multi-material structures are either fabricated using hybrid printing techniques with a combination of nozzle- and reservoir-based printing or the switching of vat or resin material during the printing process. For the former, hybrid printing can either be conducted with a customized hybrid printer or using two different printers that require a two-step printing process sequentially. For the latter, resin material contamination is inevitable as it is difficult to completely remove the residual resin stuck on the printed structure and build plate prior to submerging the build plate with the printed structure into a different resin material. Regardless, all these techniques are only capable of generating interlayer multi-material structures and the generation of intralayer multi-material structures remains challenging.

2. In another aspect, most studies reported in the literature are conducted with small-scale VP printers, rendering the potential risk of scaling up VP printing for mass production remain unknown. This is currently not an issue as VP printing is commonly used only for prototyping. However, to industrialize both the VP printing technique and the developed silicone-based material, I believe that it is crucial to investigate the VP printing of the silicone-based material on the industrial scale. On a side note, the industrial VP printer existing in the current market is often just a larger-scale printer that conducts printing in a larger printing compartment. As such, the industrial VP printer still requires semi-automatic feeding of printing material before printing and removal of printed structure after printing. It would be interesting if we could integrate VP printing into a continuous manufacturing cycle ranging from material compounding, material feeding, printing, post-processing, and finally to packaging, all within a single automated production line.

3. For fabrication material, it is vital to note that the material characteristics tend to change with the composition of the monomer precursors, enabling the customization of material characteristics based on the intended application. The hydrophilic monomers reported in this thesis are just a fraction of the many monomer precursors that are available for selection and there are many more combinations of functionalized siloxane and hydrophilic monomers to be explored. Oftentimes, fillers are also included to enhance or equip the developed material with additional features, such as enhanced mechanical properties, electrical conductivity, and magnetic properties. However, the change in material characteristics can affect the material's printability and often requires the re-optimization of printing parameters to cope with the printability of the

new material formulation, which is extremely laborious with a wide range of variables to consider. Therefore, there is a need to develop a numerical model coupled with machine learning to help predict the required printing parameters based on the resin material composition for a faster optimization process.

4. To commercialize, the shelf-life of the developed material needs to be investigated. In terms of pre-polymer, the resin material will need to remain photocurable and low viscosity throughout the storage period. For this purpose, radical inhibitor is often incorporated to prevent premature gelation, and thus, extend the storage period for VP-printable resin material. In terms of cured polymer, the printed material will need to retain its respective mechanical and chemical properties for full functionality. This applies to both the freshly printed material using stored resin and the stored printed material previously fabricated with fresh resin. In conjunction with that, both real-time and accelerated shelf-life studies need to be conducted on the pre-polymer, the cured polymer made from stored pre-polymer, and the stored cured polymer to have a better understanding of the material characteristics upon storage and the appropriate storage conditions required for the developed material.

5. For biomedical use, the developed material will need to undergo a series of sterilization processes to prevent any microbial contamination that could intervene with the human biological system. In this thesis, I employed the method to sterilize printed material with chemical disinfectant, specifically 70 % ethanol. This method might not be practical for the sterilization of a large batch of printed samples in future mass production. Therefore, there is a need to explore the compatibility of the developed material with other sterilization methods, including heat, radiation, and ozone

sterilization. It is of great importance to ensure that there is no significant change made to the material's physical, mechanical, and chemical properties after the sterilization process for full functionality.

6. In the aspect of biomimetic scaffold implants, the current method of scaffold fabrication with biomaterial ink followed by cell seeding as reported in this thesis shows difficulties for the cells to migrate to the centre of the printed structural material. The lack of cell proliferation to the deep centre of the scaffold material further restricts the size of the structural scaffold that can be used for tissue or organ replacement. Hence, there is a need for a silicone-based bioink with cells integrated directly into the ink material for VP printing. As cells are rather sensitive and fragile, both the resin material composition and the printing parameters need to be carefully optimized to ensure that the cells survive the printing process. Additionally, in this thesis, I have only confirmed the non-cytotoxicity of the developed material with *in vitro* tests. The developed material will eventually require *in vivo* tests involving animal studies to ensure its biocompatibility and performance over an extended period before moving on to clinical studies.

7. In the aspect of fluidic devices, the printing of unsupported valves and multilayer channel structures remains challenging with VP printing. This is primarily due to the absence of supporting structures, which leads to the collapse of the unsupported features. The addition of supporting structures within the printed fluidic channel is not ideal as the micron-scale channel features and the embedded nature of the printed channel make it difficult for the supporting structures to be removed after printing. However, this can be made possible with the integration of supporting structures as part

of the channel design upon further investigation. Besides, to use the printed device for advanced biological and chemical processes, there is a need to investigate the feasibility of immobilizing the fluidic channels derived from the developed material with functional receptors. The successful immobilization of channels with functional receptors, such as proteins, enzymes, or antibodies, would further expand the use of the printed fluidic devices derived from my developed material for advanced biomedical applications, including biosensing, cell sorting, and drug screening. In conjunction with that, there are more potential biological and chemical applications of the printed fluidic devices to be explored in addition to the synthesis of drug-encapsulated hydrogel beads as reported in **Chapter 4** of this thesis.

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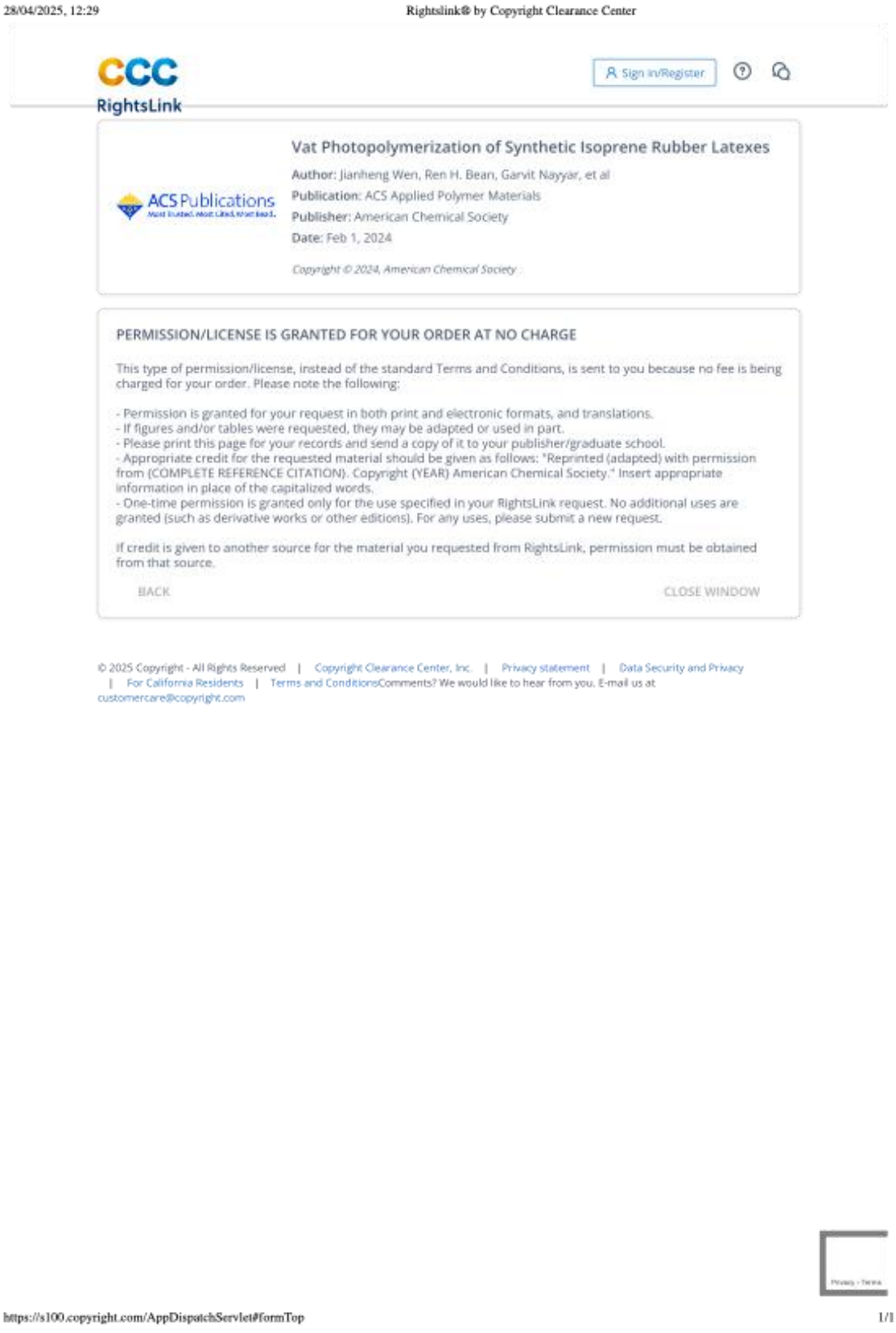
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Last updated October 2022

A.4 Figure 1.5

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A.5 Figure 1.6



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A.6 Figure 1.7a

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Article Title	Print your own membrane: direct rapid prototyping of polydimethylsiloxane.	Publication Type	e-Journal
		Start Page	2610
		Issue	15
Author / Editor	Royal Society of Chemistry (Great Britain)	Volume	14
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Last updated October 2022

A.7 Figure 1.7b

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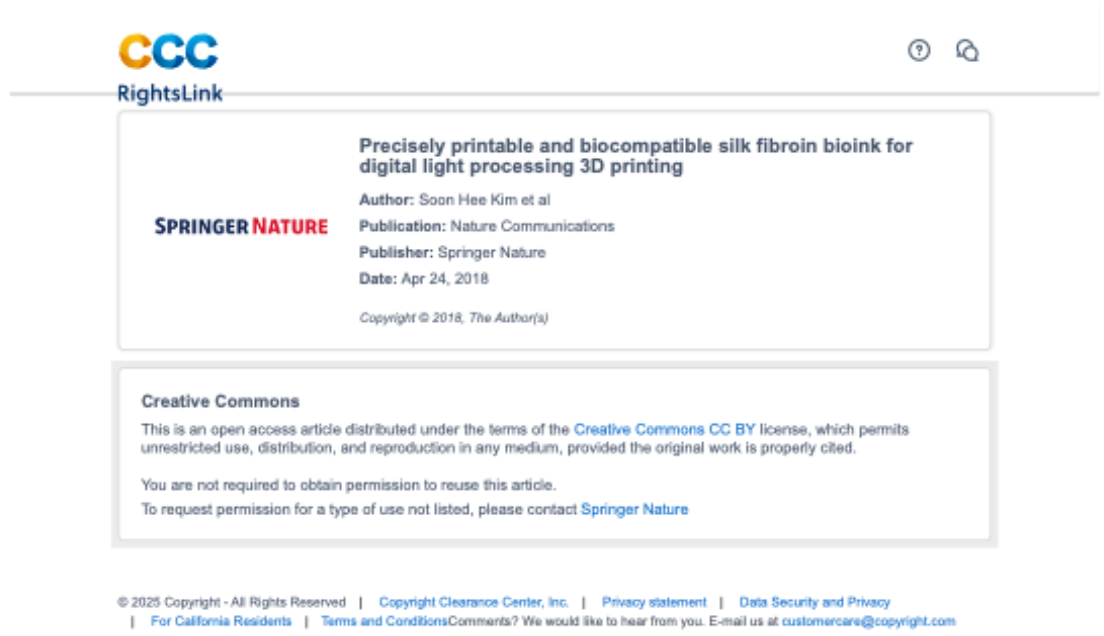
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A.11 Figure 1.9a



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G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

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Last updated October 2022

A.13 Figure 1.9c

Marketplace

This is a License Agreement between Li Yan Wong / University of Waterloo ("User") and Copyright Clearance Center, Inc. ("CCC") on behalf of the Rightsholder identified in the order details below. The license consists of the order details, the Marketplace Permissions General Terms and Conditions below, and any Rightsholder Terms and Conditions which are included below.

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Order Date	28-Apr-2025	Type of Use	Republish in a thesis/dissertation
Order License ID	1604360-1		
ISSN	2365-709X	Publisher	John Wiley & Sons
		Portion	Image/photo/illustration

LICENSED CONTENT

Publication Title	Advanced Materials Technologies	Rightsholder	John Wiley & Sons - Books
		Publication Type	e-Journal
Article Title	Fabrication and Functionalization of 3D Printed Polydimethylsiloxane-Based Microfluidic Devices Obtained through Digital Light Processing	Issue	9
		Volume	5
		URL	https://doi.org/10.1002/(ISSN)2365-709X
Date	01/01/2016		
Language	English		
Country	Germany		

REQUEST DETAILS

Portion Type	Image/photo/illustration	Distribution	Worldwide
Number of Images / Photos / Illustrations	1	Translation	Original language of publication
Format (select all that apply)	Electronic	Copies for the Disabled?	No
		Minor Editing Privileges?	No
Who Will Republish the Content?	Academic institution	Incidental Promotional Use?	No
Duration of Use	Life of current edition	Currency	CAD
Lifetime Unit Quantity	Up to 499		
Rights Requested	Main product		

NEW WORK DETAILS

Title	Development of hydrophilic silicone-based ink for the 3D vat photopolymerization printing of biomedical devices	Institution Name	University of Waterloo
		Expected Presentation Date	2025-07-16
Instructor Name	Li Yan Wong		

ADDITIONAL DETAILS

The Requesting Person / Organization to Appear on the License	Li Yan Wong / University of Waterloo

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 2	**Title of the Article / Chapter the Portion Is From**	Fabrication and Functionalization of 3D Printed Polydimethylsiloxane-Based Microfluidic Devices Obtained through Digital Light Processing
Editor of Portion(s)	Gonzalez, Gustavo; Chiappone, Annalisa; Dietliker, Kurt; Pirri, Candido Fabrizio; Roppolo, Ignazio	**Author of Portion(s)**	Gonzalez, Gustavo; Chiappone, Annalisa; Dietliker, Kurt; Pirri, Candido Fabrizio; Roppolo, Ignazio
Volume / Edition	5		
Page or Page Range of Portion	2000374	**Publication Date of Portion**	2020-09-01

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1) **Definitions.** For purposes of these General Terms, the following definitions apply:

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3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

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iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the

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B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

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B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

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iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

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15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

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Last updated October 2022

A.14 Figure 1.9d



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Publication Title	Advanced materials	Publication Type	Journal
Article Title	Desktop-Stereolithography 3D-Printing of a Poly(dimethylsiloxane)-Based Material with Sylgard-184 Properties.	Start Page	e1800001
		End Page	e1800001
		Issue	22
		Volume	30
Date	01/01/1988		
Language	English		
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Title	Development of hydrophilic silicone-based ink for the 3D vat photopolymerization printing of biomedical devices	Institution Name	University of Waterloo
		Expected Presentation Date	2025-07-16
Instructor Name	Li Yan Wong		

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REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 3	**Title of the Article / Chapter the Portion Is From**	Desktop-Stereolithography 3D-Printing of a Poly(dimethylsiloxane)-Based Material with Sylgard-184 Properties.
Editor of Portion(s)	Bhattacharjee, Nirveek; Folch, Albert; Kim, Yong Tae; Kuo, Alexandra P; Parra-Cabrera, Cesar	**Author of Portion(s)**	Bhattacharjee, Nirveek; Folch, Albert; Kim, Yong Tae; Kuo, Alexandra P; Parra-Cabrera, Cesar
Volume / Edition	30		
Page or Page Range of Portion	e1800001-e1800001	**Publication Date of Portion**	2019-05-01

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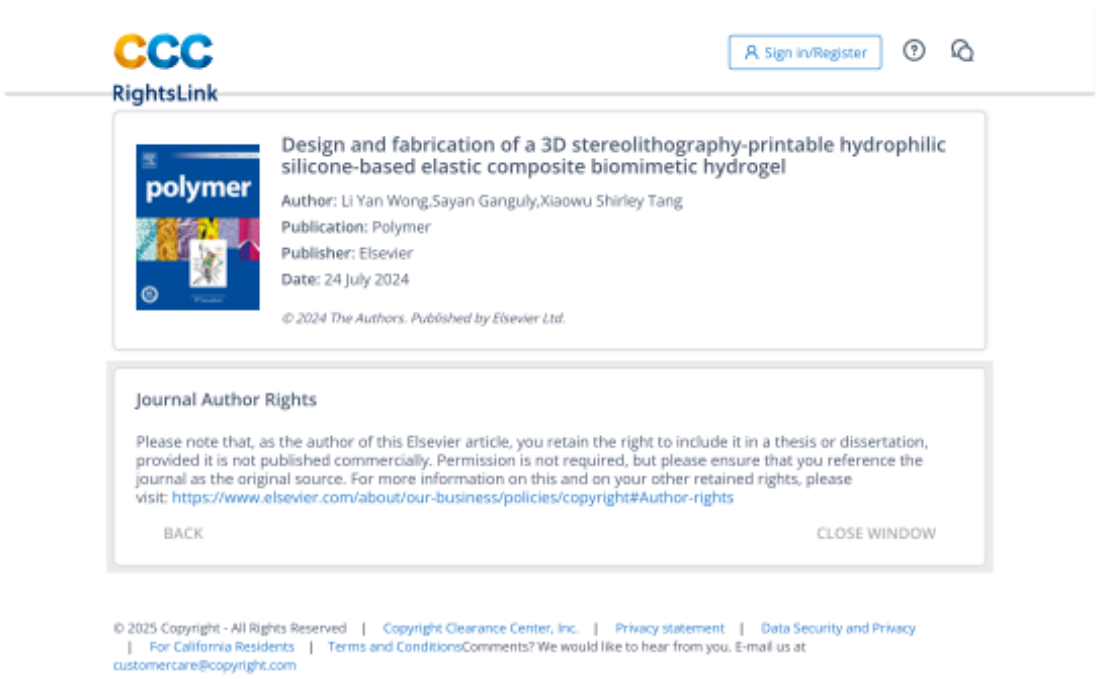
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Last updated October 2022

A.15 Chapter 2



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Design and fabrication of a 3D stereolithography-printable hydrophilic silicone-based elastic composite biomimetic hydrogel

Author: Li Yan Wong,Sayan Ganguly,Xiaowu Shirley Tang

Publication: Polymer

Publisher: Elsevier

Date: 24 July 2024

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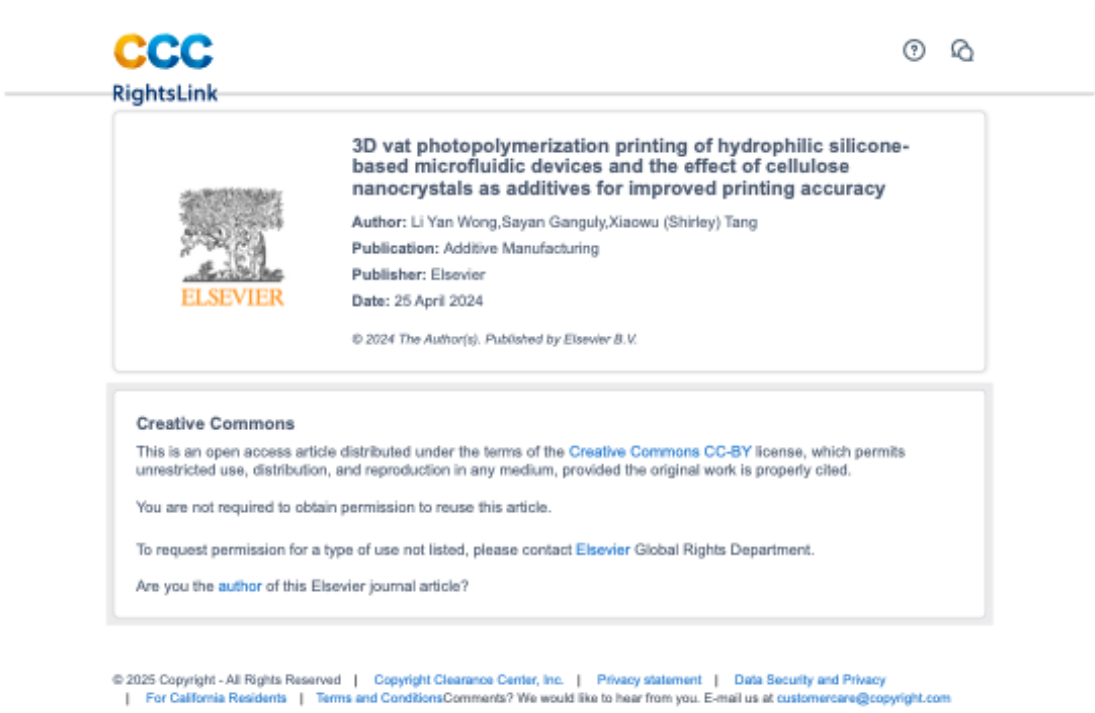
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A.16 Chapter 3



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3D vat photopolymerization printing of hydrophilic silicone-based microfluidic devices and the effect of cellulose nanocrystals as additives for improved printing accuracy

Author: Li Yan Wong,Sayan Ganguly,Xiaowu (Shirley) Tang

Publication: Additive Manufacturing

Publisher: Elsevier

Date: 25 April 2024

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A.17 Chapter 4



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Hydrophilic silicone-based ink derived from amphiphilic siloxane oligomers for the vat photopolymerization printing of embedded-channel fluidic devices

Author: Li Yan Wong,Sayan Ganguly,Xiaowu (Shirley) Tang

Publication: Additive Manufacturing

Publisher: Elsevier

Date: 25 February 2025

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References

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